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Synthesis Fe-Cr-Ti-(Al_2O_3) Nano Composite Pigment

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Abstract

The present work relates to a process for the production of nano particles pigment and relates particularly to the production of nano composite powders consisting of individual particles with sizes in the range of 10 nm to 100 nm. This process involves the mechanically activated chemical reduction of reducible metal compounds during milling, to refine and manufacture nano composite powder. Nano particle pigment for ceramic glazes was obtained by mechanochemical insertion of Fe-Cr-Ti in an α-Al_2O_3 host matrix. Iron, chromium and titanium oxides were reduced by milling with metallic aluminium with subsequent formation of additional Al_2O_3 by oxidation of aluminium. XRD (X-ray diffraction) and BET (Brunauer, Emmett and Teller) have been used for investigation of phases and particle size of powder.

Keywords

Mechanochemical, Nano Composite Powders, α-Al_2O_3, Cr-Fe-Ti

1. Introduction

Chemical production methods, such as thermal decomposition and precipitation, reactive sintering and, more recently, co-precipitation, sol-gel and *in situ* reduction reactions are currently being studied for the preparation of a wide range of powders. State of the art on mechanosynthesis of alumina can provide large quantities of ceramic powders for industrial applications [1]-[5]. Solid-state displacement reactions proceed generally by diffusional transformations whereby two or more reactants form new product phases. Such reactions are of considerable interest for producing ceramic/ceramic or metal/ceramic composites *in situ* with novel microstructures and possibly improved properties. The synthesis of metal/oxide composites using gas/solid equilibrium or thermite

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reactions was driven by combustion synthesis or by reactive ball-milling (mechanosynthesis) of a powder mixture of aluminum (or another metal) and a metal oxide [6]. Alumina has been much used in structural ceramic applications because of its excellent mechanical properties, good chemical stability, and high temperature characteristics. These $Al_2O_3/Cr_2O_3/Fe_2O_3/TiO_2$ composites demonstrated superior mechanical properties to those of the matrix phase due to outstanding ability to resist high-temperature erosion at temperatures up to 1000˚C [7]. Many alumina-based composites were thus synthesized by reduction reactions induced during ball-milling. Materials obtained by mechanosynthesis are characterized by crystal sizes typically in the 10 - 100 nm range and are therefore classified as nanostructured [6]. Nano-pigments are organic or inorganic substances, insoluble, chemically and physically inert into the substrates or binders, with a particle size less than 100 nm [8]. Searching for a suitable preparation method of nanometer particles and studying the structure and other properties of nanometer materials are among the important issues involved for nanometer science applications. The present work aimed at the development of new ceramic pigments employing new technologies of production. Pigments have been prepared by mechanosynthesis (Cr, Fe and Ti) in α-Al_2O_3 host matrix in order to obtain new color tonalities for chemically and thermally stable substances.

2. Material and Methods

2.1. Pigment Preparation

The pigment compositions are given in **Table 1**. The composite batches were prepared from reagent grade powders: chromium oxide (Cr_2O_3, 99.8%), titanium oxide (TiO_2, 99.7%), alumina (Al_2O_3, 99.8%), Iron oxide (Fe_2O_3, 99%) and metal aluminum (Al, 99.4%). The powders (18 grams) were introduced in the vial together with the grinding balls (2 kg with diameter 25 mm, giving a ball-to-powder ratio of 40:1), both of carbon steel. The vial was sealed. Ball milling was carried out under the argon atmospheric condition with 1.5 bar pressure for 30 h.

2.2. Process Control Agent (PCA)

PCA is used for preventing excessive cold welding during mechanical milling of a powder mixture, that cause coarsening of powders. Intensity of cold welding of ductile material is high. PCA is most important agent for reaching nano-powder, most of them are organic material that absorbed by surface and prevent from powder agglomeration. PCA used in this study was stearic acid 0.03 wt%.

