SYNTHESIS OF WILLEMITE PIGMENTS DOPED WITH DIFFERENT D-CHROMOPHORE ELEMENTS – Co AND Ni (PART 1)

SYNTÉZA WILLEMITOVÝCH PIGMENTŮ DOTOVANÝCH RŮZNÝMI D-CHROMOFOROVÝMI PRVKY – C_O A N_I

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Summary

The aim of the present paper is to study the possibilities to synthesize willemite ceramic pigments with respect to their possible use as pigments in the silicate industry. The preparation of high temperature ceramic pigments using colorless stable crystal carcasses turns out to be quite a suitable method in order to its colored by introducing different chromophores. This paper reports experiments carried out on the synthesis of willemite pigments with the participation of following chromophore ions: Co^{2+} and Ni^{2+}, which give blue, resp. green and blue – green coloration using the technology of solid phase sintering. X-ray phase analysis, electron spin resonance spectroscopy, electron microscopy and hot stage microscopy were used mainly in order to investigate the structure, phase composition, chromophore ions valency state, etc. The results obtained indicated that it's depend mainly on the sintering temperature and type of chromophore ion. The best pigments obtained were added to white faience glaze.

Keywords

Willemite pigments, chromophore ion, ESR spectroscopy, X -ray phase analysis

Introduction

The ceramic pigments are inorganic colored finely dispersed powders which, adding to certain medium, impart specific color and change some properties [1–4]. Besides their coloring ability, the ceramic pigments are resistant to atmospheric and chemical influences, high temperature, decomposing effect of silicate melts and light. These colored inorganic substances have high coefficient of refraction, they are insoluble in water and binding materials but can be dispersed within them, thus imparting certain color to them.

Willemite, Zn_2SiO_4 (trigonal singony) with phenakite (beryllium orthosilicate, Be_2SiO_4) structure is an orthosilicate with all atoms in general position and composed by a framework of tetrahedra accommodating zinc and silicon in three different fourfold crystallographic sites: two slightly different zinc sites Zn1 (1.950 Å) and Zn_2 (1.961 Å), and Si (1.635 Å), so resulting in rhombohedral symmetry with lattice parameters a = b ~13.948Å, and c ~9.315 Å [5–9].

If zinc oxide is substituted with nickel oxide, blue pigments can be obtained which successfully compete with the more expensive cobalt pigments. The introduction of FeO results in yellow and brown pigments and MnO – pink, purple and grey [10]. Attempts were made to substitute not only ZnO but also SiO_2 with other acidic oxides like SnO_2, TiO_2, ZrO_2 [10]. In our previous works we have successfully proved the effect of CoO as an oxide giving a saturated blue color during the synthesis of pigments [11,12].

Materials and methods

Materials

The determination of composition recipes for the production of willemite ceramic pigments is based on the main mineral willemite.

The chemical materials used in the synthesis are: CoO, NiO, ZnO, $SiO_2.nH_2O$ and NaF (as a mineralizer diminishing the temperature of synthesis and accelerating the processes of new phase formation).

The raw material used for introduction of SiO_2 in the system $SiO_2.nH_2O$ is significantly more reactive than the ordinary quartz sand. Its degree of dispersity of the particles is in the range of 2–7 μm. After annealing in a platinum crucible the initial SiO_2 and H_2O content in the $SiO_2.nH_2O$ compound was determined. This is namely: SiO_2 – 76,3% and H_2O – 23,7%.

Methods

The resulting ceramic pigments were examinated mainly using X-ray analyses, electron microscopy, Hot stage microscopy. The color was determined spectrophotometrically using Lovibont Tintometer RT 100 Colour.

Phase composition of the synthesized ceramic pigments was determined using X-ray diffraction (XRD) with a Bruker D8 diffractometer operating at 40 kV and 40 mA with CuKα radiation.

An electron spin resonance spectroscopy (ESRS) study was performed on a spectrometer type B-ER-420 of Bruker-Physic, working in the X-range at a frequency of 9.8 GHz at room temperature.

The color of pigments is determined by tintometer (Lovibont Tintometer RT 100 Colour) and presented in the CIELab color space as defined by the International Commission on Illumination (CIE).

