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Metal-Spinel Composites $(M^0_x Fe^0_{1-x})_\alpha - (M_y Fe_{3-y} O_4)_{1-\alpha}$ with $M=Co, Ni$ Synthesis and Physical Properties

S. Läkamp, T. Bouakham and G. Pourroy

*Institut de Physique et Chimie des Matériaux de Strasbourg, Groupe des Matériaux Inorganiques,
23 rue du Loess, 67037 Strasbourg cedex, France*

Abstract. Composite materials made up of cobalt-iron alloy (or nickel -iron alloy) and Co (or Ni) doped magnetite are synthesized in an aqueous media. The procedure employed is a low temperature reaction in alkaline KOH solution which involves the disproportionation of $Fe(II)$ into Fe^0 and $Fe(III)$ and a reduction of $Co(II)$ or $Ni(II)$. The composition of the final product depends on the initial and final concentrations of reagents and KOH. Pure cobalt - containing composites are obtained in a narrow range of KOH concentration. The metallic phases have the α -Fe (b.c.c. structure) or α -Mn structure, and the lattice parameter of the cobalt - containing magnetite lies between 8.396(2)Å and 8.405(2)Å. Nickel - containing composites without hydroxides are obtained for higher KOH concentrations, 14-15 mol/liter. For lower and higher KOH concentration, hydroxides or amorphous phases precipitate. The coercive field increases when $[Co]/[Fe]$ increases.

1. INTRODUCTION

Particles of magnetic metals (Fe, Co and Ni) on the one side, oxides of these metals in the form of magnetite or doped magnetites on the other side have been widely studied. We have developed several studies in this field and have found that it is possible to synthesise composites made of metal phase embedded in the magnetites. The synthesis is based on the disproportionation of $Fe(OH)_2$ into Fe^0 and Fe_3O_4 (1). $Fe(OH)_2$ also disproportionates when $Co(II)$ or $Ni(II)$ are involved. The metallic phase is thus an iron -cobalt or iron - nickel alloy and the oxide a cobalt or a nickel doped magnetite [2-3]. We describe in this paper the effect of KOH concentration on the purity and structures of composite materials. The effect on the hysteresis curve is then described. Finally, a comparison between cobalt and nickel is given.

2. EXPERIMENTAL SECTION

Aqueous solutions of $Co(II)$ and $Fe(II)$ chlorides, $FeCl_2 \cdot 4H_2O$ and $CoCl_2 \cdot 6H_2O$ were prepared at room temperature. Aqueous KOH solutions were refluxed in a stainless steel vessel equipped with a mechanical stirrer on hot plate. The temperature was measured by means of a stainless steel thermometer placed in the center of the vessel. The metal chloride solution was added to the KOH by means of a peristaltic pump at a rate of 10 ml/min. After a maturation time of 20 minutes, the black precipitate formed was then filtered, washed with boiling water and ethanol and dried at 40°C in air.

3. RESULTS

Let us define $[KOH]_i$ and $[KOH]_f$ as the concentration of KOH before and after the addition of metal chloride solution, $[M]_i$ and $[M]_f$ the concentration of the metal ions (iron and cobalt (or nickel)) before and after being added to the KOH solution.

3.1 $[KOH]_i$, $[M]_i$: region of pure metal - composites

3.1.1 The cobalt case

We have varied the $[KOH]_i$ and $[M]_i$ values from 6 to 15 mol/liter and from 0.4 to 2 mol/liter for two $[Co]_i/[Fe]_i$ values, 0.1 and 0.33. The volumes were chosen so that $[KOH]_f/[KOH]_i = 1.6$ and $[M]_f/[M]_i = 2.7$. Pure composites made up of only the

