Manufacturing Solution for Producing Cobalt-ferrite Films

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Abstract An extraction-pyrolytic technique and its usage for obtaining pure products from secondary manufacturing solutions are considered in this paper. Nanostructure ferrite thin films were prepared using the extraction-pyrolytic technique. It was shown that the extraction from modeling liquid of waste solution allows obtaining the pure single phase product. Fe2CoO4 magnetic films with grain sizes 18–20 nm were obtained by cycling pyrolysis of wet films deposited by the spin coating technique.

Keywords Composite Oxides, Wet Technique, Nanosize Materials, Homogeneity

1. Introduction

Currently great attention is given to the synthesis of nanosize materials. It is known that the presence of impurities influences greatly the characteristics of nanostructure materials, therefore expensive high-purity substances are used in their synthesis. The essential requirements for producing high quality functional materials are the achievement of chemical and phase composition homogeneity and set elements proportion. These requirements have been taken into account under the development of an extraction-pyrolysis technique for preparation of pure and homogeneous materials.

The usage of conventional techniques for acquiring composite oxide materials such as electron-beam evaporation, chemical vapor deposition, laser ablation techniques and the sol-gel method provide different properties of materials. Among the various techniques the wet chemical method such as sol-gel [1] and spray pyrolysis [2] provide the soft condition of composite oxides synthesis, These technologies would allow preparing the composite oxides under lower temperature and shorter time period for synthesis. They would offer an easy, scalable and cost-effective method for the preparation of films with ultra-fine particles [3].

With respect to polycrystalline films the properties depend on the grain boundary effects and orientation of the grains. The impurities incorporated during the growth are localized as usual at the grain boundaries and modulate the physical properties of materials. Therefore, the development of new a technology for the synthesis of composite oxide materials without impurities and under soft deposition conditions would be meaningful.

2. Materials and Methods

Polycrystalline or amorphous ferrite films are of commercial interest due to their low production cost. In this respect, the technology for synthesizing polycrystalline cobalt ferrite films with high perpendicular magnetic anisotropy and high magnetooptical effects emerged as a more important point [4]. The surface roughness of the polycrystalline films would be significantly larger than those of nanocrystalline materials. Therefore, syntheses of fine-grain ferrite films at lower temperature are the subject of the current research. Structural anomalies and disordering associated with the magnetic films having such small grains would influence the magnetic properties significantly.

For the synthesis of polycrystalline ferrite films we propose the extraction-pyrolysis method which consists in extraction of meaningful components from aqueous solutions of inorganic salts with the following mixture of the liquid extracts in the set ratio and deposition of solution on the substrate and thermal treatment [5].

The inorganic salts usually contain impurities. but the extraction process allows the cleaning of the impurities from the components. The concentrations of metals in extracts have been checked by the atomic absorption method. The following mixing of the extracts provides the exact
The possibility of deep cleaning of cobalt and iron during the extraction stage was tested on a model sulfate-chloride solution corresponding to the composition of the manufacturing solution of cobalt production plant (Norilsk metallurgy). The stock solution includes 3.5 g/l Cu, 3.0 g/l Fe, 65.0 g/l Co. The technological scheme for obtaining of the iron and cobalt extracts is shown in Fig. 1.

At the first stage the Fe and particularly Cu were extracted from the stock solution of metal salts by adding an equivalent amount of 4 M NaOH solution to the total content of iron and copper. The volume ratio of the phases was Org:W = 1:5.

As a result, following complete extraction of iron the Fe extract (1) contains 21% of the copper. The cleaning of Fe-extract from the copper was performed by using 10% solution of H₂SO₄. On the second stage the extraction of copper from cobalt solution was repeated with extractant (VIC) and alkali addition. Cobalt has been extracted from water solution (2) after copper extraction. The resulting Fe and Co extracts do not contain impurities.

The efficiency of the extraction increases a counter current flow process is used.

Magnetooptical values were calculated from the Faraday rotation and absorption spectra.

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The application of microwave heating for the Co-ferrite
thin films thus obtained have same peculiarities in comparison with traditional induction heating. It is known that the high velocity of heating to 200 °C/min promises the conservation of ultra fine structure of materials and allows to accelerate the processes of phase formation.

3.2. Thermal Decomposition of Extracts

The thermal decomposition of extracts in air atmosphere leads to the resultant simple and composite oxides. The thermal decomposition of extracts usually passes through 3 stages and concludes at 450–500 °C.