2.3. XRD and Particle Size Distribution

The milled products were characterized by X-ray diffraction (XRD), (Siemens, D-500) using Cu Kα (Kα, 0.1541 nm) radiation at 40 kV and 20 mA setting and in 2θ range from 5˚ to 70˚). The mean crystallite size was calculated from the method described elsewhere [9] [10]. Using the full width at half maximum (FWHM) of the X-ray peaks corrected for instrumental broadening and taking into account strain effects. The particle size distribution analysis was performed using a laser particle size analyzer (Mastersizer 2000, Malverm, UK). Scanning electron microscopy was performed by a VEGA/TESCAN model.

2.4. Colorimetry

The L^*, a^* and b^* color parameters of samples were measured using the Spectrophotometer SP64, in the 360 - 750 nm range. The CIE-$L^*a^*b^*$ colorimetric method, recommended by the CIE was followed. In this method, L^*

Table 1. Chemical composition of raw materials.

Raw materials	Volumetric fraction	Weight for 18 gr mixture
Al_2O_3	86.66	14.95
Al	8.33	0.98
TiO_2	5	0.92
Fe_2O_3	2.5	0.57
Cr_2O_3	2.5	0.57

is the lightness axis [black (0) white (100)], b^* is the blue (–) yellow (+) axis and a^* is the green (–) red (+) axis [11]. These colorimetric coordinates must be analyzed jointly to determine the final color of pigments, especially the a^* and b^* coordinates.

3. Results and Discussions

A new, cost effective process for the production of nano powdres which is based on mechanically activated chemical reaction of a metal compound with a metal oxide. The process involves subjecting a mixture of a metal compound and a metal oxide to mechanical activation to increase the chemical reactivity of the reactants and/or reaction kinetics such that a chemical reaction can occur which produces a solid nano-phase substance. The insertion of color centers (Cr-Fe-Ti) was performed according to the reaction (Equation (1)):

$$\begin{aligned} &\text{X Fe}_2\text{O}_3 + \text{xCr}_2\text{O}_3 + 2\text{xTiO}_2 + 20/3\text{xAl} + \text{wAl}_2\text{O}_3 \\ &= 2\text{x}[\text{Cr} + \text{Ti} + \text{Fe}] + (\text{w} + 10/3\text{x})\,\text{Al}_2\text{O}_3 \\ &([\text{Cr} + \text{Ti} + \text{Fe}] = 5\%\ \text{v/v};\ \text{Al}_2\text{O}_3 = 95\%\ \text{v/v}) \end{aligned} \tag{1}$$

α-Al_2O_3 has been added to the reagents in order to reach the volumetric fraction of 95% v/v for the matrix and 5% v/v for the chromophores. The redox reaction is performed by mechanical attrition, the metallic aluminium is oxidized and Al_2O_3 is formed simultaneously: Fe, Ti and Cr oxides are reduced and the ions Fe(II), Ti(III) and Cr^{5+} are intended to be inserted in α-Al_2O_3 lattice. The XRD diffraction spectrum of powders (Al_2O_3 95% v/v+ $Fe_2O_3/Cr_2O_3/TiO_2$ 5% v/v) after 15 h and 30 h milling is reported in **Figure 1**.

The reduction of iron oxide releases energy which is used to reduce chromium oxide. Titanium with aluminium react after 15 h [12]. Products of the reaction are not obtained directly, intermediate phases are formed: a high-pressure form of TiO_2 appears at the beginning of milling and disappears after 15 h milling, so does an Al-Ti intermetallic compound. According to **Figure 1**, after 15 hours of milling, alumina phases and Fe-Cr related phases and inter-metallic Al-Ti phase will appear. Also, related aluminium phase is not observed in figure that shows that aluminum metal has been used. High intensity of related peaks illustrates this issue. With continuing milling, alumina phase intensity will increase. The main diffraction peaks of α-Al_2O_3 are present; a value of 34 nm for the α-Al_2O_3 crystallites is obtained by the Scherrer method [10], using the full width at half maxi-

