

## EVALUATION OF SOLUTION COMBUSTION METHOD IN THE SYNTHESIS OF Fe-ZrSiO<sub>4</sub> BASED CORAL PIGMENT

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**Abstract:** Auto-ignited gel combustion process has been used for producing a red hematite-zircon based pigment. The combustible mixtures contained the metal nitrates and citric acid as oxidizers and fuel, respectively. Sodium silicate (water glass) was used as silica source for producing zircon phase. X-Ray Diffractometry, Electron Microscopy and Simultaneous Thermal Analysis were used for characterization of reactions happened in the resulted dried gel during its heat-treatment. L\* a\* b\* color parameters were measured by the CIE (Commission International de l'Eclairage) colorimetric method. This research has showed that solution combustion was unable to produce coral pigment as the end product of combustion without the need for any further heat treatment process.

**Keywords:** Coral Pigment, Solution Combustion, Zircon, Mineralizer, Sodium Silicate.

### 1. INTRODUCTION

Zircon is an important refractory material, which also finds application as a ceramic matrix in the high temperature pigments such as coral [1, 2]. In this pigment hematite as the color agent can be encapsulated by zircon clusters (core-shell phenomenon) and red ceramic pigments with high chemical and thermal resistance produce [3]. In the last few years, a significant amount of research has been performed on chemical methods to improve the properties of inorganic materials. Homogeneity in atomic scale, could give fine particles with uniform size distribution and large surface area [4]. Sol-gel process and other methods based on chemical reactions produce amorphous zircon powders which are further heat treated to develop crystalline zircon. A wide range of temperatures for zircon formation from amorphous powders have been reported, depending on the preparation conditions. Thus the lowest temperature found for complete zircon formation is about 1250°C (with a holding time of 2h) [1], using a new synthesizing method like solution combustion that is characterized by fast heating rates, short reaction times and relatively simple setting up was thought to be useful method for synthesizing zircon-based pigments. In addition, this process is less complicated than the other chemical method. The products of synthesis by combustion can be in powder form and usually

powders produced by this method are used as end products. In some cases it has been demonstrated that products by this process are superior to those prepared by conventional methods. Compared to solid-state reactions, the products of this synthesis method usually are more homogeneous. Besides, the most important advantage of this type of combustion reaction is the continuous formation of well-crystallized fine powders utilizing both external heating and the chemical energy released during combustion [2]. The synthesis of zircon phase at a lower temperature than conventional method is a notable feature of this method. Therefore, we decided to investigate the ability of solution combustion method for synthesizing coral pigment based on zircon-hematite. We had predicted that core-shell coral pigment as the end product of combustion without the need for any further heat treatment process. In the synthesis of zircon a wide variety of silicon-containing compounds such as fumed silica, tetraethylorthosilicate (TEOS), quartz, and colloidal silica had been used. At the present work sodium silicate (water glass) was used as a source of silica. Sodium silicate is very fine and highly reactive silica source.

### 2. EXPERIMENTAL

ZrCl<sub>4</sub> (Riedel-Dehaën), Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Merck number: 1.03898.1000), Sodium silicate (water

glass, Merck number: 5621.2500) and  $C_6H_8O_7 \cdot H_2O$  (Citric acid, Merck number: 8.18707.1000) were used as starting materials.  $Zr(NO_3)_4$  was prepared by dissolving of  $ZrCl_4$  in nitric acid. To produce one mol zircon, according to this equation  $SiO_2 + ZrO_2 \rightarrow ZrSiO_4$ , one mol of silica has to react with one mol zirconia. A molar ratio of hematite to zircon was measured to be (0.15). The adjustment of the pH was done by drop wise addition of ammonia to the solution. This neutralized solution (pH=7) was heated on a hot plate with continuous agitation to evaporate excess water, leading ultimately to thermal dehydration of the system and a viscous transparent gel. To achieve a perfect ignition of gel, this reaction was performed in an electric kiln which was preheated at 500°C. It is shown that external heating source can accelerate the combustion phenomenon [2]. The calcination of the samples was done at 850°C for 2h in closed aluminosilicate crucibles. Finally 3wt% LiF, NaF,  $MgF_2$  and KF were added separately to the resulting powder as the mineralizer and the samples were named ( $P_{Li}$ ,  $P_{Na}$ ,  $P_{Mg}$  and  $P_K$  respectively).

