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$_2$O$_3$ 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°C. The best pigments have been added to white faience glaze.

Key words: pink pigment, zircon, color

1. INTRODUCTION

It is well known that the pigments from the ZrO$_2$ – SiO$_2$–Fe$_2$O$_3$ 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 fluoride 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$_2$O$_3$ 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$_2$O$_3$ at a molar ratio ZrO$_2$ : SiO$_2$ : Fe$_2$O$_3$ = 1:1:1. The zirconium dioxide used was chemically pure (ZrO$_2$ - 99,35%) and X-ray diffraction revealed that mineralogically it consisted of pure baddeleyite. The silicon dioxide used was washed and ground (50µm) from Kaolin JSCo- Bulgaria. X-ray diffraction indicate that it was pure gartz (SiO$_2$ - 99,62%). Fe$_2$O$_3$ was used as analytical reagent - MERCK. The concentration of the chromophoric ion is 5 at.% Fe from Fe$_2$O$_3$ used. As mineralizers have been used 6% wt. LiF + 4% wt. NaCl and 6% wt. Na$_2$SiF$_6$ (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 CuKα 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.

\[ ^{57}Co \text{ (Rh)} g \]

- source of radioactivity of 10 mCi have been used. Particle size determination have been determined by PHILIPS - TEM - EM 301G at 80kV.

3. RESULTS AND DISCUSSIONS

Figure 1 shows X-ray diffraction intensities of an iron (III) containing pigment with mineralizer Na$_2$SiF$_6$ 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. NaCl, the phase picture does not significantly differ, but samples at 1000°C are strongly sintered. The obtained results indicate that Na$_2$SiF$_6$ 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: \( a = b = 6,605902 \pm 0,001035 \) Å, \( c = 5,983344 \pm 0,001321 \) Å. The calculated parameters of pure ZrSiO$_4$ are: \( a = b = 6,604 \pm 2 \) Å, \( c = 5,979 \pm 2 \) Å (8).

Figure 2 shows the ESR spectrum of a sample with mineralizer Na$_2$SiF$_6$ 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 \( g \approx 2.05 \) and width \( \Delta H_{pp} = 250 \) G. and low intense one with \( g > 2.1 \) and \( \Delta H_{pp} = 500 \) 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 mostly 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. /\( g \approx 2.05 \) and \( \Delta H_{pp} = 250G/\) in the same time a new symmetric signal in the spectra of samples obtained at higher temperatures is observed with \( g \approx 2.9 \) and \( \Delta H_{pp} = 1400 \) G. These parameters are typical for magnetically

**TABLE 1  NOMINAL COMPOSITIONS OF THE PIGMENTS.**

<table>
<thead>
<tr>
<th>Index</th>
<th>Constituents , % wt.</th>
<th>Mineralizers , % wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO$_2$</td>
<td>SiO$_2$</td>
<td>Fe$_2$O$_3$</td>
</tr>
<tr>
<td>Sample 1</td>
<td>56.19</td>
<td>6.29</td>
</tr>
<tr>
<td>Sample 2</td>
<td>58.68</td>
<td>28.74</td>
</tr>
</tbody>
</table>

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- $\alpha$-SiO$_2$ respectively.

Figure 2.- ESR spectrum of sample 2 with Na$_2$SiF$_6$ used as mineralizer; heat treatment 1000 °C for 4 h.
coupled Fe\textsuperscript{2+} ions in silicate matrices. This result shows that the high synthetic temperatures of the pigments favor the Fe\textsuperscript{3+} inclusion in Zr-matrix. In any way the Fe\textsuperscript{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\textsuperscript{3+} coordination state i.e. not any contribution from Fe\textsuperscript{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\textsubscript{eff}) = 517 KOe and a relative peak intensity (I\textsubscript{rel}) = 90\%. It is clear that the checked Moessbauer parameters are closed to the 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: isomer shift (IS) = 0.38 mm/s, quadrupole splitting (QS) = 0.8 mm/s and I\textsubscript{rel} = 10 \%. The spectrum is a quadrupole doublet, which is typical for Fe\textsuperscript{2+} 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 0.5-2.0 \mu m. 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 (30 \mu m) 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\textsuperscript{3+}-ions incorporation has been proved. The optimal synthesis temperature has been established to be 900°C, utilizing Na\textsubscript{2}SiF\textsubscript{6} as an effective mineralizer. ESR and Moessbauer spectroscopy studies show that the iron is only in Fe\textsuperscript{3+}-state with parameters close to \alpha-Fe\textsubscript{2}O\textsubscript{3}. X-ray diffraction data shows that the main phase is ZrSiO\textsubscript{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.

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