$(Fe,Cr)_2O_3$ BLACK CERAMIC PIGMENT PRODUCTION AND CHARACTERIZATION FROM COST-EFFECTIVE RAW MATERIALS

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ABSTRACT

In this study, hematite waste from the steel rolling industry and ferrochrome were used as less expensive raw materials for the synthesis of $(Fe,Cr)_2O_3$ black pigments to be used in porcelain tile bodies. The effects of raw material particle size, mineralizers and stepwise calcination on the pigment colour properties were investigated. The obtained colour values were reported as *L*a*b** parameters, measured by a UV-Vis spectrophotometer. When fine particle size raw materials with mineralizers were used and calcined in a stepwise manner, black ceramic pigment with very similar *L*a*b** values to commercial black pigments was produced.

1. INTRODUCTION

Black ceramic pigments are extensively used and represent nearly 25 wt.% of total inorganic pigment consumption. Fe-Cr black pigments are either in a spinel or corundum structure. Black pigments based on the spinel system are widely used to decorate glazed wall and floor tile, since they remain stable when mixed with the glaze and fired at high temperatures. Spinel-based black pigments are derived from cobalt ferrochromite, $(Fe,Co)(Fe,Cr)_2O_4$ or nickel ferrochromite, $(Ni,Fe)(Fe,Cr)_2O_4$ compounds. In contrast, black pigments based on the corundum system are synthesised by traditional solid state reaction method to obtain a $(Fe,Cr)_2O_3$ solid solution, but this pigment is mainly used in colorants in porcelain stoneware tile manufacture because of its instability when glazed to decorate traditional wall and floor tile [1,2]. Structurally, the pigment is a substitutional solid solution with a corundum-type crystalline network. The Fe^{3+} and Cr^{3+} cations occupy two-thirds of the octahedral vacancies in the compact hexagonal network formed by the oxygen anions, and are randomly distributed according to their proportion in the mixture.

Most of the synthetic pigments are prepared with metallic oxides or salts of the desired metals and they must be of industrial chemical purity, which makes them rather costly. Use of less expensive natural raw materials [3-6] and/or industrial wastes [7-9] containing valuable metals in the pigment production is important in order to reduce pigment cost. Many investigations of the ceramic pigments have sought ways to replace the conventional raw materials with less expensive ones [10,11]. In this study, an attempt was made to synthesize cost-effective black ceramic pigment by using a hematite waste from the steel rolling industry and a ferrochrome for colouring porcelain tile bodies.

2. EXPERIMENTAL

$(Fe,Cr)_2O_3$ black pigments were produced using the conventional ceramic method. For this purpose, the hematite waste (Erdemir T.A.S., Turkey) and ferrochrome (Gensa A.S., Turkey) were used as raw materials. Industrially available $(Fe,Cr)_2O_3$ black pigment was supplied by Ferro for comparative purposes. The as-received hematite waste and ferrochrome were ground separately to the different particle sizes by planetary ball-milling using water and then dried. The mixtures containing 50:50 hematite waste and ferrochrome were prepared by using different particle size hematite waste and ferrochrome and homogenized using a planetary ball mill for 15 min. The slurry was then dried at 100ºC for 24 h; the dried mixture was pulverised and the powder was calcined for 5 h at 1200ºC. Stepwise calcination was performed by calcination first at 1100ºC followed by 1200ºC, or first at 1000ºC followed by 1100ºC and 1200ºC in a laboratory furnace under air atmosphere. The total calcination time in every case was 5 h. The calcined pigments were milled with water for 2 h in a ball mill, washed, filtered and then dried at 100ºC. The average particle sizes of the milled pigment were about 6 µm, this being similar to that of commercial pigment.

In order to evaluate the colour development, 3 wt.% ground pigments were added to a porcelain tile body composition, supplied from a ceramic factory (Toprak Seramik

A.S, Turkey). The mixtures were prepared by wet ball-milling for 15 min. and were dried at 100ºC. The dried porcelain powder mix was pressed into 4 cm diameter pellets at 40 MPa and then fired at 1190ºC, with a 45 min. from cold-to-cold firing cycle in an electric furnace.

The chemical compositions of the raw materials and pigments were determined using an X-ray fluorescence spectrometer (XRF, Rigaku ZSX Primus). The crystalline phases in the raw materials and pigments were identified using an X-ray diffractometer (XRD, Rigaku Rint 2200-Series). The average particle size of the raw materials and pigments were measured via the laser diffraction method (Malvern Mastersizer 2000, UK).

