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Sol-gel synthesis and characterization of cobalt chromium spinel $CoCr_2O_4$

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In the present work, the sinterability and formation of cobalt chromium spinel ($CoCr_2O_4$) by the aqueous sol-gel process are investigated. The metal ions generated by dissolving starting materials of metals in diluted acetic acid were complexed by 1,2-ethanediol to obtain precursors for mixed-metal ceramics. The phase purity of the synthesized compounds was characterized by powder X-ray diffraction analysis (XRD) and infrared spectroscopy (IR). The microstructural evolution and morphological features of the obtained products were studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The SEM and optical characterization of this compound has shown that the sol-gel-derived material may be successfully used as an effective cobalt-based ceramic pigment.

Key words: sol-gel synthesis, cobalt chromium spinel, pigments, glazes

INTRODUCTION

Cobalt-based ceramic pigments are widely used for coloured glazes in the ceramic industry for floor or wall whitewares and in the bulk coloration of polished, unglazed, porcelainzed stoneware. They are characterized by a high resistance to light, environment, high temperature and chemicals. These pigments are also used in many industries because of their different colour, fine particle size, good hiding power, acid acceptance and compatibility with many organic and inorganic systems. The palette of their colours is very wide: blue, green, yellow, violet, brown and black [1–3].

There is a wide range of various historical cobalt pigments. Some of them were more important in the history of painting, others were more often used for decorating ceramic works or producing ceramic glaze [1, 3–12]. For example, cobalt yellow (Aureolin, $K_3[Co(NO_2)_6]$) appeared in trade as a pigment in 1860. In those years it was the only steady bright yellow glazing colour used in the colour assortment together with the Indian yellow. Because of its remarkable effect, this pigment is perfectly suitable for various painting techniques: aquarelle, tempera and oil. Also, it is used in glass, porcelain painting, and enamel. The most important violet cobalt pigments are different phosphates: cobalt violet brilliant light ($CoNH_4PO_4 \cdot H_2O$) and cobalt violet dark ($Co_3(PO_4)_2$). These pigments have been known since the end of the 18th century.

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Cobalt cerulean blue ($CoO \cdot nSnO_2$) was discovered in 1789. This pigment was used in enamel art and porcelain painting. The colour of the pigment varies from bluish green to greenish blue, depending on the molar ratio of aluminium and chromium. Cobalt green bluish ($CoO \cdot ZnO$) was synthesized in 1778 and became more widely used in the 19th century. The pigment is resistant to light and suitable for all painting techniques. Blue cobalt pigments are also of significant importance in art history. Cobalt blue dark and cobalt blue light ($CoO \cdot Al_2O_3$) pigments were in use even in ancient Egypt for decorating pottery.

Cobalt blue greenish ($Cr_2O_3 \cdot CoO \cdot Al_2O_3$) was produced in the middle of the 19th century and used for decorating porcelain. The colour of this pigment varies from bluish green to greenish blue, depending on the molar ratio of aluminium and chromium [13]. However, the chemical composition of the blue greenish cobalt pigment does not correspond to the one given in the Kremer Pigmente catalogue and has been slightly corrected. According to the XRD results, the cobalt blue greenish pigment is cobalt chromium spinel $CoCr_2O_4$, but not a mixture of separate oxides $Cr_2O_3 \cdot CoO \cdot Al_2O_3$. Moreover, no phases containing aluminium have been determined. It is possible that alumina exists as a separate amorphous phase [13]. In this paper, we present results of a systematic study of the novel aqueous sol-gel synthesis method to pure cobalt chromium spinel ($CoCr_2O_4$).

EXPERIMENTAL

The cobalt chromium spinel ($CoCr_2O_4$) was synthesized by the aqueous glycolate sol-gel method. The gels were prepared using stoichiometric amounts of analytical-grade cobalt nitrate hexahidrate $Co(NO_3)_2 \cdot 6H_2O$ and chromium nitrate nonahidrate $Cr(NO_3)_3 \cdot 9H_2O$, as Co^{2+} and Cr^{3+} raw materials, respectively. For the preparation of precursor samples by the sol-gel process, $Co(NO_3)_2 \cdot 6H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ were dissolved in 100 mL of distilled water at 55–60 °C. The resulting mixture was stirred for 1 h at the same temperature. In the following step, 1,2-ethanediol (2 mL) as a complexing agent was added to the reaction solution. After concentrating the solutions by evaporation at 65 °C under stirring, the Co–Cr–O nitrate-acetate-glycolate sol turned into a greenish transparent gel. The oven-dried (105 °C for 10 h) precursor gel powders were ground in an agate mortar and preheated for 3 h at 700 °C in air. After grinding in an agate mortar, the powders were additionally sintered in air for 10 h at 1 000 °C without intermediate grinding. The flow chart of the sol-gel synthesis of cobalt chromium spinel is presented in Fig. 1.

