ISSN : 0974 - 7486 Volume 7 Issue 2

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 7(2), 2011 [90-93]

Encapsulation of nano hematite into zircon-silica matrix as a non toxic red ceramic pigment

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Received: 6th October, 2010 ; Accepted: 16th October, 2010

ABSTRACT

The hematite as a natural and non toxic red ceramic pigment has been known since prehistoric times but color shade of hematite becomes unstable with temperature and need to protect with a suitable matrix. The best red shades are obtained by the inclusion of hematite in silica casings. Zircon has the best thermal and chemical stability but it is more rare and expensive than silica, so in this research a fraction of zircon is substituted with silica crystals. A Sol-Gel method has been applied in order to improve the inclusion efficiency of hematite into silica and zircon crystals; Iron sulfate was used as Fe precursor and matrix agents were zirconium chloride and colloidal silica. Continuous changes in color were measured by comparing L*-a*-b* values of the heated samples. TEM analysis on calcined powders shows hematite single crystals with spherical morphology and diameter of 5-10nm that were occluded with silica-zircon crystals successfully. Due to its chemical and thermal stability, the pigment of hematite-silica-zircon system may be considered as a suitable red pigment for ceramic manufacturing by fast firing cycles.

KEYWORDS

Ceramic;
Inclusion pigment;
Non toxic red pigment;
Hematite-silica-zircon;
Nano composite.

INTRODUCTION

In ceramic applications including glazes, ceramic bodies and porcelain enamels, pigments are dispersed in the media and must do not dissolve. In conclusion, powders used for coloring ceramics must show thermal and chemical stability at high temperature and must be inert to the action of molten glass (frits or sintering aids)[1]. These characteristics limit ceramic pigments to a very small number of refractory systems which are fully reacted and relatively inert to the matrix in which they are dispersed[2-4]. This need for great chemical and thermal stability has dominated research and development in recent years especially towards new red or pink pigments. In particular the interest is directed to the development of inclusion pigments which make utilizable colouring substances suffering the industrial thermal and chemical conditions by occluding them in a stable glassy or crystalline matrix (heteromorphic pigments). The inclusion or encapsulation of a reactive, colored or toxic crystal into a stable crystalline matrix, gives a protection effect to the crystal guest by the host crystal. The

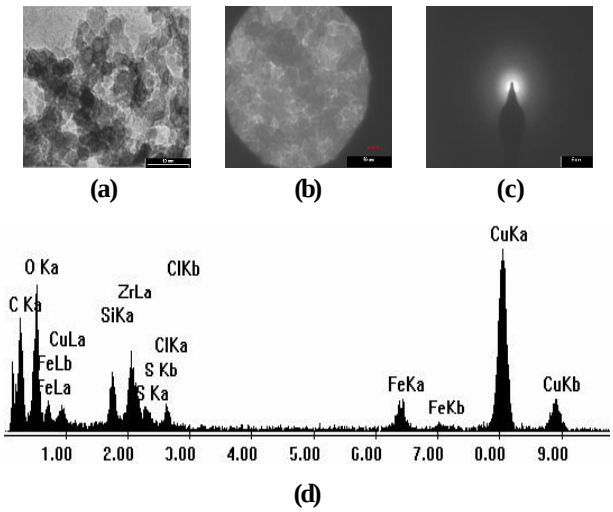

Figure 1 : TEM Micrographs of the dried powders and its EDX a) image, b) selected area diffraction zone, c) X ray pattern of it that indicates amorphous powder and d) EDX

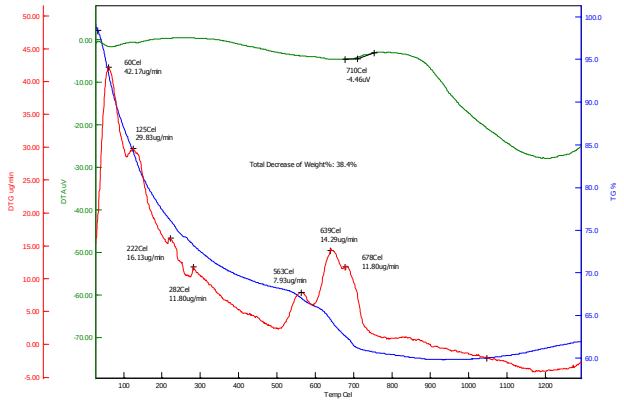

Figure 2 : Simultaneous thermal analysis (TG and DTA) of the dried powder. Data Name: NO:1.tgd, Module:TG/DTA, Sample name: dr hosseini, Sample weight: 1.740 mg, Reference name: empty pan, Reference weight: 0.000 mg. Comment:- Operator: icpc, Gas 1: none, Gas 2: Air, Pan: alumina. Temperature program:- Cel Cel Cel/min min s 1*30 1300 15 0 0.5

guest crystals are inactivated into the matrix[5-7].