The $L^*a^*b^*$ colour parameters of coloured porcelain tile samples were measured with a UV-Vis spectrophotometer (Minolta 3600 d). In this system, L^* is the degree of lightness and darkness of the colour in relation to the scale extending from white ($L^* = 100$) to black ($L^* = 0$); a^* is the scale along the axis from green ($-a^*$) to red ($+a^*$), and b^* is the scale along the axis from blue ($-b^*$) to yellow ($+b^*$).

3. RESULTS AND DISCUSSION

The results of the chemical composition of the raw materials are shown in Table 1. Table 1 clearly shows that the hematite waste is mainly composed of Fe_2O_3 (97.5 wt.%). On the other hand, metallic ferrochrome has about 65 wt.% Cr content and about 25 wt.% Fe content.

Raw material	Fe_2O_3	Al_2O_3	SiO_2	Fe	Cr	C	Mg	Al	Si	Others	*LOI
Hematite waste	97.5	0.8	0.9	-	-		-	-	-	0.4	0.5
Ferrochrome	-	-	-	25	65	7.0	1.2	0.6	1.2	-	-

Table 1. Chemical composition of the studied raw materials (wt.%).

The results of the chemical composition of both the pigment produced from 50% hematite waste and 50% ferrochrome (50H50F) mixtures calcined at 1200ºC and commercial black pigment (CP) are shown in Table 2.

Pigment	Fe_2O_3	Cr_2O_3	Al_2O_3	SiO_2	MgO
50H50F	54.0	38.8	4.5	2.7	-
CP	59.1	36.5	2.7	1.3	0.4

Table 2. Chemical composition of pigments produced by calcining 50% hematite waste and 50% ferrochrome (50H50F) mixtures at 1200ºC and commercial black pigment (CP) (wt.%).

Fig. 1 shows the XRD patterns of both the commercial and synthesized 50H50F pigments prepared by using fine particle size hematite (7 μm) and ferrochrome (8 μm). The XRD results showed that the synthesized pigment and commercial black pigment

contained only $(Fe_{1-x}Cr_x)_2O_3$ solid solution phases. The generated free Cr_2O_3 from ferrochrome reacts with hematite to produce the $(Fe_{1-x}Cr_x)_2O_3$ solid solution phase (F). In the phase diagram of Fe_2O_3 and Cr_2O_3, these oxides can be observed to generate a complete solid solution for all the range of compositions up to 1400ºC [12].

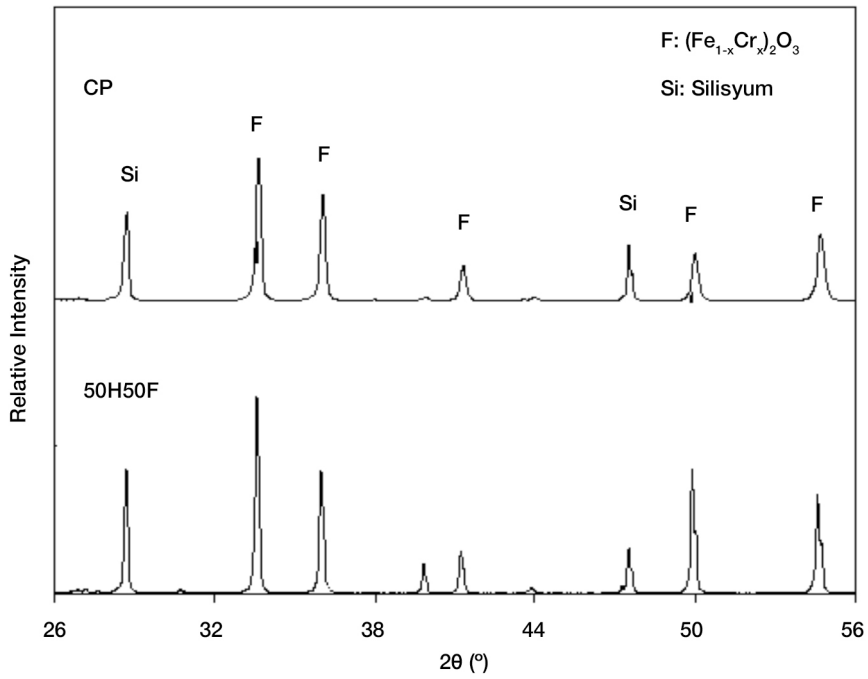

Figure 1. XRD patterns of both the commercial (CP) and synthesized pigments (50H50F). (Note that Si was used as an internal standard).

Table 3 shows *L*a*b** values of the porcelain tile containing 3% pigments prepared by using different particle size raw materials and calcination at 1200 °C. According to Table 3, the hematite waste particle size did not affect the colour of the pigment, but reducing the particle size of ferrochrome reduced the L* and b* values. $(Fe,Cr)_2O_3$ solid solution phase forms by diffusion of Cr^{+3} and O^{-2} ions into the Fe_2O_3 particles [13]. Since ferrochrome is in metallic form, chromium should oxidize first before reacting with hematite. It may be stated that reducing ferrochrome particle size enhances oxidation and subsequent reaction with hematite. Thus, studies were continued using fine particle size hematite waste and ferrochrome.