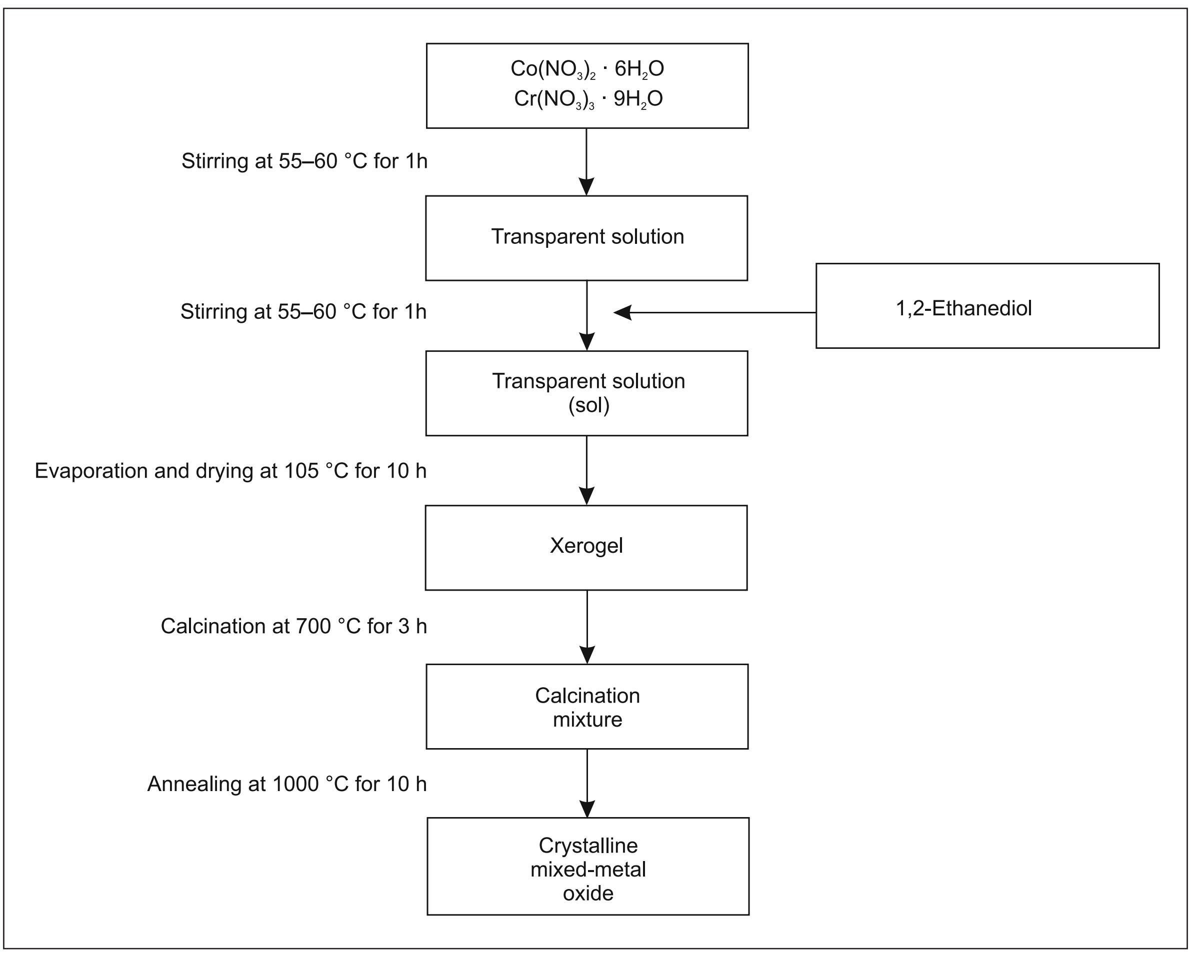

Fig. 1. Scheme of sol-gel synthesis of $CoCr_2O_4$

The sol-gel derived pigment along with lead oxide (Pb_3O_4) and silica (SiO_2) were used for the preparation of cobalt-based glaze [14]. The following molar ratio of the ingredients was selected: Pb_3O_4 : SiO_2 : pigment = 2.85 : 1.9 : 0.25. The glaze was formed on a terracotta surface (3 × 2 cm). The pigment was mixed with a small amount of distilled water, pasted on the terracotta plate and dried for 10 h at room temperature. The glaze was annealed at 1 000 °C for 2.5 h.

Powder X-ray diffraction (XRD) measurements were performed at room temperature with a DS Bruker AXS diffractometer (CuK_α radiation: λ = 1.5418 Å). The infrared spectra in the range 4 000–400 cm^{-1} were recorded on a Perkin-Elmer FT-IR Spectrum BX II FTIR spectrometer. Samples were prepared as KBr pellets (1.5%). Scanning electron microscopy (SEM) was used to study the morphology of the samples. The SEM analysis was performed under vacuum in the specimen chamber of an EVO 50 XVP scanning electron microscope equipped with the EDX detecting system. The transmission spectra were recorded with a Perkin-Elmer Lambda 35 UV VIS spectrophotometer. A Veeco Bioscop II atomic force microscope (AFM) was also used for the characterization of the synthesized glazes. An optical Leitz microscope and a Canon EOS 300 D digital camera were used for the surface characterization of the obtained glazes.

RESULTS AND DISCUSSION