Silica may be considered to have a relatively low price giving it a potential to be used in occluded pigments as a matrix, due to its thermal and chemical stability towards glassy phases.

The aim of this work was to study the optimization of synthesizing red inorganic pigments for ceramic applications. In order to improve the inclusion efficiency of hematite into silica and zircon matrixes, the aqua sol-gel route has been applied as chemical processes which improve microstructural characteristics and control particles morphology[8-10].

EXPERIMENTAL

Samples of the SiO_2 – $1.4Fe_2O_3$ –$ZrSiO_4$ were prepared using the Sol-Gel method. A concentrated aqua solution was prepared by adding iron sulphate ($FeSO_4.7H_2O$, Merck) in the dionized water, refluxing at 70°C for 30 minute. Then, the required colloidal silica and zirconium chloride (Merck) was added to the aqueous solutions by Drops of concentrated solution. The system was continuously stirred and kept at 70°C until the pH stabilized equal to 5. The resulting light yellow gel was dried at 110°C and then fired. In order to determine the effects of firing temperature, the powders were fired at temperatures ranging from 900 to 1100°C in an electrical furnace with a soaking time of 3 h. The fired samples were micronised, wet milled in water and finally dried at 110°C.

To identify the crystalline phases that were present in the raw and fired samples, X-ray diffraction patterns were collected using a conventional powder technique in a Siemens Diffractometer (D500 mod) employing Cu Ka Ni-filtered radiation. To define the color developed about the samples, a UV-Vis spectrophotometer with analytical software for color measurements (PERKIN ELMER Spectrometer Lambda 19, UV/VIS/NIR, Standard Observer: 10°) has been used. L*, a*, b* color parameters have been measured following the CIE (Commission International de l'Eclairage) colorimetric method. In this method, L* is the lightness axis (black 0) → white (100)), a* is the green (-) → red (+) axis, and b* is the blue (-)→ yellow (+) axis. Powders microstructure characterization and morphology of the occluded hematite has been studied by transmission electron microscopy (Jeol JEM 2010).

RESULTS AND DISCUSSION

Morphology of the hematite particles can be detected just by TEM analysis because they are very fine and occluded by the matrix. The spherical nano hematite crystals have been successfully occluded in silica and zircon particles after firing. Figure 1 report the TEM images of not calcined sample. In this case, sample is constituted of very fine and spherical particles. Location of Iron chloride crystals were not been detected. It seems that they are occluded by the amorphous phase because the X ray pattern of the dried powder in figure

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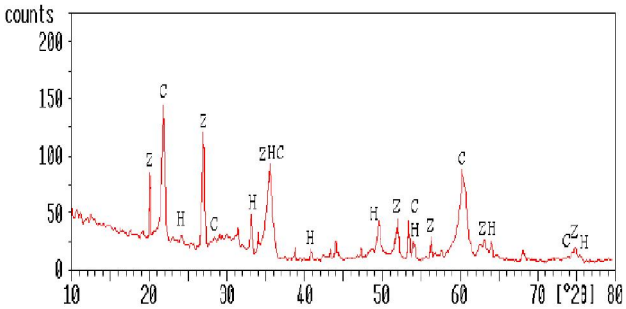


Figure 3 : XRD patterns of a) dried powder b) fired sample after calcination in 1000°C, H: Hematite, C: Cristobalite, Z: Zircon

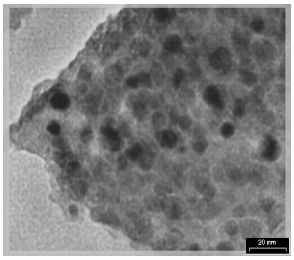
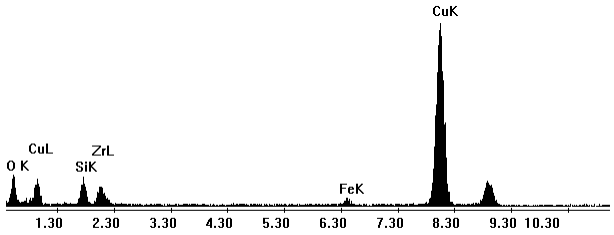
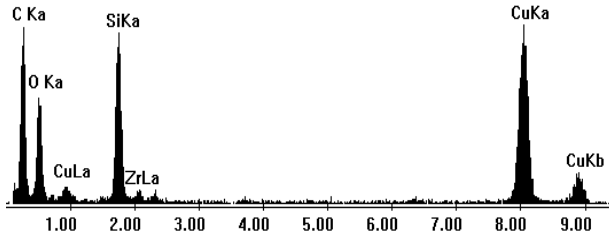