The sintering behavior of the ceramic pigments under investigation was studied by means of optical hot stage microscopy (HSM) with an ESS HSM-1400 MISURA (Italy). This instrument allows measurements up to 1 400 °C of the sample volume alterations.

All samples were measured non-isothermally by using a programmed constant linear thermal scan with a rate of 10 °C min^{-1} up to °1 400 C.

Experimental procedures

The following willemite pigment compositions have been prepared:

– Cobalt-willemite pigments: $xCoO.(2-x)ZnO.SiO_2$,

– Cobalt-willemite pigments with dopants: 0,1NiO, 0,1MnO and $0,1Fe_2O_3$,

– Nickel-willemite pigments: $xNiO.(2-x).ZnO.SiO_2$,

where x = 0.125, 0.250, 0.375, 0.50, 0.625, 0,75, 0.875 и 1,00.

The quantities of the materials in the recipe for a 100 g batch were weighted with the help of balances with a resolution of 0.1 g. Then the samples were mixed together and homogenized with a planetary mill FRITSCH Pulverisette–6 (Germany) in a dry environment.

The firing was carried out in a laboratory tube furnace with a heating rate of 300–400 °C h^{-1} in air environment and using porcelain crucibles. The firing regime consisted of an isothermal soaking at the final temperature with a holding time of 2 hours. All pigments were heat treated at temperatures of 900, 1 000 and 1 100 °C.

Results and discussions

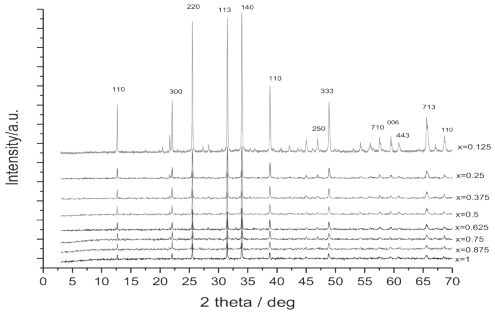
Co –doped willemite pigments

Co – doped willemite pigments have been investigated mainly by the methods of X-ray analyses, colour measurement and electron spin resonance spectroscopy (ESRS).

X-ray analyses

In figure 1 are presented X-ray spectra of pigments with different CoO concentration treated thermally at 1 000 °C. The calculated crystal lattice constants vary slightly around 80–1 000 nm. The lattice parameters do not reveal significant differences due to the substitution of Zn with Co caused by ion radiuses of the nearby ion in the tetrahedral coordination (Zn^{2+} – 0.74 Å, Co^{2+} – 0.65 Å). A solid solution, wilemite-cobaltin is obtained due to isovalent substitution of the two ions – Zn^{2+} and Co^{2+}.

Fig. 1: XRD spectra of willemite – cobaltin pigments with composition xCoO.(2-x)ZnO.SiO_2, synthesized at a temperature of 1 000 °C

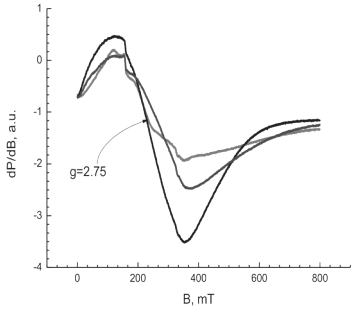


Electron spin resonance spectroscopy (EARS) study

In Figure 2 is presented the ESR spectrum of a pigment in the system 0.5CoO.1.5ZnO.SiO_2.

The ESR spectra of sample 0.5CoO.1.5ZnO.SiO_2. were measured in the temperature range of 120–295 K. At room temperature is observed an anti-symmetric broad signal with an effective g-factor around 2.75 and a linewidth around 218 mT. The signal becomes wider with a decrease of the temperature and at low temperatures the signal described above becomes overlapped with relatively broad signals beyond the existing resolution.

Fig. 2: ESR spectrum of the sample 0.5CoO.1.5ZnO.SiO_2 at 295 K (black curve), 210 K (blue curve) and 120 K (red curve).



The single anti-symmetric signal determined at 295 K is typically contributed to high-spin exchange bonded Co^{2+} in a field with an octahedral distortion [13].