The XRD pattern of sol-gel derived $CoCr_2O_4$ ceramics heated at 1 000 °C for 10 h is shown in Fig. 2. According to the XRD analysis, a fully crystallized single-phase oxide $CoCr_2O_4$ of a well-pronounced spinel crystal structure was formed (PDF [22-1084]). No impurity phases in the sample were detected. IR spectroscopy was used as an additional tool for the structural characterization of the ceramics obtained by the aqueous sol-gel method. The IR results are consistent with the crystallization process observed by XRD measurements. The IR spectrum of $CoCr_2O_4$ is shown in Fig. 3. One can see that the IR spectrum of the sample calcined at 1 000 °C does not show any band attributable to carbonates. The IR spectrum of sol-gel synthesized $CoCr_2O_4$ ceramics shows broad absorption bands arising from O–H stretching and bending vibration of water due to the exposure of the sample to the atmosphere at ~3 500–3 300 cm^{-1} and ~1600 cm^{-1}, respectively. Besides, in the IR spectrum of $CoCr_2O_4$, two intensive absorption lines in the region of 700–530 cm^{-1} could be attributed to the typical metal–oxygen (M–O) vibrations [15, 16]. The band located at ~680 cm^{-1} probably belonged to the tetrahedral (CoO_4) and the peak observed at ~540 cm^{-1} to the octahedral (CrO_6) fragments in the spinel.

Figure 4 shows the SEM micrograph of synthesized ceramic specimen. SEM investigation showed that the sol-gel-derived $CoCr_2O_4$ was composed of rather large (~8–10 μm) differently shaped crystallites. Most particles were plate-like crystallites. Besides, these particles were formed with a very well pronounced agglomeration, indicating a good connectivity between the grains. Finally, the results of EDX analysis clearly showed that the molar ratio of metals corresponded to the formation of $CoCr_2O_4$. The determined molar ratio of metals was Co : Cr = 14.52(6) : 30.67(8), which is very close to the nominal composition. The image presented in Fig. 5 is