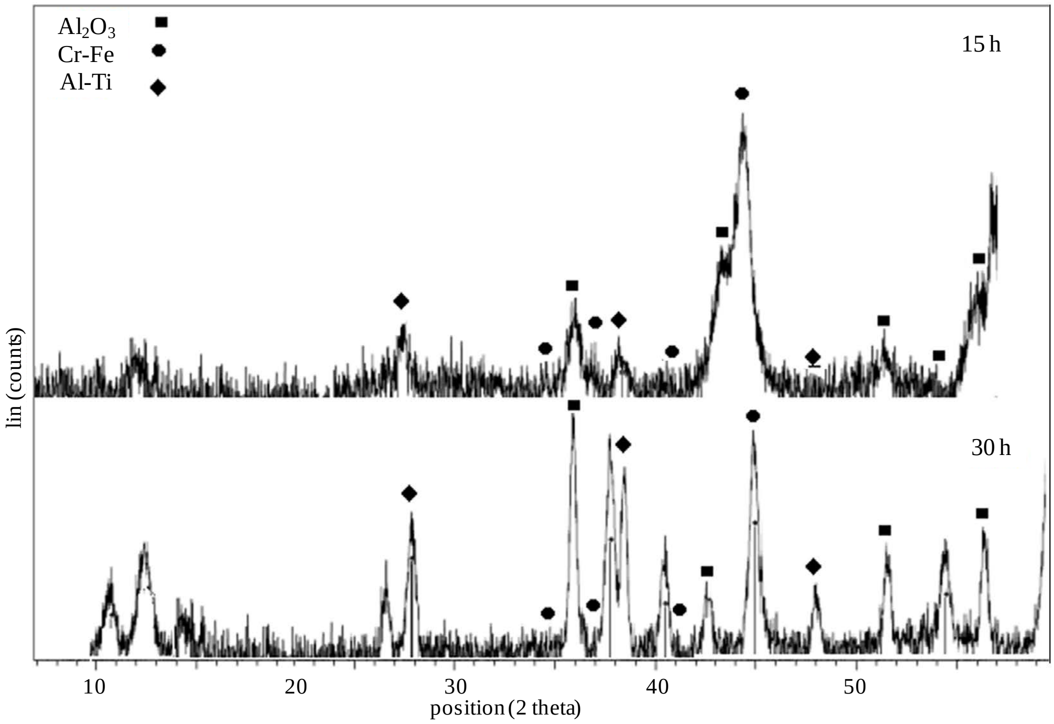
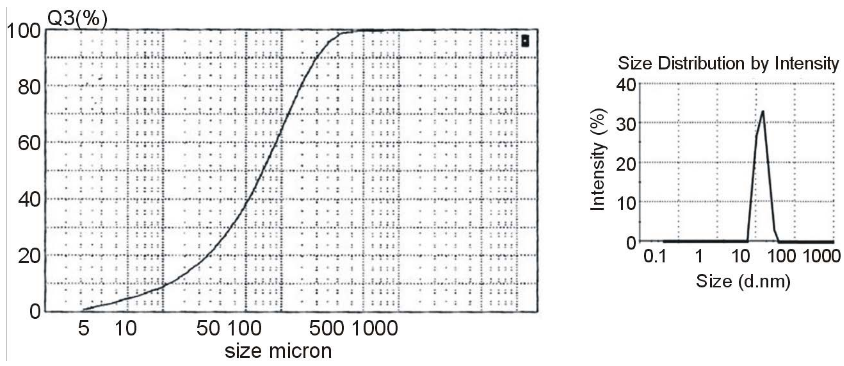


Figure 1. XRD spectrum of pigments obtained by mechanomaking [α-Al_2O_3, (x)] after 15 h and 30 h milling.

mum (FWHM) of the X-ray peaks corrected for instrumental broadening and taking into account strain effects. The presence of chromophores causes a decrease in α-Al_2O_3 cell volume (244.8 Å^3 against 254.7 Å^3 for pure in α-Al_2O_3), that could show a successful doping of corundum lattice. The smaller atomic radius of Fe (0.126 nm), Cr (128 nm) compared with that of Al (0.143 nm) reduced the lattice parameter. However, after the product process, the dissolved Fe/Ti/Cr atoms react with Al to form Ti-Al and Fe-Cr intermetallic. The powder size distribution for this sample before and after milling is reported in **Figure 2**.

