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Nano encapsulation of hematite into silica matrix as a red inclusion ceramic pigment

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ABSTRACT

The hematite as a natural and non toxic red inorganic 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 matrixes. A co-precipitation method has been applied in order to improve the inclusion efficiency of hematite into silica crystals; iron sulfate was used as Fe precursor and precipitating agent was ammonia. Effects of the single flux agent (NaF and NaCl) and binary flux agent (NaF·NaCl), have been studied. Continuous changes in color were measured by comparing L^*-a^*-b^* values of the heated samples. TEM analysis on heat treated powders shows some hematite single crystals that were occluded with silica crystals successfully. Due to its chemical and thermal stability, the hematite/silica pigment may be considered as a suitable red pigment for ceramic manufacturing by fast firing cycles.

1. Introduction

In ceramic applications including glazes, ceramic bodies and porcelain enamels, pigments are dispersed in the media and must not be dissolved. 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 [2–7]. 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 coloring 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.

Hematite–silica heteromorphic pigment based on silica crystals that protect the occluded red α-Fe_2O_3 chromophore crystals, is usually utilized even if the traditional preparation led to powders that suffer the glaze composition and the sintering temperature. In particular, in order to achieve high efficiency of chromospheres agent encapsulation, the matrix sintering and/or crystallization must be synchronized with nucleation and growth of the occluded chromophore agent. Crystallization, sintering and inclusion process are thus considered to take place simultaneously and consequently, the control of particle size of raw powder is one of the main steps to control [6].

In this work, in order to improve the inclusion efficiency of hematite into silica matrix, co-precipitation routes have been applied as chemical processes which improve microstructures characteristics and control particles morphology [1,3,6]. In particular the effect of the ammonia precipitant agent has been evaluated. Several additives (mainly alkaline or alkaline earth halides, etc.) known as mineralizers, are also used in the ceramic route with the aim to obtain pigment at lower temperatures and/or within lower soaking times. In this research, the addition of mineralizers, NaF and NaCl in different ratio, have been also investigated in order to optimize the pigment calcinations temperature and obtain a better control on the color developed in an industrial glaze.

2. Experimental procedure

Samples of $1SiO_2$–$0.2Fe_2O_3$–0.2Mineralizer (if case) composition have been prepared by co-precipitation (P) route (Fig. 1). A 0.5 M aqueous solution of final composition has been prepared adding iron sulfate ($Fe_2SO_4 \cdot 7H_2O$, Aldrich) in the required mole ratio to aqueous suspension of colloidal silica (LUDOX, 30% in SiO_2). In mineralized samples 0.2 mol of NaF, NaCl, NaF·NaCl or NaF·2NaCl (all Aldrich) have been added to the aqueous solutions before reaction. Concentrated ammonia solution droplets are then added to the mixture, continuously stirred and main-

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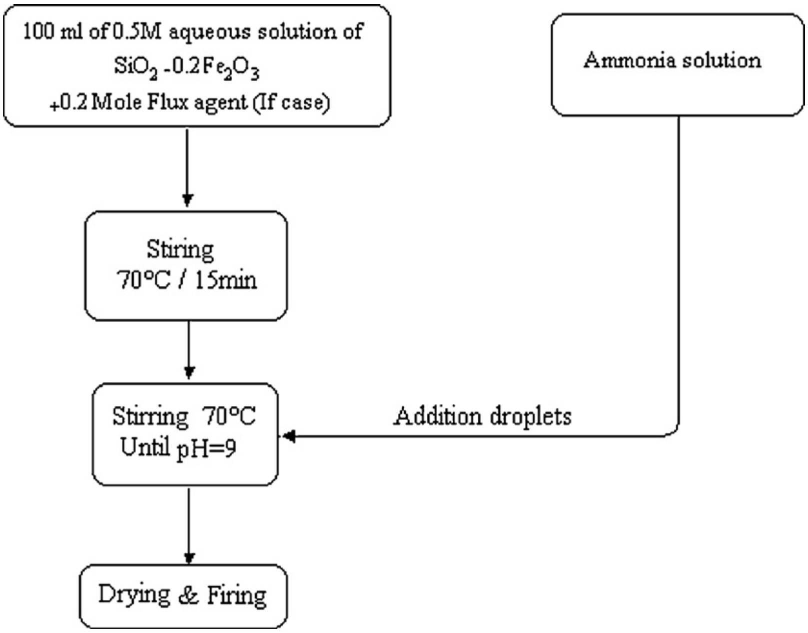

Fig. 1. Flux diagram of coprecipitation method used.

tained at 70 °C till pH is stabilized to 9. The dark green coprecipitate obtained has been then dried at 110 °C and fired. During the co-precipitation and drying steps, the green color, due to the iron (II) presence, changes partially into red color due to iron oxidation exposed at free atmosphere. In order to avoid the bulk oxidation of the samples the precipitated powders have not been filtered but directly dried and heat treated [6].

