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Arch. Metall. Mater. **62** (2017), 2B, 1231-1234

DOI: 10.1515/amm-2017-0183

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SYNTHESIS AND CHARACTERIZATION OF BLACK $CoFe_2O_4$ PIGMENTS USING MOOH (M = Fe AND Co) NANOROD

We studied the coloration and phase transformation of various iron based pigment with cobalt substitution method and heat treatment. First, we synthesized well defined one dimension β-Fe/CoOOH nanorods using the solid solution method. Yellowish β-Fe/CoOOH nanorods were transformed into reddish intermediate states and, finally, black $CoFe_2O_4$ pigments was obtained. Divalent cobalt ions easily occupied tetrahedral sites. The prepared pigments were well characterized in terms of physical properties by using UV-vis, CIE *Lab* color parameter measurements, SEM (scanning electron microscopy) and XRD (powder X-ray diffraction). In addition, the magnetization property of the prepared $CoFe_2O_4$ pigment was confirmed by VSM (vibrating sample magnetometer).

Keywords: β-Co/FeOOH, $CoFe_2O_4$, black pigment, substitution, solid solution

1. Introduction

Iron-based pigments are promising materials due to their non-toxic properties and relative inexpensiveness [1-3]. Especially, various colorations such as yellow (α-FeOOH, β-FeOOH), red (α-Fe_2O_3) and black (Fe_3O_4) were can be possible depending on the various crystal structures [3-5]. However, problem of their aggregation, low coloration, and thermal instability at high temperature have limited this material in application in the industry. To enhance the thermal stability and to tune the material coloration, we proposed a color tuning system that includes controlling of the size/shape, silica coating, and calcining temperature [6-9].

Recently, we found that the length of β-FeOOH is well correlated to the yellow coloration and length [10]. In addition, β-FeOOH transformed into reddish α-Fe_2O_3 rather than into a black Fe_3O_4 spinel structure at high temperature because the Fe ion prefers trivalent oxidation states and its colors change to red or brown [9,11]. In general, the spinel ferrite structures have two kinds of lattices for cation occupancy, A and B sites, which have tetrahedral and octahedral coordination, respectively. The spinel structure is retained by divalent metal ions occupying the tetrahedral sites. The black color of the Fe_3O_4 spinel structure changed easily to brown under oxidation condition due to the instability of the iron oxidation states. Another important black spinel pigment, $CoFe_2O_4$, is considered a stable black pigment because Co ions prefer the divalent state to the trivalent states [12].

For this paper, we synthesized stable black pigments that were prepared by heat treatment of yellow color pigments using a mixed metal system.

2. Experimental

Synthesis of β-Co/FeOOH and $CoFe_2O_4$ nano powders. The starting materials, ferric chloride ($FeCl_3 \cdot 6H_2O$, 97%), and cobalt (II) chloride ($CoCl_2.6H_2O$, 95%) were purchased from Daejung. All the materials were used as received without further purification. Mixed metal, β-Co/FeOOH powders were prepared using a modified version of a method from the literature [10]. 2.7 g of $FeCl_3 \cdot 6H_2O$ was dissolved in 100 mL of DI water with the addition of 2.37 g of $CoCl_2 \cdot 6H_2O$. Then, the temperature was increased to 80°C in an oil bath for 24 hours. The mixture cooled naturally to room temperature. The product was centrifuged successively with DI water and then dried at 40°C in an oven for one day. The as-prepared samples were calcined in air at different temperatures in a range from 500 to 900°C for 2 hours with a heating rate of 5°C/min. The prepared samples were characterized by X-ray diffraction (XRD, Rigaku D/max 2500v/pc), scanning electron microscopy (SEM, JEOL-6710F), and UV-vis spectrometry (UV-2600, Shimazu, Japan).

3. Results and discussion

Now, black pigments of $CoFe_2O_4$ were prepared using the yellowish mixed metal system of MOOH (M = Fe, Co) with heat treatment. Previous our result, the yellow color was controlled by the size and shape of the β-FeOOH[10]. First, we prepared mixed metal samples by substituting for cobalt ion in β-FeOOH using the solid solution method. Fig. 2 provides an SEM image and the XRD patterns of the β-Co/FeOOH samples.