The spectrum recorded at 120 K reveals the appearance of lines caused by the ultra-fine structure of the Co^{2+} ions (I = 7/2) overlapped with the broad signal contributed as already mentioned above to exchange bonded Co^{2+} ions. The ultra-fine structure becomes visible at low temperatures because of the significant broadening of the dominating at 295 K signal.

Measurement of the colour

The results of colour characteristics study are given in Table 1. Summarizing the results one could clearly state that in the system CoO.ZnO.SiO_2 blue pigments have been successfully obtained.

Table 1. Color characteristics of the synthesized Co-willemite pigments at temperatures of 900 °C and 1 000 °C

Pigments	R	G	B	L*	a*	b*
$CoO.ZnO.SiO_2$ (900 °C)	23.4	70.0	116.3	28.7	2.1	–31.4
$CoO.ZnO.SiO_2$ (1 000 °C)	16.1	92.2	168.6	38.5	8.4	–47.2
$CoO.ZnO.SiO_2$.0,1MnO (900 °C)	58.1	80.3	96.2	32.8	–4.0	–12.0
$CoO.ZnO.SiO_2$.0,1MnO (1 000 °C)	40.6	85.1	126.7	35.3	–0.3	–28.6
$CoO.ZnO.SiO_2$.0,1Fe_2O_3 (900 °C)	43.5	56.7	65.1	23.5	–3.2	–7.2
$CoO.ZnO.SiO_2$.0,1Fe_2O_3 (1 000 °C)	40.2	73.4	108.4	29.6	–0.1	–24.4
$CoO.ZnO.SiO_2$.0,1NiO (900 °C)	43.4	70.2	104.4	29.3	1.3	–22.6
$CoO.ZnO.SiO_2$.0,1NiO (1 000 °C)	51.2	100.4	161.6	41.6	3.9	–37.5

With an increase of the firing temperature the values of the parameter L* are accordingly increasing as well (the color of the pigments becomes lighter) and the quantity of the blue color decreases. The best blue color (–b* = –47,2) has been obtained with the pigment sample $CoO.ZnO.SiO_2$ thermally treated at 1 000 °C. As a whole the introduction of additives of 0,1% NiO, MnO, Fe_2O_3 in the system $CoO.ZnO.SiO_2$ leads to diminishing of the blue color.

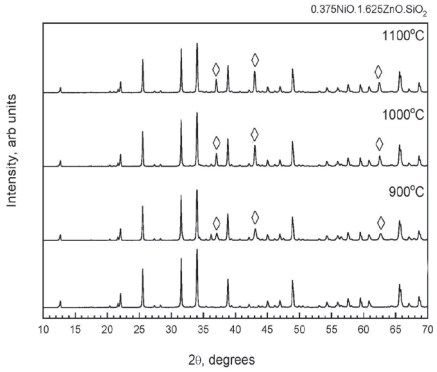
Ni –doped willemite pigments

Ni –doped willemite pigments were studied mainly by means of X-ray analyses, colour measurement and by hot stage microscopy.

X-ray analyses

The X-ray spectra of synthesized Ni-willemite ceramic pigments in the system 0,375NiO.1,625ZnO.SiO_2 at the different temperatures of synthesis (900, 1000 and 1 100 °C) are presented in Figure 3.

Fig. 3 X-ray spectra of synthesized Ni-willemite pigments in the system 0,375NiO.1,625ZnO.SiO_2: main phases - solid solution between willemite and NiO, ◊ - NiO (PDF 652901)



The performed analysis reveals that even at 900 °C are present peaks of the main phases- willemite, solid solution between willemite and residual NiO.

The diffraction pattern shows well defined peaks with positions corresponding to the standard model JSPDS PDF 46-1316 possessing a willemite structure. At all firing temperatures have been registered weak peaks of NiO where a trend of their increase together with the concentration increase of NiO has been determined. According to the XRD experiment the optimal synthesis temperature of these pigments has been found to amount to 1 000 °C.

The results of colour characteristics study are given in Table 2.