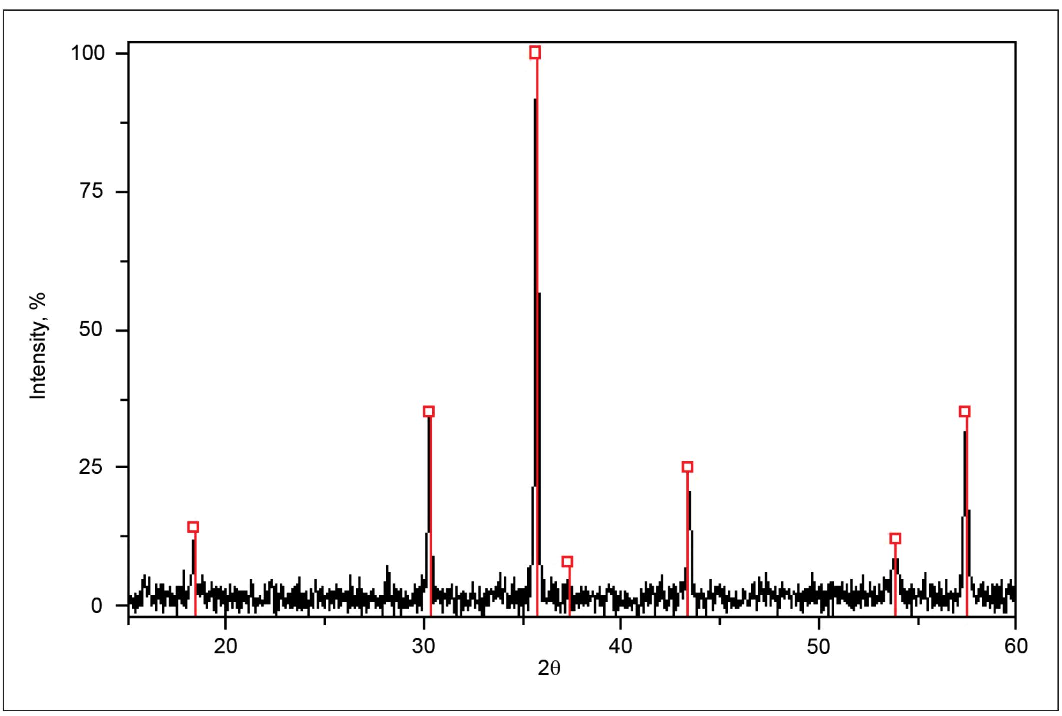

Fig. 2. X-ray diffraction pattern of $CoCr_2O_4$ ceramics synthesized using sol-gel method at 1 000 °C. Annealing time was 10 h. □ – reference data for $CoCr_2O_4$ PDF [22–1084]