In order to determine the effects of the firing temperature and mineralizer compositions, the powders have been fired at temperatures ranging from 800 to 1100 °C in an electrical furnace with soaking time of 3 h. Fired samples have been micronized and washed in a ball-mill in water media and dried at 110 °C.

In order to identify the crystalline phases present in the raw and fired powders, X-ray diffraction patterns have been collected using a conventional powder technique in a Siemens Diffractometer (D500 mod) with Cu Kα Ni-filtered radiation. In order to define the color developed by the samples, a UV–vis spectrophotometer with analytical software for color measurements (PERKIN ELMER Spectrometer Lambda 19, UV/VIS/NIR, 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 hematite morphology have been studied by transmission electron microscopy (Jeol JEM 2010 with GIF gatan Multiscan Camera 794 and Software Digital Micrograph 3.1).

3. Results and discussion

3.1. Thermal evolution of crystalline phases by XRD analysis

XRD results and CIE $L^*a^*b^*$ color parameters of powdered pigments are reported in Table 1. All the raw powders present ammonium sulfate due to precipitant agent used. The precipitation produces an amorphous phase where oxygen bridges between metal ions and hydroxyl plays an important role together the possibility of crystallization of neutral salts in drying [8].

In all dried samples, there are not any peaks of FeOOH or silica precursor. This can be due to production of very fine or amorphous FeOOH that cannot be detected by XRD. Regarding the heat treated powders, the use of mineralizers affect the silica crystallization and promotes tridymite phase formation instead of crystobalite; the use of two mineralizers allow the crystallization of tridymite crystals also in dried powders (Fig. 2) although the crystalline structure changes on heating from hexagonal to monoclinic. Comparing the CIE $L^*a^*b^*$ values, it seems that stronger red shade is obtained by using two mineralizers, especially in the ratio NaF·2NaCl at calcinations temperature as lower as 800 °C. In fact, the a^* parameter,

Table 1
Crystalline phases and CIELab values of powder samples as a function of calcination temperature.

Mineralizer	T (°C)	Phase composition (XRD)	Color $L^*/a^*/b^*$
Without	Raw	Ma	Maroon
	900	H	45.8/25.8/23.4
	1000	H, C(w)	43.5/25/23.1
	1100	H, C(s)	41.9/24.2/22.8
NaF	Raw	Ma	Green-yellow
	900	H, C(w)	45.1/26.8/21.3
	1000	H, C, T(w)	43.0/25.4/20.1
	1100	Local melting H, C(w), T_m	Brown
NaCl	Raw	Ma	Green-yellow
	900	H, C(w)	44.9/26.5/21.1
	1000	H, C(w), T	42.5/25.3/19.4
	1100	Local melting, H, T_m	Brown
NaF·NaCl	Raw	Ma, N(w), S, T_H	Light green
	800	N(w), H, T_m(w)	46.4/26.6/22.1
	900	N(w), H, T_m(s)	44.8/25.2/20.3
	1000	Local melting, H, T_m	Brown
NaF·2NaCl	Raw	Ma, N, S, T_H	Brown
	800	N(w), H, T_m	43.2/28.9/24.1
	900	N(w), H, T_m(s)	44.2/27.8/23.1
	1000	Local melting, H, T_m	Brown

Ma: $(NH_4)_2SO_4$ (mascagnite 00-001-0363); H: hematite (00-033-0664); C: crystobalite (01-076-0937); N: Na_2SO_4 (01-075-1979); T_m: tridymite-monoclinic (01-071-0197); T_H: tridymite-hexagonal (01-089-3141); S: NH_4Cl (00-001-1037); w: weak; s: strong.