Measurement of the colour

Table 2: Colour of pigments

No	Composition	L*	a*	b*
1	0.125NiO.1.875ZnO.SiO_2	67.1	–9,84	–21,18
2	0.250NiO.1.750ZnO.SiO_2	60.8	–10.5	–22.47
3	0.375NiO.1.625ZnO.SiO_2	58.2	–12.4	–17.54
4	0.500NiO.1.500ZnO.SiO_2	53.5	–12.5	–13.78
5	0.625NiO.1.375ZnO.SiO_2	52.0	–12.65	–8.49
6	0.750NiO.1.250ZnO.SiO_2	50.9	–12.45	–6.75
7	0.875NiO.1.125ZnO.SiO_2	49.8	–10.45	–5.17
8	1.000.NiO.1.000ZnO.SiO_2	47.2	–9.01	–1.94

Figures 4 and 5 show results from hot stage microscopy (HSM). Figure 4. shows sintering curves of willemite pigment 0,25NiO.1,75ZnO.SiO_2 by hot stage microscopy (HSM) at 10 °C/min.

Fig. 4: Sintering curves of willemite pigment 0,25.NiO.1,75ZnO.SiO_2 by optical hot stage microscopy (HSM)

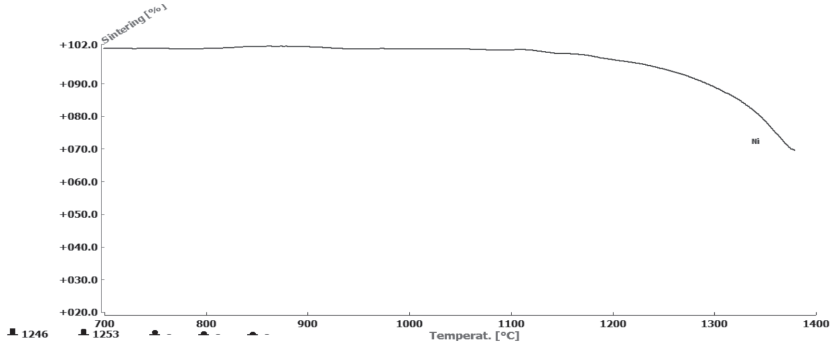
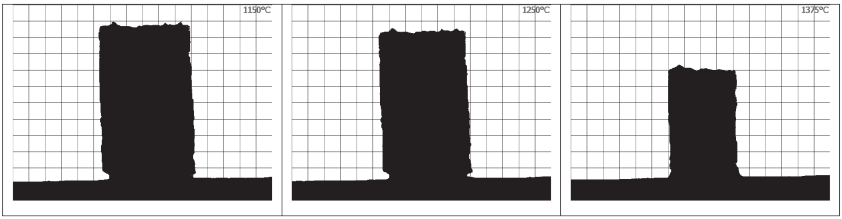


Fig. 5: Images at 1 150, 1 250 and 1 375 °C of willemite pigment 0,25.NiO.1,75ZnO.SiO_2 by HSM run



The used in this experiment powders were obtained by synthesizes at 900 °C. The studied pigment demonstrates very high temperature resistance. Up to 1 150 °C no volume changes are observed, while at 1 250 °C the sintering shrinkage is only at about 4%. At 1 375 °C the shrinkage, due to the densification, reaches at about 25%, but the sample don't show any deformation. This behavior indicates that the sintering process carries out without formation of liquid phase and is controlled by solid state reactions.

Conclusions

The synthesis of willemite ceramic pigments with added two chromophore ions: Co^{2+} and Ni^{2+} was studied. Ceramic pigments were prepared using solid phase sintering technology. Adding Co^{2+} ion a solid solution, wilemite-cobaltin is obtained due to isovalent substitution of the two ions – Zn^{2+} and Co^{2+}. It was proved that as main crystalline phase, willemite is formed at temperatures as low as 900 °C. The optimal parameters of the synthesis process have been determined. Best results are obtained with the pigment synthesized at a firing temperature of 1 000 °C. In-depth studies with electron spin resonance spectroscopy (ESRS) have been performed. It was established that the pigments synthesized could successfully be used in glazes for wall tiles.

Acknowledgements

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