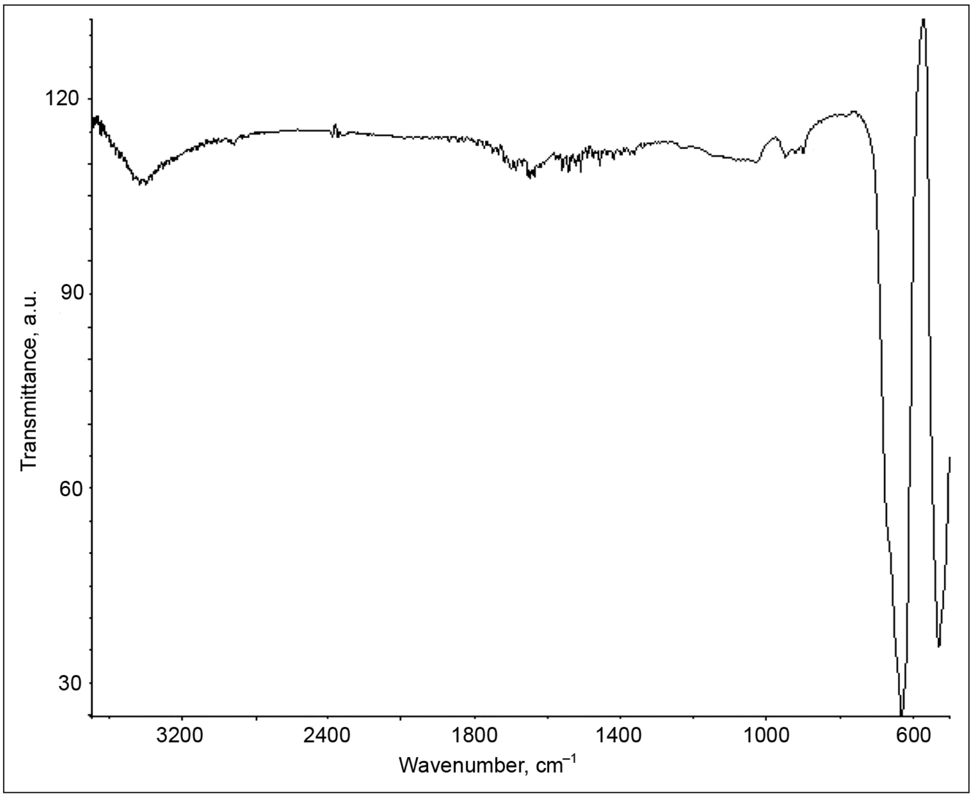

Fig. 3. Infrared spectrum of $CoCr_2O_4$

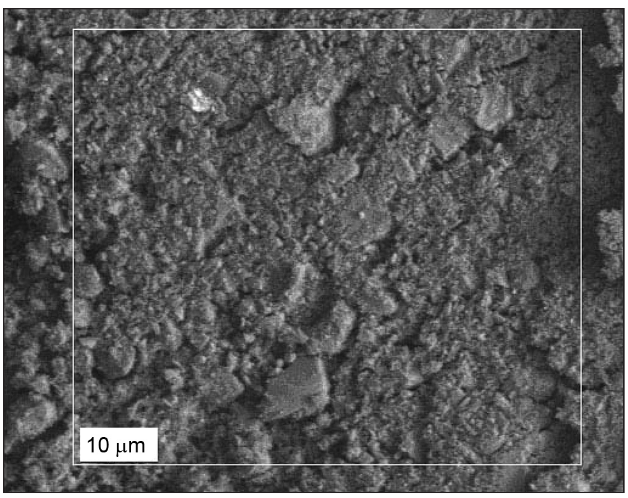

Fig. 4. Scanning electron micrograph of sol-gel-derived $CoCr_2O_4$

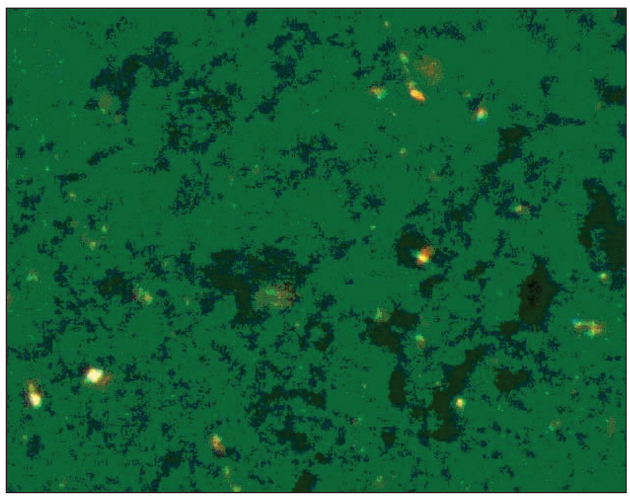

Fig. 5. Optical micrograph of sol-gel-derived $CoCr_2O_4$. Magnification 10×

an optical micrograph of $CoCr_2O_4$ synthesized by the sol-gel method. It could be noted from Fig. 5 that the characteristic green colour of the cobalt pigment $CoCr_2O_4$ was dominating. The light spots on the micrograph could be generated by the beam. However, dark-blue areas are also seen, i. e. the green colour in the pigment is distributed unevenly. Thus, we can conclude that the sol-gel-derived $CoCr_2O_4$ pigment could be a source of cobalt blue greenish glaze.

The sol-gel-derived pigment was mixed with Pb_3O_4 and SiO_2 for the preparation of cobalt-based glaze. The glaze was formed on the surface of terracotta at 1 000 °C after 2.5 h. The optical reflectance spectrum of the glaze sample was measured at room temperature in the range 400–750 nm. The samples exhibited a high transmittance in the visible region. Figure 6 demonstrates the reflectance spectra of the glaze obtained using $CoCr_2O_4$ pigments. One can see several periodically repeating absorptions in the whole wavelength region. The absorption edge for the samples could be detected below 400 nm. In the whole wavelength region the reflectance is wavelength-dependent. In the range 500–530 nm, the cobalt-based mixed-metal glaze shows a significant increase of transmission. In the higher wavelength region (~680 nm), the absorption monotonically increases. These absorption bands are possibly due to the band gap excitation of the host lattice.