Thermogravimetric study of extract and their mixtures (Fig.2) demonstrates that water is removed at 90-150 °C, the excess of extractant is removed at 170–190 °C. Carboxylates decompose with removal of gases CO2, CO, CH4, C2H6 in the temperature range 250–470 °C. By using gas-liquid chromatography (GLC) it was found that the 90 % CO2, 8 % CO and 2 % of other gases are present in the gaseous product.

Metals concentrations of the cobalt and iron extracts were analyzed and mixed in a stoichiometric ratio Fe:Co = 2:1. The organic solution of extracts was deposited on glass by a spin coating technique and underwent pyrolysis with 5-10 times repetition in order to produce the films of cobalt ferrite. After 5–15 cycles of wetting and pyrolysis, the cobalt ferrite films were obtained with thicknesses of 100–500 nm. The as-deposited films were annealed at temperatures 350–650 °C during 1 hour in air.

It was found that the films became magnetic after pyrolysis at 450 °C. X-ray diffraction (XRD) patterns of the films annealed at different temperatures are shown in Fig.3. The XRD pattern for a film annealed at 350 °C (see Fig.3, a) have a maximum at 20 = 22° 2Θ indicating the existence of amorphous structure on the films.

With the increasing of the annealing temperature to 400–500 °C the crystallization occurred, as indicated by the appearance of the small peaks (Fig. 3, b) which was identified as a spinel structure. The broadening of the peaks testifies the presence of nanocrystalline grains in the film.

XRD investigations demonstrated the crystalline phase of FeCoO2 thin films prepared by microwave heating of extracts deposited on glass substrates. The microphotographs from a scanning electron microscope (SEM) have shown the nanosize particles with dimension of about 10 nm (Fig. 4).

3.3. Magnetic Properties of Co-ferrite Films

The plot of magnetic in-plane and perpendicular plane hysteresis loops for the films was obtained via the technique of polar Kerr effect [9]. The typical magnetic loop curve of CoFeO4 with a perpendicular magnetic anisotropy is shown in Fig.5. This indicates the presence of the perpendicular magnetic anisotropy in cobalt ferrite films with composition CoFeO4.

Ferrite films synthesized on quartz substrates by the extraction-pyrolysis technique have high values of the perpendicular magnetic anisotropy constant (Ku = 0,8-1,0*10⁵ J/m³), coercive force (Hc = 220–260 kA/m) and hysteresis squareness (S = 0,8–0,9). Hysteresis squareness was calculate as S=θF/θks, where θk – magnitude of Kerr rotation in a field H = 0, θks – in a field of saturation; θF – magnitude of Faraday rotation.
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The spectral dependence of the Faraday effect ($\theta_F$) of the Co$_{0.6}$Fe$_{2.4}$O$_4$ film has two extremes (Fig. 6): $\theta_F = 2.5$ deg/μm on $\lambda = 0.5$ μm and $\theta_F = -2.5$ deg/μm on $\lambda = 0.8$ μm.

The value $\theta_F$ on $\lambda = 0.8$ μm is much higher than Faraday rotation on 0.8 μm of other ferrite films, with the exception of Ce-substituted iron garnet films, but its magnetic properties make it the most suitable ferrite for the magneto-optical recording.

The practical interest presents the magnetooptical value $\Psi = |2\theta_F|/\alpha$, where $\alpha$ - factor of an optical absorption, for wavelength 0.63 and 0.8 microns, that is equal to 0.5 and 3 degree respectively. These values are not lower than the values obtained for cobalt ferrite films by other method [10].

The magnetization of saturation for CoFe$_2$O$_4$ films obtained by microwave pyrolysis was evaluated as 100 Gs. Perpendicular magnetic anisotropy in films was not found, but nanosize films are characterized by the Kerr and Faraday effect. Therefore they are suitable for magneto optic applications.

It is apparent from the above results that the usage of an extractive-pyrolytic method allowed to obtain cobalt ferrite films with nanocrystalline structure having high values of magnetic and magnetooptical parameters. The values of the above-stated properties meet the requirements for magneto-optical applications.

4. Conclusion

By the extraction-pyrolysis technique the pure and homogeneous films have been derived from model of manufacturing solution. This technique is low cost and suitable for deposition of films on the large surfaces or on materials with complex forms. The structure of films deposited by the extraction-pyrolysis technique is an important factor for different functional applications. For instance, for obtaining films with perpendicular magnetic anisotropy and magneto-optic materials, the extractive-pyrolysis technique allows nanosize materials and materials with controllable size of grains to be derived.

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