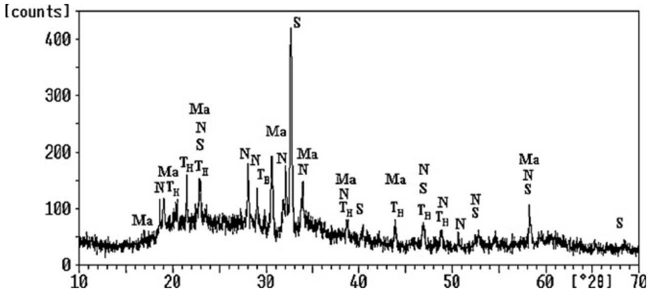

Fig. 2. XRD patterns of PI dried powder sample with NaF·NaCl mineralizer. Ma: $(NH_4)_2SO_4$; N: Na_2SO_4; T_H: tridymite-hexagonal; S: NH_4Cl.

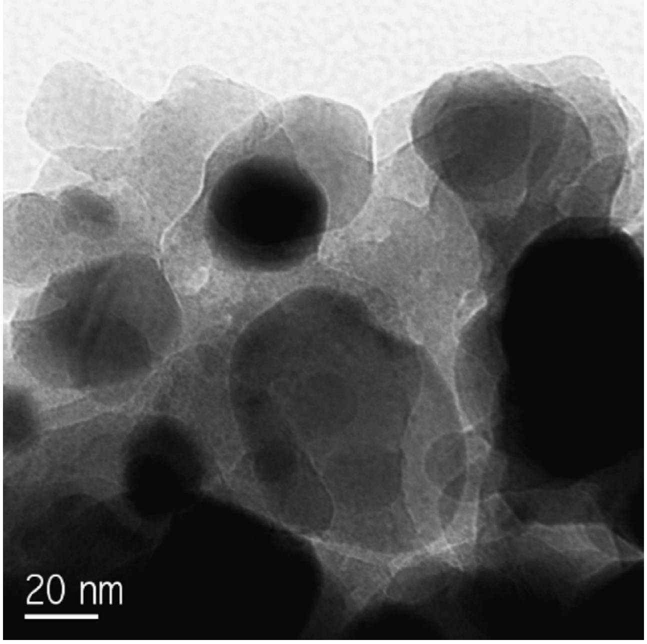

Fig. 3. TEM micrographs of unfluxed sample fired at 1100 °C/3 h.

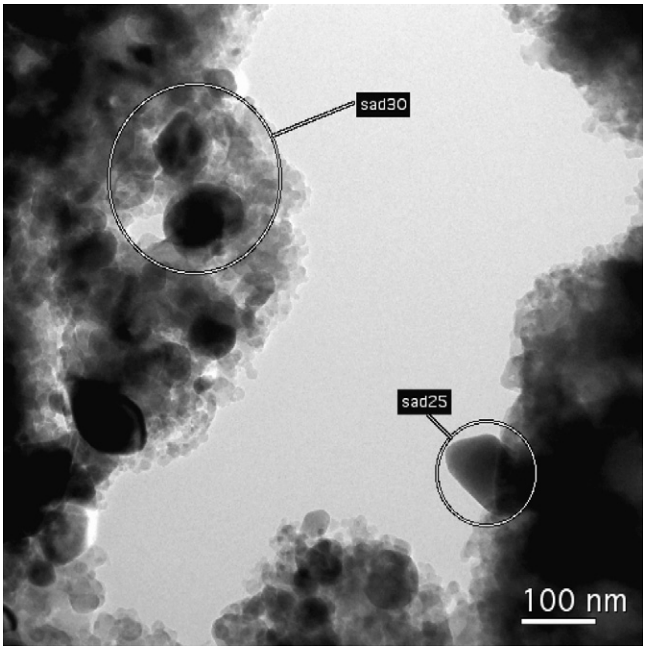

Fig. 5. TEM micrographs of NaCl fluxed powders fired at 900 °C/3 h.

indicating the predominance of the red shape, has the higher value ($a^* = 28.9$). At higher temperature (1000 °C), however, two mineralizers allow to local melting of the silica matrix due to eutectic compositions formations [9].

3.2. Microstructural analysis of samples by TEM techniques

Morphology of hematite particles can be detected only with TEM analysis. The spherical hematite crystals have been successfully occluded in silica particles after firing about all samples. Fig. 3 reports the TEM images of sample without mineralizer that has been heat treated at 1100 °C/3. In this case, sample is constituted of very fine particles even after calcinations and the morphology of hematite particles is spherical with diameter of approximately 20–30 nm. Correlating this evidence with the CIELab values (Table 1), it seems that the poor red shade of these powders is due to this nanometric size of hematite crystals [10–12].

