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Study of ceramic pigments from the ZrO_2 – SiO_2- Fe_2O_3 system

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In order to obtain high temperature ceramic pigments using colorless stable crystal carcasses turns out to be quite suitable in the case of $ZrSiO_4$ and their coloring by introducing different chromophores. In the paper presented experiments have been carried out on synthesis of zircon pigments from the ZrO_2-SiO_2-Fe_2O_3 system. The technology of solid phase sintering have been applied for their obtaining. X -ray phase analysis, ESR and Moessbauer spectroscopy have been used to define the phase composition and to checked the Fe ions valency state above the optimal temperature of synthesis. In most pigments the basic phase is obtained at even 900 - 1000^{0}C. The best pigments have been added to white faience glaze.

Key words: pink pigment, zircon, color

Estudio de pigmentos cerámicos del sistema ZrO_2-SiO_2-Fe_2O_3

La obtención de pigmentos cerámicos de alta temperatura a partir de cristales estables incoloros, puede ser muy viable en el caso del ZrSiO4 y su posterior coloración con diferentes cromóforos. En este artículo se han desarrollado pigmentos de zircón basados en el sistema ZrO2-SiO2-Fe2O3, utilizando la tecnología de sinterización en fase sólida. La composición de las fases se ha efectuado mediante análisis por DRX, ESR y Espectroscopía Moessbauer, comprobándose la valencia de los iones Fe a la temperatura óptima de sinterización. En la mayoría de los pigmentos la fase básica se obtiene en el intervalo 900-100ºC Los mejores pigmentos se han añadido a un esmalte blanco de loza

Palabras clave: pigmento rosa, zircon, color.

1.INTRODUCTION

It is well known that the pigments from the ZrO_2 – SiO_2-Fe_2O_3 system have been synthesized for the first time by Seabright (1) in 1960. From the practical point of view the pigments are attractive and many investigators continue to study them in few technological aspects up to now (2,3). It was established that in such type of ceramic pigments the role of acceptor is taken by $ZrSiO_4$ and the role of a coloring ion generally is taken by Fe^{3+} thus forming a pink colour(4-9).

Characteristic feature of the synthesis of these pigments is the usage of comparatively large amounts of mineralizers. Usually the mineralizers used are alkaline chlorides (fluorides), silicofluorides or combination from these (10), as well as alkaline or ammonium nitrate (11). When alkaline fluorides and silicofluorides are used to incorporate sufficient amount of fluorine ions in the matrix but as a results volatile SiF_4 is form. Those partly stimulate the transport of Si- ions to the site where the reaction takes place. Chlorides are used usually to lower the temperature of fairing, while nitrates form with iron ions compositions, suitable for incorporation in the structure of zirconium (12). It is necessary to note that at low concentration e.g. at about 2% of mineralizer used, the zirconium-$ZrSiO_4$ is formed but without incorporation of the coloring ion into the crystal structure (7). It is clear that to carry the synthesis in a successful way it is very important to use a mineralizer of definite type in a definite concentration.

2. EXPERIMENTAL

The aim of the present work is to study the phase evolution of the pigments from the ZrO_2 –SiO_2 - Fe_2O_3 system vs. the temperature at a constant time of treatment as well as to checked the Fe- ions state above the optimal temperature of synthesis.

The synthesis of pigments is carried out by solid state reaction using raw materials as ZrO_2, SiO_2 and Fe_2O_3 at a molar ratio ZrO_2 : SiO_2 =1:1. The zirconium dioxide used was chemically pure (ZrO_2 - 99,35%) and X-ray diffraction revealed that mineralogically it consisted of pure badddeleyite. The silicon dioxide used was washed and ground (50µm) from Kaolin JSCo- Bulgaria. X-ray diffraction indicate that it was pure qartz (SiO_2 - 99,62%). Fe_2O_3 was used as analytical reagent - MERCK. The concentration of the chromophoric ion is 5 at.% Fe from Fe_2O_3 used. As mineralizers have been used 6% wt. LiF + 4% wt. NaCI and 6% wt. Na_2SiF_6 (chem.pure), respectively incorporated in the batch in the corresponding quantities. Isothermal treatment is carried at 800°C, 900°C, 1000°C and 1100°C for 4 hours, respectively. The nominal compositions of the pigments are presented in the Table 1. The samples possess pink colour after thermal treatment.

X -ray phase analysis, Electron spin resonance spectroscopy (ESR) and Moessbauer spectroscopy have been used to define the phase composition and to checked the Fe ions valency state above the optimal temperature of synthesis. X-ray phase analysis was carried out on a Philips- ARD-15 at CuK_{α} radiation and a diffracted beam monochromator. Electron spin resonance spectroscopy (ESR) study has been carried on an spectrometer type B-ER-420 of Bruker- Physic , working in the X-range at a frequency of 9.8. GHz; room temperature experiments. Magnetic field modulation value has been at 100kHz. Moessbauer spectra have been taken in transmittance geometry with a standard spectrometer working at a regime of a constant acceleration. ^{57} Co (Rh) g - source of radioactivity of 10 mCi have been used. Particle size determination have been determined by PHILIPS - TEM - EM 301G at 80kV.