metal and the spinel phases and containing no amorphous phases are encountered in a narrow region, 11.3-14.5 mol/liter when $[\text{Co}]_i / [\text{Fe}]_i = 0.33$ (Fig. 1). The metal is mainly of b.c.c. structure for $[\text{KOH}]_i$ close to 13-14 mol/liter and mainly isomorphous to α -Mn for $[\text{KOH}]_i$ close to 11.5-12 mol/liter. The lattice constant of the b.c.c. alloy lies between $a = 2.843(1) \text{ \AA}$ for the lowest $[\text{KOH}]_i$ and $a = 2.850 \text{ \AA}(1)$ for $[\text{KOH}]_i = 14$ mol/liter which corresponds to 29(2)% up to 40(1)% of iron in the alloy respectively [4]. The crystallographic parameter of the spinel phase, always equal to $a = 8.400(2) \text{ \AA}$ is close to those of magnetite and cobalt ferrite. The chemical analysis shows that $[\text{Co}]_f / [\text{Fe}]_f = 0.33 = [\text{Co}]_i / [\text{Fe}]_i$ for the lowest $[\text{KOH}]_i$ while $[\text{Co}]_f / [\text{Fe}]_f$ gradually decreases down to 0.30 when $[\text{KOH}]_i$ is increased up to 14 mol/liter. The region becomes narrower and is shifted towards higher $[\text{KOH}]_i$, between 12 and 15 mol/liter for $[\text{Co}]_i / [\text{Fe}]_i = 0.1$. Outside this region, hydroxides are crystallized. The coercive field and the saturation magnetization vary very few, around 650 Oe and 107 emu/g

Figure 1: Phases encountered in the cobalt containing precipitate owing to the $([\text{KOH}]_i, [\text{M}]_i)$ and $([\text{KOH}]_f, [\text{M}]_f)$ regions. M and S refer to metal and spinel phases respectively.

3.1.2 The nickel case

According to the XRD patterns, pure nickel containing composites are observed in the same range of $[\text{KOH}]_i$ for $[\text{Co}]_i / [\text{Fe}]_i = 0.1, 0.2$ and 0.33 . The diffraction lines of the metal are large due to heterogeneous composition and small grains. Its lattice constant cannot be determined precisely but we can claim that the metal is nickel - rich. The oxide is pure magnetite. However, the background and thermal gravimetric measurements in vacuum show that amorphous phases occur for $[\text{KOH}]_i < 14$ mol/liter.

3.2 Variation of $[\text{Co}]_i / [\text{Fe}]_i$ and $[\text{Ni}]_i / [\text{Fe}]_i$

The effect of $[\text{Co}]_i / [\text{Fe}]_i$ and $[\text{Ni}]_i / [\text{Fe}]_i$ on the composition and properties of the precipitate was studied for $[\text{KOH}]_i = 11.5$ mol/liter and 14 mol/liter respectively. The lattice parameter of the spinel phase does not change in both cases. When $[\text{Co}]_i / [\text{Fe}]_i$ increases, we observe a decrease of the lattice parameter of metal corresponding to increasing cobalt concentration in the alloy, an increase of the concentration of the α -Mn structure with regard to the b.c.c. structure, an increase of hydroxides concentration for $[\text{Co}]_i / [\text{Fe}]_i > 0.6$ and an increase of coercive field (Fig. 3). In the nickel case, the crystallization of the metal seems to be improved when $[\text{Ni}]_i / [\text{Fe}]_i$ increase. However, nickel hydroxide is crystallized for $[\text{Ni}]_i / [\text{Fe}]_i \geq 0.5$.

Figure 2: X-ray diffraction patterns recorded at room temperature for $[\text{M}]_i = 1.6$ mol/liter. Region I a) II b) III c) IV d). ■, ◆, ● and ○ are referred to b.c.c. and α -Mn structures, β - $\text{Co}(\text{OH})_2$ and $\delta\text{-Fe}_{0.66}\text{Co}_{0.33}\text{OOH}$ respectively.

Figure 3: Variation of saturation magnetization σ_s and coercive field H_c at room temperature versus $[\text{Co}]_f / [\text{Fe}]_f$ for $[\text{KOH}]_i = 9.0$ mol/l

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