Figs. 4 and 5 indicate that the NaF and NaCl single flux agent additions influence on the iron particles growth and promote sizes, even which the diameter of spherical hematite particle becomes as longer as about 100 nm (Fig. 4). This behavior it might be due to some surfaces energy effects [4]. It seems that NaF is more effective on hematite crystal growth that it should be due to presence of evaporation of fluorinated phases as F_2, HF or SiF_4. Moreover the shapes of hematite particles have some changes, especially in case of NaF mineralizer. It is obviously that apply mentioned single mineralizer promote some crystalline plants results other shapes such as lozenge and or hexagonal.

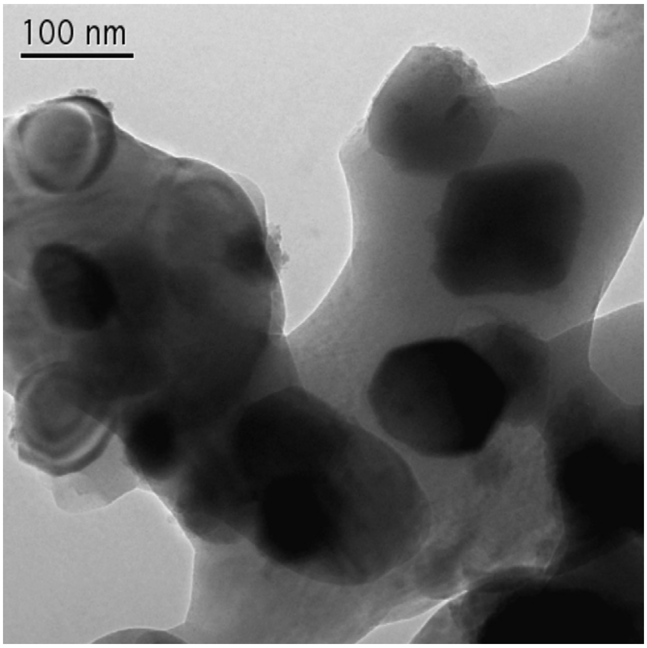

Fig. 4. TEM micrographs of NaF fluxed powders fired at 900 °C/3 h.

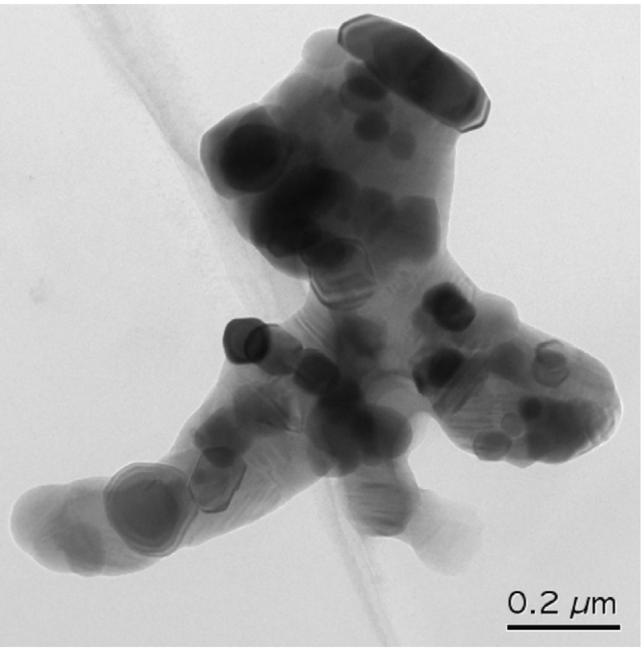

Fig. 6. TEM micrographs of NaF·2NaCl fluxed powders fired at 900 °C/3 h.

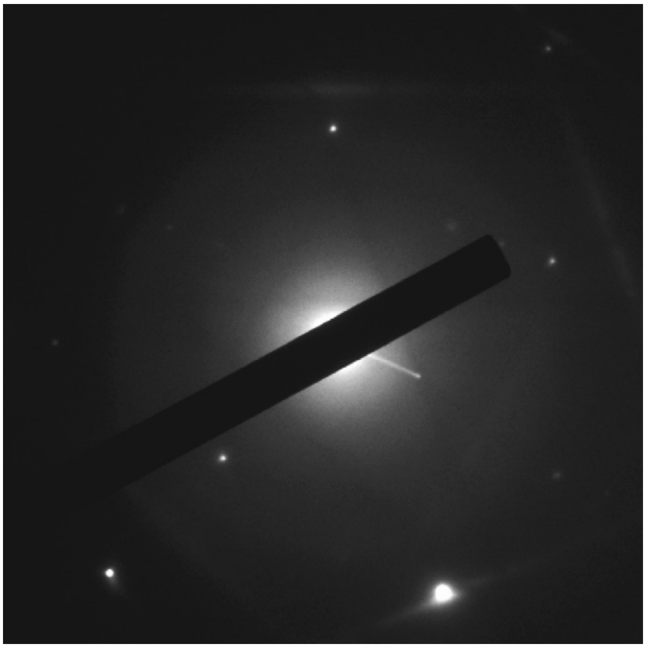

Fig. 7. Selected area diffractions (SAD) image has been obtained from camera lens number 25 on hematite particle that have been shown in Fig. 5 (sample with NaF fired at 900 °C/3 h).