TABLE 1 NOMINAL COMPOSITIONS OF THE PIGMENTS.

Index	Constituents , % wt.			Mineralizers , % wt.		
	ZrO_2	SiO_2	Fe_2O_3	LiF	NaCI	Na_2SiF_6
Sample 1	56,19		6,29	6	4	-
Sample 2	58,68	28,74	6,58	-	-	6

3. RESULTS AND DISCUSSIONS

Figure 1 shows X-ray diffraction intensities of an iron (III) containing pigment with mineralizer Na_2SiF_6 used at different temperatures. At 800°C diffraction peaks of the basic phase $ZrSiO_4$ clearly can be checked. There are some diffraction patterns due to ZrO_2 (monoclinic) phase is registered, as well. With the increase of temperature even at 900°C we can checked an almost entire synthesis of $ZrSiO_4$ and small amount of ZrO_2. No changes is noticed in the intensity of the responses at 1000°C. The excess ZrO_2 is formed as a result of the reaction of part of the SiO_2 with the mineralizers, whereby a volatile SiF_4 is formed. This mechanism has been studied thoroughly by Eppler [3], who presumes that SiF_4 plays a transport role carrying part of the Si^{4+} ions to the site of the reaction, i.e. the ZrO_2 layer.

It can be accepted that the temperature of 900°C is optimal one of the phase synthesis. When using a mineralizer of the type - 6% wt. LiF + 4% wt. NaCI, the phase picture does not significantly differ, but samples at 1000°C are strongly sintered. The obtained results indicate that Na_2SiF_6 is a more appropriate mineralizer with regard to the synthesis of $ZrSiO_4$ as zircon is fully synthesized at 900°C already, whereas in the case of LiF, NaCl, there is much more ZrO_2 at the same temperature.

The calculated parameters of the elementary $ZrSiO_4$ cell are have been defined, applying the program TREOR 91 suitable for powder identification on the base of XRD measurements (13). The following results have been obtained: a = b = 6,605902 ± 0,001035Å , c= 5,983344 ± 0,001321Å. The calculated parameters of pure $ZrSiO_4$ are : a = b = 6,604 ± 2 Å, c = 5,979 ± 2 Å (8).

Figure 2 shows the ESR spectrum of a sample with mineralizer Na_2SiF_6 treated at 1000°C. In the spectrum of the pigment two types of signals are observed due to Fe^{3+} ions with coordination numbers 6 and existing in different moieties: a symmetric intense signal with g ≅ 2.05 and width ΔHpp = 250 G. and low intense one with g > 2.1 and ΔHpp = 500 G. These ESR data are indicating that the intense signal might be assigned to magnetically coupled Fe^{3+} from separate ferric-oxide phase, while the broad one with g > 2.1 is due most likely to ferric-oxide phase with nanodimensions found insupermagnetic state. With the temperature raise of the synthesis decrease of the intensity of the narrower signal is observed, although no changes of its parameters is registered. /g ≅ 2.05 and ΔHpp ≅ 250G/. In the same time a new symmetric signal in the spectra of samples obtained at higher temperatures is observed with g ≅ 2.9 and ΔHpp ≅ 1400 G. These parameters are typical for magnetically

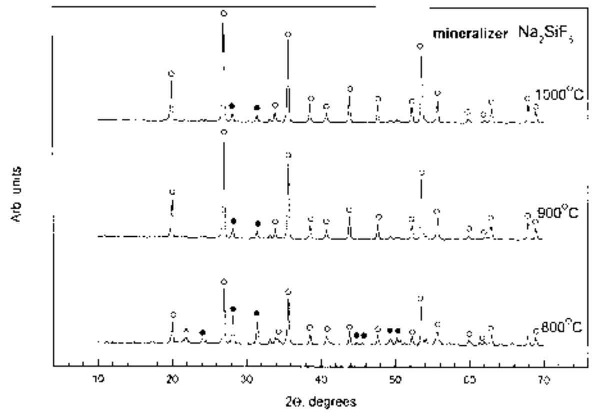

Figure 1.- XRD patterns of pigments with 5at% Fe content after treatment from 800 °C to 1000°C for 4 hour; the checked crystalline phases are : o - $ZrSiO_4$; • -ZrO_2 (monoclinic) and x- α-SiO_2, respectively.