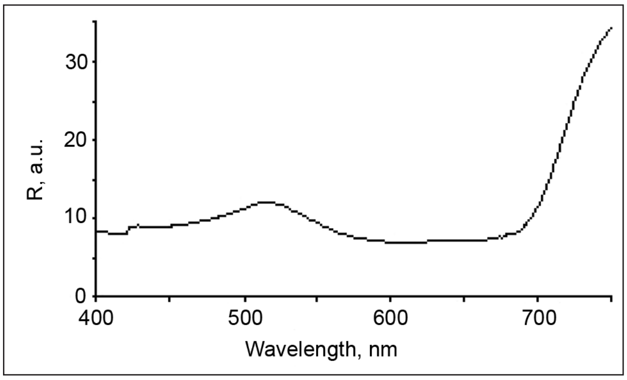

Fig. 6. Optical reflectance spectrum of glaze containing $CoCr_2O_4$ pigment

The surface picture of the obtained cobalt ceramic glaze was taken with a digital camera and is shown in Fig. 7. One can see that the obtained glaze has a very intensive and expressive greenish colour. Therefore, the cobalt blue greenish glaze could be obtained only using the $CoCr_2O_4$ pigment without adding alumina. Figure 8 shows a SEM micrograph of a new cobalt-based glaze obtained at 1 000 °C, in which the surface of terracotta is evenly coated with cobalt-based glaze. The surface microstructure of the ceramic sample contains differently oriented amorphous particles of the pigment. Such morphological features of glazes are usually observed in most cases. However, an atypical roughness of the surface could be also determined. Figure 9 shows the AFM image of the novel cobalt-based glaze. Interestingly, the surface of the glaze sintered with $CoCr_2O_4$ pigment is rather smooth. The roughness of glaze with cobalt chromium spinel is about 10–20 µm.

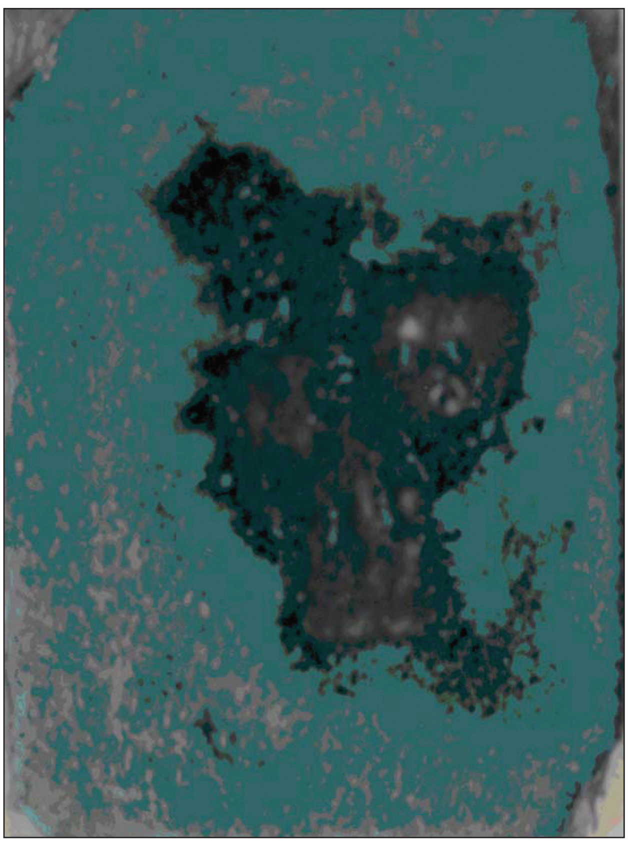

Fig. 7. Photograph of sol-gel-derived glaze containing $CoCr_2O_4$ pigment

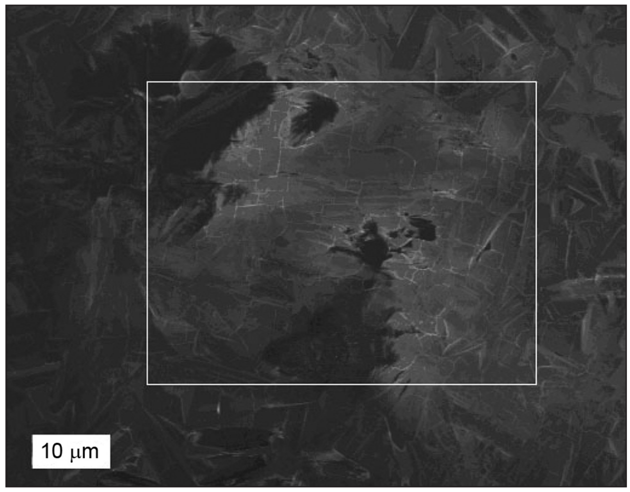

Fig. 8. Scanning electron micrograph of glaze obtained using sol-gel-derived $CoCr_2O_4$ pigment