Simultaneous thermal analysis (STA) of the gel was carried out with a thermo analyzer (Netzsch-1640 model) at a heating rate of 20°C/min in static air. X-ray diffraction patterns (XRD) of the gel and the calcined powders were recorded with an X-ray diffractometer using  $Cu-K_{\alpha}$  radiation (Philips-3710). The powder morphology was investigated by a scanning electron microscope (Philips-XL30). The specific surface area was measured by a micromeritics surface area analyzer (Gemini), using nitrogen adsorption.  $L^*$   $a^*$   $b^*$  color parameters of 5wt% enameled samples in a tile glaze were measured following the CIE colorimetric method using (Color-Eye, 7000A) spectrophotometer. In this method  $a^*$ ,  $b^*$  and  $L^*$  represent the green - red, the blue - yellow and the brightness axis of a sample, respectively.

### 3. RESULTS AND DISCUSSION

In general fuels serve two purposes, a) They are the source of C and H, which on combustion form  $CO_2$  and  $H_2O$  and liberate heat. b) They form complexes with the metal ions facilitating homogeneous mixing of the cations in solution [5]. Complexing agents can be added to the

precursor solutions to avoid the formation of single oxides or precipitation. The reactivity of solution combustion depends on the fuel/oxidizer molar ratio (F/O). The fuel/ oxidizer molar ratio is determined by summing the total oxidizing and reducing valencies in the fuel compounds and dividing by the sum of the total oxidizing and reducing valencies in the oxidizer compounds [6,7]. In this experiment F/O molar ratio initially was chosen lower than 1 ( $F/O < 1$ ), however, after adding ammonia, the stability of the solution disappeared and precipitation of solid materials occurred. The above-mentioned problem was prevented by changing the F/O ratio to 1 ( $F/O=1$ ). It seemed that increasing the amount of citric acid as a complexing agent in the solution hindered metal ions from hydrolyzing, leading to stability and homogeneity in the starting materials. The auto-ignition nature of the combustion process of the gel was studied by thermal analysis (STA), with the results shown in Fig.1. The small exothermic peak with a weight loss of ~40% was attributed to combustion reaction procedure. The sharper exothermic one at about 500°C was associated with a weight loss of about 20wt% which seems to be due to burning of remaining organic residues. According to the results the amorphous fluffy product of ignition process contained residual carbon, which means that ignition reaction did not advance completely. This process was repeated for several times to achieve the perfect ignition and to get rid of residual carbon. However, the result was the same, so apparently the ignition reaction can not be completed in this system. Therefore, the fluffy powder of the combustion reaction was decarbonized in oxygen atmosphere at 650°C for 2h in an electric kiln.

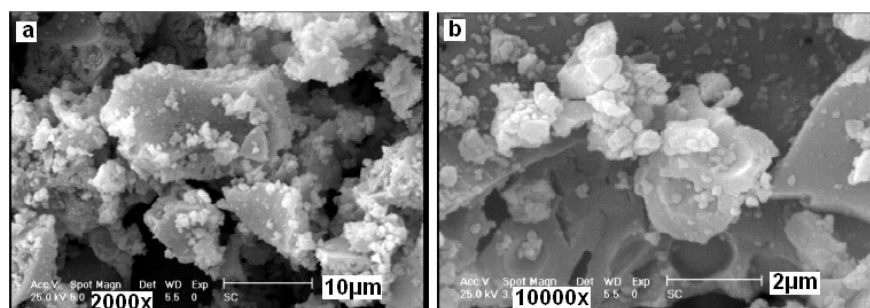


Fig. 1. STA trace of the gel.