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It can be observed that the β-FeOOH structure (JCPDS NO. 00-034-126) is present for this sample.(Fig. 2a) Upon substitution with cobalt ion, a clear decrease in the unit cell parameters was observed, suggesting that this cation is incorporated into the β-FeOOH particles in a trivalent state rather than a divalent one, because the ionic radii for Co (III) cations in high-spin configuration (0.525 Å) is lower than that of high spin Fe (III) (0.65 Å) [15]. It is certain that the valence of the elemental Co in the samples is 3+. Fig. 2b provides SEM images of the β-Co/FeOOH nanorods, which mainly exhibit a rod-like structure with length of 500 nm.

To identity and confirm the prepared samples, we measured the colorimetric and reflectometric techniques. It is well known that there are many different ways to define individual colors; the most commonly utilized method is the CIE *Lab*, by which each color is defined by means of three parameters, L*, a*, and b*. These three parameters measure the brightness (white/black), and the red/green and yellow/blue color intensities, respectively [15].

TABLE 1

The CIE *Lab* values of β-Co/FeOOH in various temperature

Temperature (°C)	**CIE *Lab* value**		
	L*	**a***	**b***
25°C	+55.96	+15.95	+35.14
500°C	+31.46	+25.58	+15.77
800°C	+25.34	–0.43	–0.59
Commercially available $CoFe_2O_4$	+26.9	+0.4	–2.3

β-Co/FeOOH shows a yellow color tone with b* value (b* = +35.14), as can be seen in Fig. 3 and in Table 1. The b* value of β-Co/FeOOH is relatively low because of the substitution for cobalt ion in β-FeOOH.

Fig. 4 provides XRD patterns of the heat-treated samples. In Fig. 4a, for the β-Co/FeOOH samples at 500°C, α-Fe_2O_3/CoO is generated from $Co(OH)_2$ and $Fe(OH)_3$. In the case of β-FeOOH, the phase is transformed into α-Fe_2O_3 at high temperature because the iron ion easily oxidizes into the trivalent state. On the

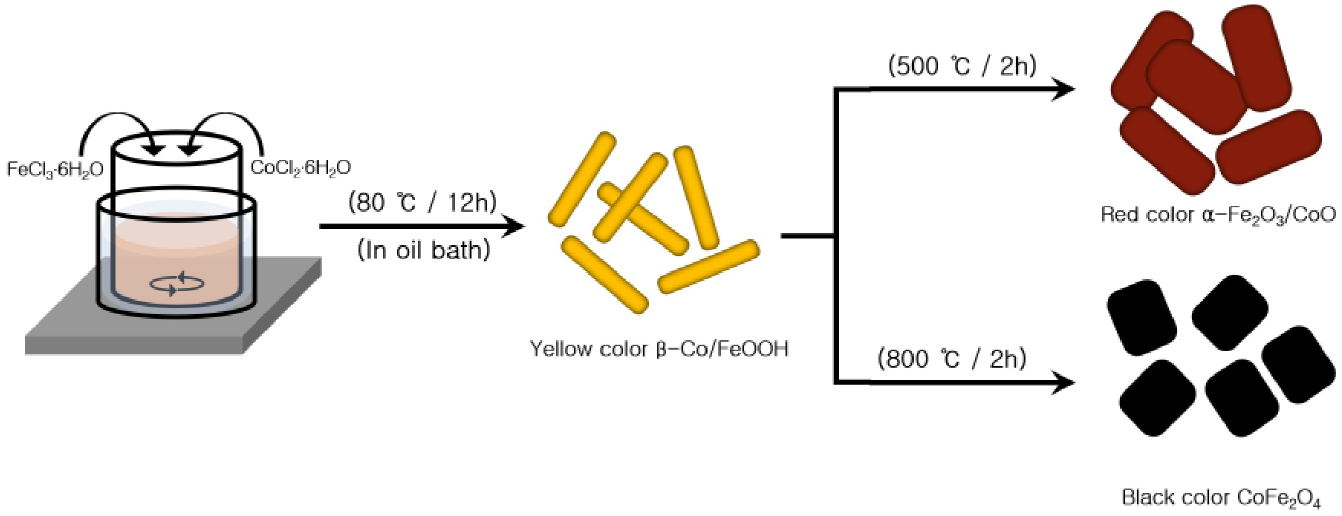

Fig. 1. Schematic illustration of the formation of the $CoFe_2O_4$ black pigment with heat-treatment