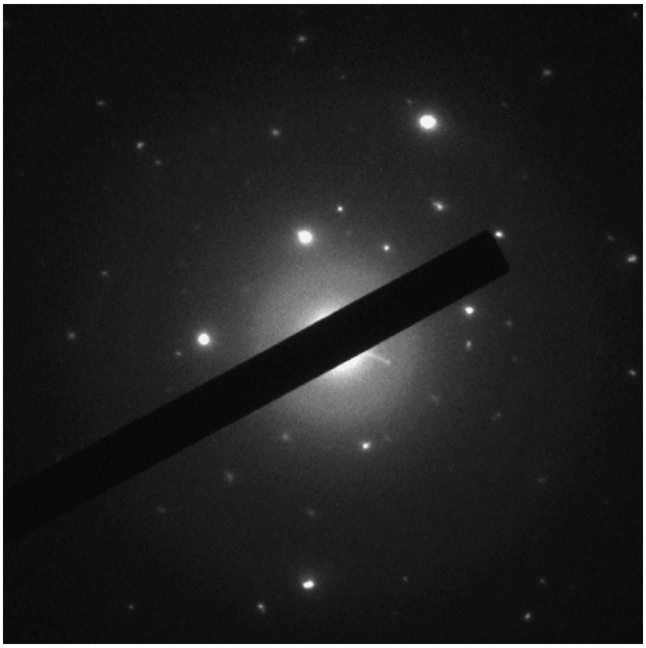

Fig. 8. Selected area diffractions (SAD) image has been obtained from camera lens number 30 on hematite particle that have been shown in Fig. 5 (sample with NaF fired at 900 °C/3 h).

The use of NaF·NaCl and NaF·2NaCl binary mineralizers result in more changes on spherical shape of the hematite crystals and tend it to rectangle particles that are shown in Fig. 6, about NaF·2NaCl mineralizer. Therefore binary mineralizers result better morphology and particle size around 50–100 nm as can be concluded base in Table 1.

Selected area diffractions (SAD) on random hematite particles were shown in Figs. 7 and 8 in order to confirm that nano hematite are single crystals in all samples, even about bigger particles which had been shown in Fig. 5.

3.3. *Colorimetric analysis of samples by CIELab values*

Colorimetric results in Table 1 indicate that single mineralizer addition produce similar results but NaF produces slightly better red shades, perhaps because hematite shows bigger size in this case [11–12]. 0.2 Weight percent of Synthesis pigment by NaF·2NaCl mineralizer and heat treated at 900 °C (with 44.2/27.8/23.1 CIELab values) in conventional stoneware body tile, results 41.28/30.68/23.74 CIELab values.

4. Conclusion

In order to prepare a hematite–silica inclusion red ceramic pigment by a co-precipitation process, silica particles sintered and crystallized to crystobalite and or tridymite (depend on applied mineralizer) occluding and covering the small crystalline particles of in situ formed nano hematite. X-ray diffraction patterns and transmission electron microscopy results indicate that:

1. Spherical hematite nano particles were provided with diameter of approximately 20–30 nm by ammonia as a precipitant agent and without mineralizer.
2. The dimensions of the hematite particles depend on the mineralizers used.
3. The morphology and dimensions of the hematite particle directly affect the shade of the red pigments obtained; the silica structure does not influence shade.
4. The use of mineralizers effects the silica crystallization and promotes tridymite phase formation instead of crystobalite.
5. The use of binary mineralizers allows the crystallization of tridymite crystals also in dried powders.
6. The stronger red shade is obtained by using two mineralizers, especially in the ratio NaF·2NaCl at calcinations temperature as lower as 800 °C.
7. It seems that NaF is more effective on hematite crystal growth than NaCl.
8. In situ formed nano hematite is single crystals by mentioned method.

Due to its chemical and thermal stability, this heteromorphy pigment may be considered to be a suitable red pigment for ceramic applications.

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