Fig. 2 shows the XRD pattern of the as-received powder and the resulted sample after de-carbonization. As it can be seen, hematite ( $\alpha$ - $\text{Fe}_2\text{O}_3$ ), maghemite ( $\gamma$ - $\text{Fe}_2\text{O}_3$ ), tetragonal zirconia and sodium chloride have been crystallized during this process. The presence of maghemite in the sample arises from partial reduction of hematite. The presence of NaCl is due to the reaction between sodium silicate and zirconium chloride during the procedure. This salt acts as mineralizer in all the samples. As can be seen (in Fig. 2), zircon has not formed as the end product of the combustion process. Hematite is the color agent for coral pigment; however it seems that a part of it, due to residual carbon and non-oxide atmosphere has been transformed to maghemite. Therefore, it seems that solution combustion is not a suitable method for producing coral pigment. High ignition temperature was not enough to produce zircon phase as a final product, therefore our prediction was not confirmed. Also residual organic materials led to decrease in the amount of hematite phase and the formation of various polymorph of iron oxide formed. Fig. 3 shows the morphology of the de-carbonized product. Powder consists of porous and irregularly shaped aggregates with different size.



**Fig. 2.** XRD pattern of a) as-received powder b) de-carbonized powder.



**Fig. 3.** SEM micrographs of the de-carbonized powder (at different magnifications).

Exothermic reaction, associated with the decomposition of nitrates and the oxidation of fuel produced the large volume of gases and therefore a porous product (Fig. 3). Specific surface area of this powder was  $27\text{m}^2/\text{g}$ . To achieve zircon phase at lower temperature the effect of various mineralizers on encouragement of zircon crystallization was examined by addition of mineralizers into the milled de-carbonized combustion product. XRD patterns (Fig.4) indicates the influence of lithium, magnesium, sodium, and potassium sources in this regard. As illustrated in Fig. 4, lithium florid was the most effective mineralizer among the other mineralizers on the formation of zircon and hematite phases. As mentioned before NaCl as extra mineralizer was the same for all the samples. The quality of synthesized pigment depends considerably on the crystallized zircon and hematite; these minerals were considered as critical parameter for assessment of the efficiency of mineralizer. According to this criterion, the following order can show the efficiency of the used mineralizers:

With regard to the formation of zircon:

$\text{LiF} > \text{MgF}_2 > \text{NaF} > \text{KF}$

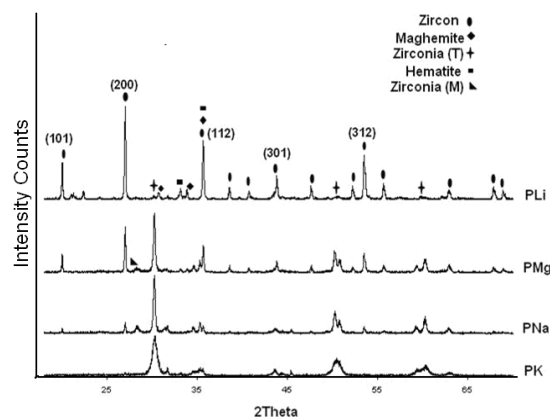
With regard to the formation of hematite:

$\text{LiF} > \text{MgF}_2 > \text{NaF} > \text{KF}$

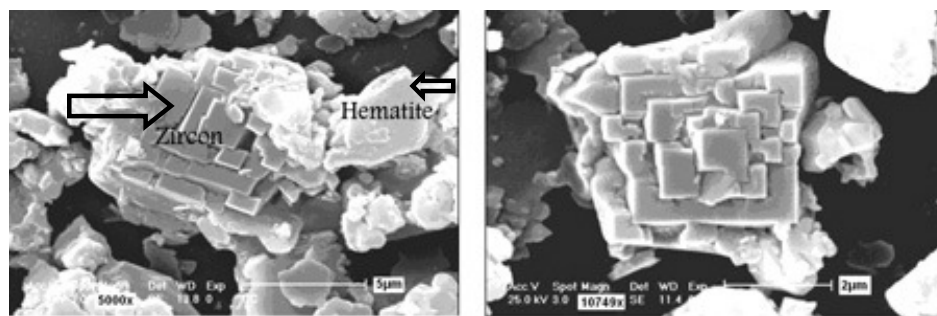
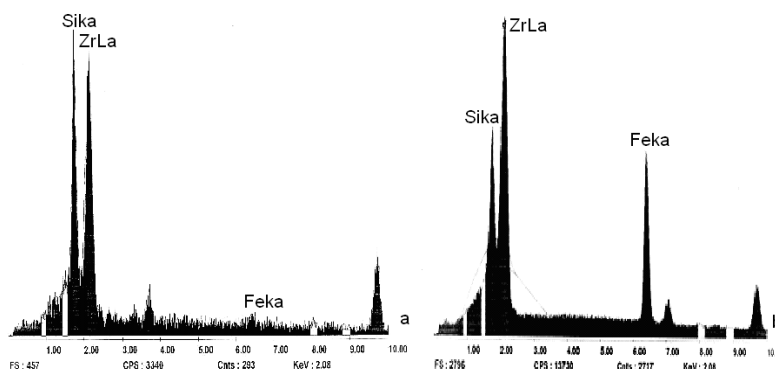
In fact, hematite (color agent) has not formed in presence of NaF and KF. On the other hand, maghemite has been crystallized in all samples. The presence of this mineral in the heat-treated powder indicates that some of the iron oxide particles have been reduced during firing procedure, which led to the formation of an unwanted maghemite phase. However, none of the fired glazes, containing these prepared samples, showed the desirable coral appearance (Table 1). Fig. 5 shows the SEM micrographs of  $\text{P}_{\text{Li}}$  pigment. EDX analysis indicates that plate like crystals are zircon (Fig. 6).

**Table 1.** CIE L\*a\*b\* parameters of fired samples and reference pigment 5wt% enameled in a tile glaze.

Sample	a*	b*	L*
PLi	15.771	22.217	78.357
PMg	8.871	24.699	78.239
PNa	5.973	20.485	80.141
PK	5.637	21.469	82.939
Reference sample (Wanxing GS 669)	30.293	24.349	47.466

**Fig. 4.** XRD patterns of different mineralizers.

Zircon and hematite particles in this microstructure have formed separately. In other words core-shell phenomenon was not achieved

**Fig. 5.** SEM micrographs of  $P_{Li}$  pigment (at different magnifications).**Fig. 6.** EDX analysis of a) zircon particles b) hematite particles.

and hematite particles were not encapsulated within zircon crystals [3]. The free iron oxide particles were dissolved in the ceramic glaze and red coral pigment was not achieved. CIE L\*a\*b\* parameters of enameled samples in comparison with an enameled reference coral pigment (Wanxing, GS 669, China) is given in Table 1. All samples fast fired at 1050°C for 5 minute. As shown in Table1, even the best-synthesized sample ( $P_{Li}$ ) has a considerable lower red parameter ( $a^*$ ) and higher lightness ( $L^*$ ) hue than the reference ones.

#### 4. CONCLUSIONS

Solution combustion method was not a desirable method for obtaining coral pigment. Because of incomplete ignition and residual carbon, part of hematite particles (color agent) transformed to un-wanted maghemite phase. In addition effective inclusion of hematite particles in zircon clusters was not achieved. Zircon phase was not obtained as final product from solution combustion method, although adding flux agent (mineralizer) helped to form zircon phase. LiF was the best mineralizer for producing zircon and hematite phases amongst all the other mineralizers used.

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