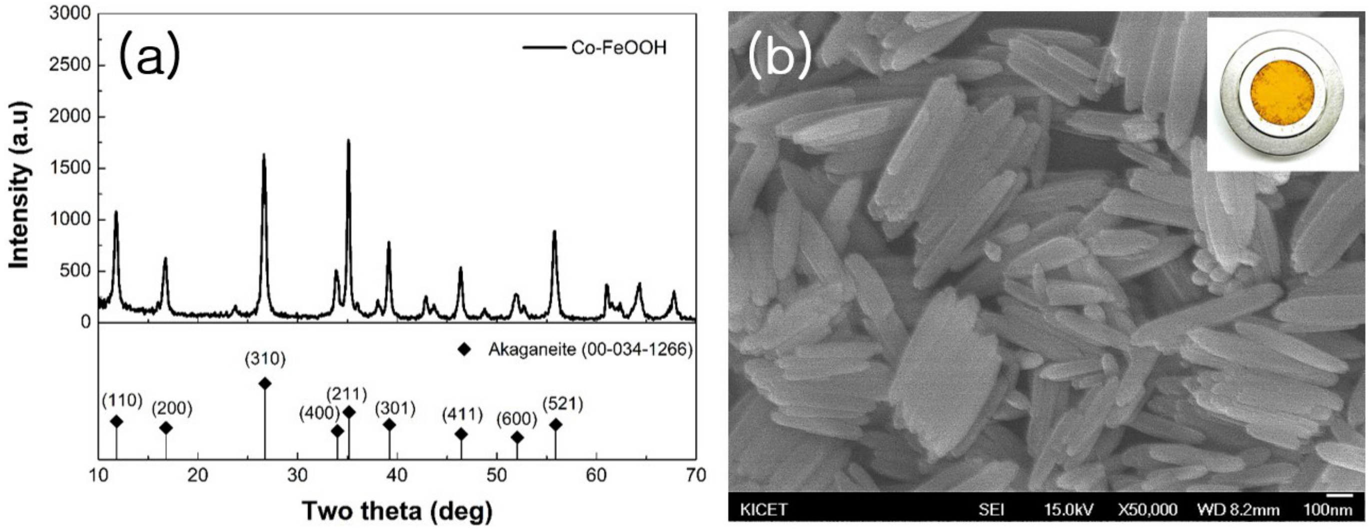

Fig. 2. (a) XRD patterns and (b) SEM image of β-Co/FeOOH samples

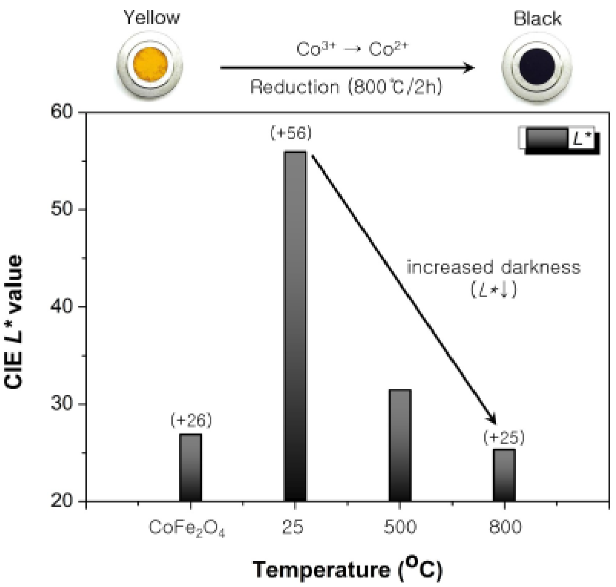

Fig. 3. CIE L* value of samples at various temperatures

other hand, for the β-Co/FeOOH sample, this heat treatment permits isolation of the small reduction maximum above ascribed to Co(III) → Co(II) reduction, which is clearly recorded for the CoFe$_2$O$_4$ sample at 800°C Fig. 4b. In this sample, the measured peaks match the CoFe$_2$O$_4$ standard pattern (JCPDS No.00-022-1086), while diffraction peaks that could be attributed to other iron oxide or oxyhydroxide phases are not observed ($CoO + \alpha\text{-}Fe_2O_3 \rightarrow CoFe_2O_4$). CoFe$_2O_4$ can be found to have a spinel structure. Commonly, the CoFe$_2$O$_4$ material is mostly considered to be an inverse spinel compound with most of its divalent cobalt ions occupying octahedral sites [13].