This figure shown that size distribution powder before milling is very wide, and covers a large part of the range of the experimental apparatus (from 5 up to 900 µm). Powder after milling is 10 - 100 nm. Center of the distribution particle is about 50 nm. SEM micrographs (see **Figure 3**) seem to confirm these results: at lower magnification, a narrow size distribution of particles is shown, ranging from a few nanometer to one hundred nanometer, the larger particles seeming to be formed by aggregation of smaller particles. This is confirmed by SEM images at higher magnification: in fact, powders look like aggregates of small particles with dimensions up to 500 nm. For investigation of heating effect on color grain during heating of product, pigment powder has been heated at 900˚C and 1000˚C. Results of colorimetry are listed in **Table 2** that shown exact color coordinates of the pigment. Before heat treatment, pigment was black color and after heat treatment at 900˚C pigment was brown. Heat treatment at high temperature at 1000˚C cause that color change to turbid brown.



(a) (b)

Figure 2. Particle size of composite powder: (a) Before milling; (b) After milling.

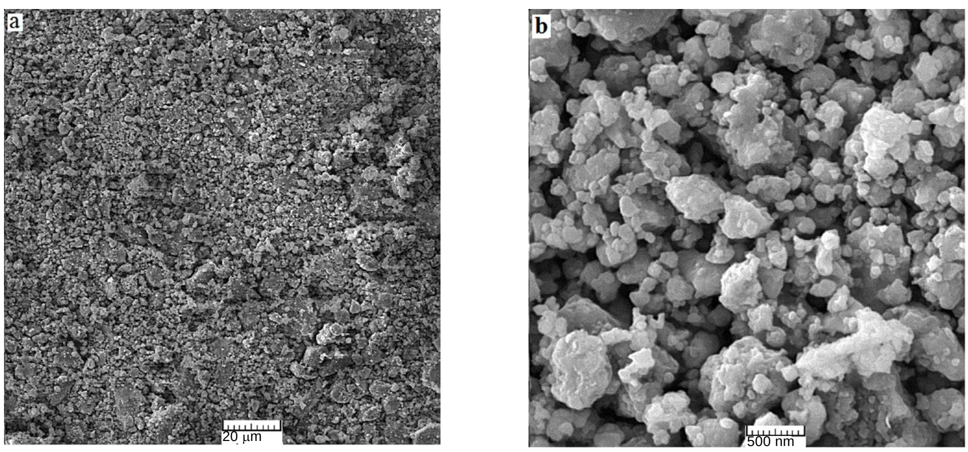


Figure 3. SEM micrographs of pigments obtained by mechanosynthesis at different magnifications.

Table 2. Chromatic coordinates of the pigments after calcinations at 900˚C and 1000˚C.

Sample No.	L^*	a^*	b^*
Before heat treatment	1	4	−9
After heat treatment 900˚C	25	28	32
After heat treatment 1000˚C	36	40	48

4. Conclusion

In this study, nano composite pigment by mechanochemical method was produced. Additive oxides such as iron, chromium and titanium during milling due to reduction by aluminum metal placed in crystal network of alumina. Aluminum metal was not seen in XRD observation due to completion of oxidation-reduction experiment. Color of this nano pigment was black that after conducting heat treatment due to presence of color producer agents such as iron and titanium changed into brown. This could be not only due to the appears of a smaller amount of $FeAl_2O_4$, but also due to a less significant insertion of Fe, Cr and Ti ions in the corundum lattice (the small effectiveness in both dopant ions insertion and spinel formation are confirmed by the presence of free metallic Fe and Ti in the pigment, responsible for the brownish tonality of the resulting color, although variation in α-Al_2O_3 volume cell for doped pigments obtained by mechanosynthesis could indicate an effective insertion of Fe/Cr/Ti ions in the corundum lattice). Only the choice of the proper parameters for the mechanosynthesis process, in particular the applied energy in the attrition, could result in the optimization of the production of nanocrystalline powders with new and industrially exploitable color formulations. This composite can be used such as pigment in ceramic glaze.

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Nomenclature and Units

nm: nano metere
kg: kilogram
mm: millimeter
kV: kilo volt
mA: milliampere
Å: angstrom