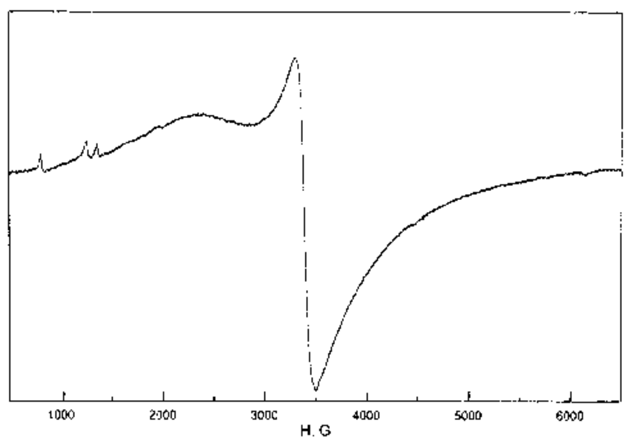

Figure 2.- ESR spectrum of sample 2 with Na_2SiF_6 used as mineralizer; heat treatment 1000 °C for 4 h.

coupled Fe^{3+} ions in silicate matrixes. This result shows that the high synthetic temperatures of the pigments favor the Fe^{3+} included in Zr-matrix. In any way the Fe^{3+} ions are distributed irregularly so exchange coupling interactions are realized. In Figure 3 is shown a Moessbauer spectrum of sample 2 with 5 at.% Fe content after thermal treatment at 1000°C for 4h. It is well seen that the whole iron content is in the Fe^{3+} coordination state i.e. not any contribution from Fe^{2+} state can be checked. The basic component is of a sextet spectrum with parameters as follows: isomer shift (IS) = 0.369 mm/s, quadrupole splitting (QS) = 0.204 mm/s, effective magnitude of the magnetic field (H_{hf}) = 517 KOe and a relative peak intensity (Irel) = 90%. It is clear that the checked Moessbauer parameters are closed to the iron nucleus in α-Fe_2O_3 state. According to (14) the hematite possesses a close packed oxygen lattice of FeO_6- octrahedra and the spectrum is asymetrical ($D_{1,2}$; $D_{5,6}$) and also secondary assimetrical with respect to the center (see Figure 3 for fit results). It can be conclude, that the iron atoms in oxygen surroundings form clusters or high dispersed separated phase, with Moessbauer parameters typical for α-Fe_2O_3. Several coordination spheres at least having the structure of hematite are necessary to enhance Moessbauer spectra, typical for this oxide phase.

A second iron containing phase without hyperfine magnetic interaction is registered, as well. This is a contribution to the Moessbauer spectrum with parameters as follows: IS = 0.38 mm/s, QS = 0.8 mm/s and Irel = 10 %. The spectrum is a quadrupole doublet, which is typical for Fe^{3+} ions. It can be accepted that a small part of the iron atoms do not form big particles enough to form magnetic order structures. The large width of the quadruple doublet is impressing in the spectrum center, which is an evident indication for a different surroundings of the iron atoms. Obviously, here we can observe a substitution or bonding effect with oxygen including only some iron atoms.

The results of the TEM-study show that pigments synthesized with mineralizer are observed crystals of zircon with dimensions of 0,5-2,0μm. In both cases a certain tendency to aggregation is observed, which is more pronounced in Sample 1.

The synthesized pigments previously were washed and ground (30μm.) and then they were added to white zircon faience glaze (obtained from Coloronda Ltd. - Spain) - 5% quantity, the tiles were thermally treated in an industrial furnace at 1025°C for 50 min. The samples possess pink colour after thermal treatment.

4.CONCLUSIONS

The capability for the synthesis of a pink zirconium pigment with Fe^{3+}-ions incorporation has been proved. The optimal synthesis temperature has been established to be 900°C, utilizing Na_2SiF_6 as an effective mineralizer. ESR and Moessbauer spectroscopy studies show that the iron is only in Fe^{3+}- state with parameters close to α-Fe_2O_3. X-ray diffraction data shows that the main phase is $ZrSiO_4$ which is a suitable one for iron ions incorporation. From the practical point of view the pigments can be successfully applied for glazes intended for faience articles.

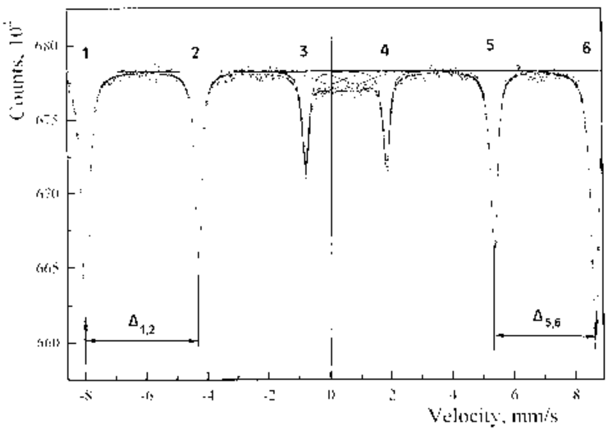

Figure 3.-Moessbauer spectrum of sample 2 at room temperature; thermal treatment conditions of the sample are marked in the text.

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