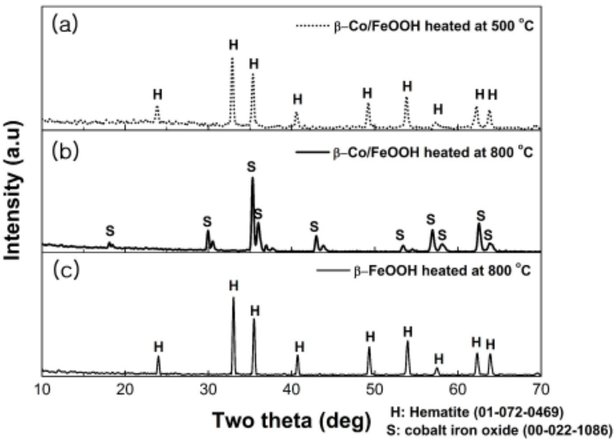

Fig. 4. XRD patterns of β-Co/FeOOH and β-FeOOH after heated at 500 and 800°C. (a) 500°C, (b) 800°C, (c) β-FeOOH heat treatment at 500°C

The *Lab* color coordinate data for the samples are listed in Table 1, along with those of the commercially available CoFe$_2$O$_4$ pigments for comparison. The L* values, which correspond to the black chromaticity in the positive direction of the Co^{2+} substituted samples, were similar to those of commercially available CoFe$_2$O$_4$. In addition, the L* value gradually decreased when the sample calcination temperature was 800°C (L* = +25.34). Moreover, the a* value and the b* value can be seen to have levels that come close to 0, the similar to those of the commercial sample.

The magnetic properties of the prepared CoFe$_2$O$_4$ were characterized by VSM. Fig. 5 shows the magnetic hysteresis loops of the CoFe$_2$O$_4$ samples measured at room temperature. The spinel structure was confirmed at approximately 1.7 emu/gm under an applied field of >10KOe.

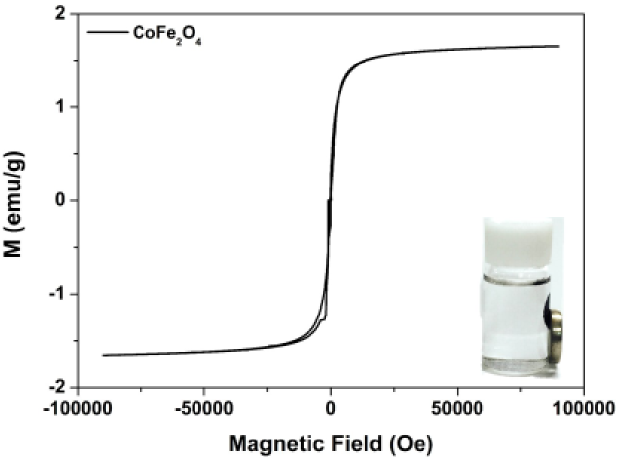

Fig. 5. Magnetic hysteresis loops of prepared CoFe$_2$O$_4$ samples measured at room temperature

4. Conclusions

In summary, we presented the synthesis of black CoFe$_2$O$_4$ pigment with yellowish β-Co/FeOOH nanorods. First, the mixed metal nanorods were synthesized via hydrolysis and solid solution method; nanorods had lengths of approximately 500 nm. With heat-treatment at 800°C, we finally obtained a black color CoFe$_2$O$_4$ pigment of which the coloration changed with the phase from β-Co/FeOOH to CoFe$_2$O$_4$. We determined that the black value (L* = 25.34) reached its highest value at 800 °C. Also, the magnetic properties of the spinel structure were confirmed by VSM.

Acknowledgments

This work was supported by Industry Technology Innovation Program (10052730) fund by the Ministry of Trade, Industry and Energy (MOTIE), Republic of Korea.

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