Average particle size of ball milled raw materials d_{50} (µm)		CIE-L*a*b* values of coloured porcelain tile samples		
Hematite	**Ferrocrhome**	***L****	***a****	***b****
26	31	34.8	1.7	2.1
7	8	34.7	1.3	1.0
7	31	34.7	1.6	1.9
26	8	34.2	1.7	1.4

*Table 3. L*a*b* values of coloured and fired porcelain tile samples containing 3 wt.% 50H50F pigment, by milling different particle size distribution of raw materials.*

The 50H50F composition was calcined under various conditions without mineralizer and using 0.5% KNO_3 as mineralizer, and the effect of these pigments on the colour values of the porcelain tile is given in Table 4. It can be said that stepwise calcination improves pigment strength and this improvement becomes even more significant by using KNO_3.

Pigment	Calcination temperature (ºC)	L*	a*	b*	ΔE
CP	-	32.0	1.0	0.5	-
50H50F	1200	34.7	1.3	1.0	2.6
50H50F + 0,5% KNO_3	1200	33.9	0.9	0.8	2.5
50H50F	1100-1200	33.5	1.3	1.1	1.4
50H50F + 0,5% KNO_3	1100-1200	33.2	1.2	0.8	1.1
50H50F	1000-1100-1200	33.6	1.3	1.1	1.6
50H50F + 0,5% KNO_3	1000-1100-1200	32.3	1.2	0.7	0.7

*Table 4. L*a*b* values of coloured porcelain tile samples containing 3 wt.% pigment, synthesised by calcining 50H50F mixture at temperatures between 1000°C and 1200°C.*

The positive effect of stepwise calcination was probably due to thermal expansion mismatch between oxide scale and the metallic ferrochrome. That is, once the oxide scale is formed and the temperature is raised, the larger thermal expansion coefficient of ferrochrome (11-13x10^{-6} ºC^{-1}) than Cr_2O_3 (9.6x10^{-6} ºC^{-1}) [14] would create tensile stresses and cracks on the Cr_2O_3 scale and this enhances oxygen diffusion through the scale causing further oxidation. This explanation is supported by comparing optical micrographs of ferrochrome oxidized directly at 1200°C and stepwise between 1000-1200°C (Fig. 2). While 1200°C calcined sample shows a distinct metallic grey colour, the stepwise calcined sample showed black oxide scale due to substantial presence of $(Fe,Cr)_2O_3$ solid solution. Samples containing the mineralizer and calcined in 3 steps resulted in the lowest ΔE (0.7) when compared with the commercial pigment.

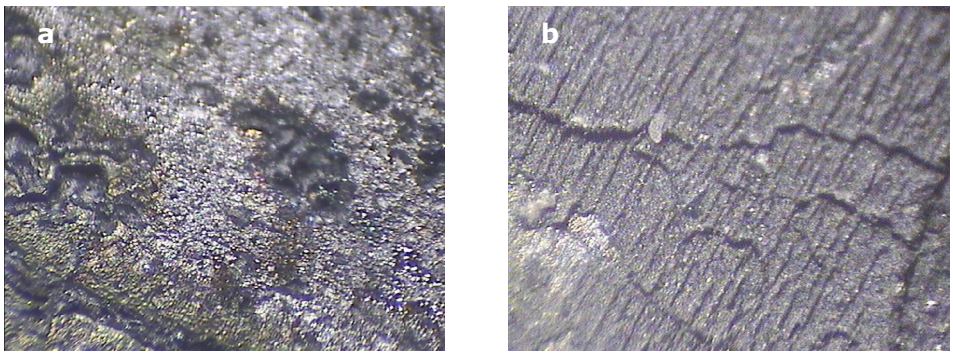

Figura 2. Optical micrograph of ferrochrome calcined (a) directly at 1200ºC and (b) stepwise at 1000-1100-1200ºC. The total calcination time was 5 h.

4. CONCLUSIONS

Regarding the use of hematite waste and ferrochrome as cost-effective raw materials for the production of $(Fe,Cr)_2O_3$ black ceramic pigment, the main conclusions are:

1. Fine particle size and using mineralizer positively affect the colour development.
2. Stepwise calcination improves the oxidation behaviour of ferrochrome and thus enhances colour development.
3. Black pigment with similar *L*a*b** values to commercial black pigment can be produced by using cost-effective ferrochrome and hematite waste.

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