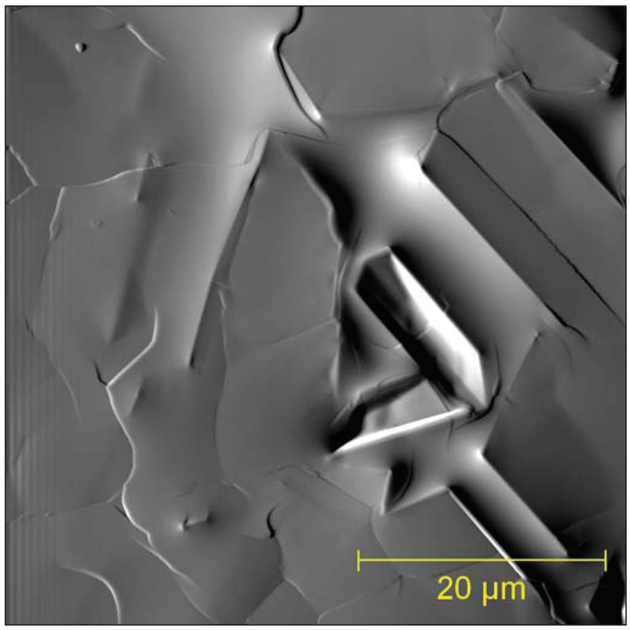

Fig. 9. AFM image of glaze obtained using sol-gel-derived $CoCr_2O_4$ pigment

CONCLUSIONS

In this work, a new cobalt-based pigment $CoCr_2O_4$ has been synthesized using an environmentally benign aqueous sol-gel chemistry technique. According to the XRD analysis, a fully crystallized single-phase oxide $CoCr_2O_4$ of a well-pronounced spinel crystal structure was formed. The IR and EDX results were consistent with the crystallization process observed by XRD measurements. SEM investigation has shown that the sol-gel derived cobalt chromium spinel is composed of rather large (~8–10 µm) differently shaped crystallites. Most particles were plate-like crystallites with a very well pronounced agglomeration, indicating a good connectivity among the grains. The glaze obtained using sol-gel-derived $CoCr_2O_4$ showed rather good colour characteristics. This glaze had an intensive and expressive greenish colour. Thus, the cobalt blue-greenish pigment has been successfully prepared without adding Al_2O_3. The proposed sol-gel method of obtaining the new cobalt-based pigment in aqueous media is inexpensive and thus appropriate for the large-scale production of such type of ceramics.

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KOBALTO CHROMO ŠPINELIO $CoCr_2O_4$ SINTEZĖ ZOLIŲ–GELIŲ METODU IR APIBŪDINIMAS

Santrauka

Vandeniniu zolių–gelių metodu susintetintas naujas kobalto pigmentas $CoCr_2O_4$. Rentgeno spindulių difrakcinės analizės rezultatai parodė, kad gautas vienfazis kobalto chromo špinelio struktūros junginys. Infraraudonųjų spindulių spektroskopijos ir skenuojančios elektroninės mikroskopijos rezultatai patvirtino Rentgeno spindulių difrakcinės analizės išvadas. SEM tyrimai parodė, kad susidarė pakankamai dideli (~8–10 µm), dažniausiai plokštuminiai, linkę aglomeruotis kristalitai. Šio pigmento pagrindu gauta glazūra pasižymėjo pakankamomis spalvinėmis charakteristikomis – glazūra buvo intensyviai ir ekspresyviai žalsva. Taigi kobalto melsvai žalsvas pigmentas buvo sėkmingai susintetintas ir be Al_2O_3 priedo. Šie rezultatai parodė, kad zolių–gelių metodas, pritaikytas naujo kobalto pigmento sintezei, yra nebrangus ir tinkamas dideliems tokio tipo keraminių medžiagų kiekiams sintetinti.