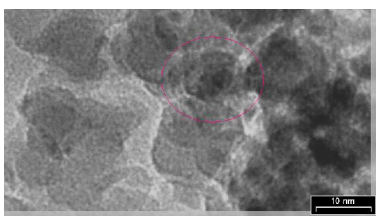
Figure 4 : TEM Micrographs of the fired powders at 1100°C/3h



(a)



(b)



(c)

Figure 5 : TEM Micrographs of the fired powder at 1000°C/ 3h, and EDX analysis of the (a) black spherical circles and (b) grey background of this powder

TABLE 1 : CIELab values of powder samples (a) dried gel and (b) calcination temperature was 1000°C

	Standard	L*	a*	b*	C*	h°
	D65	82.304	-2.448	60.57	60.622	92.314
a	A	84.925	6.291	59.44	59.772	83.958
	CWF_2	84.523	-2.472	68.33	68.379	92.072
	D65	57.797	19.069	19.08	26.974	45.014
b	A	61.133	22.142	24.22	32.819	47.572
	CWF_2	59.22	14.084	21.97	26.1	57.342

1c did not show any light dot related to a crystalline plate. Figure 2 is related to the STA analysis and shows all of the reactions have been take placed before 800°C and total decrease of weight percent is 38.4%. The main reaction in mentioned aqua Sol-Gel method was:

$$2FeSO_4 + ZrCl_4 \rightarrow Zr(SO_4)_2 + 2FeCl_2$$

Due to heat treatment obtained zirconium sulfate and Iron chloride have been decomposed and oxidized to very fine particles of zirconium oxide and hematite respectively. Therefore the real precursor of red colored agent of this synthesized pigment (hematite) is Iron chloride that it will affect on hematite morphology[5]. It seems that very fine and aggressive zirconium oxide particle in situ react with nano silica particle while the crystal growth and diffusion have been taking placed. High surface area energy of the fine particles has been caused to reducing of reaction temperatures.

CIELab values of dried gel and fired powder samples are reported in TABLE 1. Base on the D65 standard of colorimeter results in TABLE 1, the red factor equals to 19.069 and it is very near to yellow factor (19.08). These data report that the obtained pigment after calcinations has red brown shade.

According to XRD results, it can be seen in figure 3; interested three phases of hematite, cristobalite and zircon have been crystallized after calcination in 1000°C in the samples and before of this temperature just hematite can be detected (not shown).

Figure 4 and 5 are TEM Micrographs of the fired powders at 1100°C/3h and at 1000°C/3h respectively. Those present the size, morphology and location of the hematite particles that have been occluded in the silica-zircon matrix. Even, it can be seen the planes of a hematite crystal that are regular like single crystals. TEM Micrographs shows black spherical circles with 5-10 nm diameters in the sintered and uniformed of grey

matrix. EDX analysis of the black spherical circles has been detected elements of iron, zirconium and silicate, therefore figure 5a indicate that black spherical circles are hematite particles with spherical shapes and presence of Zr and Si is due to encapsulation of hematite by the matrix, as can be seen similar to egg (red sign). Figure 5b is related to EDX analysis of grey background of the same powder (far from black spherical circles) and shows the matrix contain just Zr and Si without any dissolved Fe ions. Increasing of sintering temperatures at 1100°C/3h did not show any effect on hematite morphology but it might be important about red shade because of oxygen reduction[3].

CONCLUSION

In order to prepare a hematite–cristobalite-zircon inclusion red ceramic pigment, Sol-Gel process with the colloidal silica, Zirconium chloride and iron (II) sulfate were been synthesized.

Nano-sized and homogeneous hematite particles were obtained into sintered cristobalite-zircon matrix after heat treatment at 1000°C/3h and 1100°C/3h. Occluded hematite particles have been spherical shapes with 5-10 nm diameters. Changes of sintering temperatures did not show any effect on hematite morphology but it was important about red shade, inclusion efficiency and thermal-chemical stability of the pigments. Due to its high inclusion efficiency, this heteromorphic pigment may be considered to be a suitable red pigment for ceramic applications.

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