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VARIATION IN MAGNETIC PROPERTIES OF SOL-GEL-SYNTHESIZED COBALT FERRITES

SPREMINJANJE MAGNETNIH LASTNOSTI KOBALTOVIH FERITOV, SINTETIZIRANIH PO SOL-GEL POSTOPKU

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Single-phase cobalt ferrite ($CoFe_2O_4$) was synthesized with a sol-gel reaction between 10.59 g of cobalt nitrate and 29.40 g of iron nitrate using 480 mL of 10 % polyvinyl alcohol (PVA) in water. Their magnetic squareness and coercive field were slightly reduced with the increase in the annealing at 800 °C from 2 h to 6 h. To examine the reproducibility of ferrite products of the PVA sol-gel method, the synthetic condition was repeated 28 times. After annealing for 4 h, $CoFe_2O_4$ samples from different batches exhibit variations in the magnetic properties. The coercive field has a large distribution because of its sensitivity to the particle agglomeration, whereas the squareness fluctuates in a narrower range from 0.22 to 0.29. Since the squareness is the ratio of the remanence to the saturation magnetization, the particle agglomeration tends to increase both values while keeping this ratio rather unchanged.

Keywords: cobalt ferrites, PVA sol-gel, annealing time, magnetic squareness, coercive field

Enofazni kobaltov ferit ($CoFe_2O_4$) je bil sintetiziran s sol-gel reakcijo med 10,59 g kobaltovega nitrata in 29,40 g železovega nitrata z uporabo 480 mL 10-odstotne raztopine polivinil alkohola (PVA) v vodi. Njihova četverokotna magnetna oblika in koercitivno polje sta se rahlo zmanjšala s podaljšanjem žarjenja na 800 °C iz 2 h na 6 h. Da bi preiskali ponovljivost feritnih proizvodov iz PVA sol-gel metode, je bila sinteza ponovljena 28-krat. Po žarjenju 4 h so kazali vzorci $CoFe_2O_4$ iz različnih serij razliko v magnetnih lastnostih. Koercitivno polje kaže velik raztros zaradi občutljivosti za aglomeracijo delcev, medtem ko se četverokotnost oblike spreminja v ožjem področju od 0,22 do 0,29. Ker je četverokotnost razmerje med remanenco in nasičeno magnetizacijo, aglomeracija delcev povečuje obe vrednosti, medtem ko razmerje ostaja skoraj nespremenjeno.

Ključne besede: kobaltov ferit, PVA sol-gel, čas žarjenja, magnetna četverokotna oblika, koercitivno polje

1 INTRODUCTION

Cobalt ferrite ($CoFe_2O_4$) is under research and development for its applications in magneto-optical recording media, magnetic refrigerants, microwave absorbers and stress sensors.[1,2] Bulk $CoFe_2O_4$ has an inverse spinel structure consisting of a cubic close-packed (fcc) arrangement of oxide anions, O^{2-}. The tetrahedral and octahedral interstitial sites in the lattice are partially occupied by the Co^{2+} and Fe^{3+} cations, respectively.[1,2] Like the other spinel ferrites (e.g., $NiFe_2O_4$, $MnFe_2O_4$, $ZnFe_2O_4$, $CuFe_2O_4$) and barium ferrites, $CoFe_2O_4$ nanoparticles can be synthesized with the sol-gel method.[3–17] In a sol-gel reaction, homogeneous $CoFe_2O_4$ nanoparticles are produced in-situ with a controlled decomposition of precursors, while the chelating gel is dried during the heat treatment at a relatively low temperature. Gatelyte et al.[7] demonstrated that the characteristics of $CoFe_2O_4$, $NiFe_2O_4$, $ZnFe_2O_4$, $YFeO_3$ and $Y_3Fe_5O_{12}$ produced with aqueous sol-gel reactions under the same synthesis condition were comparable.

According to our previous sol-gel synthesis using polyvinyl alcohol (PVA) as the chelating agent,[8] the magnetic properties of $CoFe_2O_4$ are influenced by PVA contents for two reasons. Firstly, the single-phase $CoFe_2O_4$ obtained in the case of sufficient PVA gives rise to a relatively high coercive field because of its strong magnetic anisotropy. In the case of a diluted PVA solution, the second phase (e.g., α-Fe_2O_3) may also be present, reducing the overall coercive field. The other reason is the dependence of the cluster size on the PVA contents used in the sol-gel reaction. The cluster size, on the other hand, dictates the coercive field and magnetization of $CoFe_2O_4$.[9,15] The role of the PVA gel is to cleave atoms during the reaction. An increase in PVA improves the crystallinity of $CoFe_2O_4$ without an excessive particle agglomeration.

The temperature of the heat treatment of the as-synthesized products also affects the magnetic properties of $CoFe_2O_4$. Our previous result agrees with the other experimental works indicating that both the coercive field and the magnetic squareness (the ratio of the remanence to the saturation magnetization) of $CoFe_2O_4$ are initially increased with an increase in the annealing temperature up to 700–800 °C and then reduced with further increases in the temperature.[8,15–19] The growth and agglomeration of $CoFe_2O_4$ particles at high temperatures result in a decrease in the coercive field and an increase in the saturation magnetization. The squareness is, therefore, reduced due to this high-temperature regime. In addition, Toksha et al.[15] reported a decrease in the coercive field and an increase in the saturation magnetization due to an increased particle size after prolonged annealing. Recently, Sajjia et al.[14] employed the response surface methodology to simulate the optimum heat treatment to obtain single-phase $CoFe_2O_4$ and minimize the cost of electricity.

To implement a sol-gel synthesis of ferrites on a commercial scale, another aspect of concern is the reproducibility of the products from different batches. Although this issue is hardly addressed in research papers, it is particularly important since ferrites of the order of a hundred grams or less are usually obtained with a laboratory-scale sol-gel synthesis. In this research, the condition for preparing the single-phase $CoFe_2O_4$ from the previous work[8] is reproduced in order to study the variation in magnetic properties observed after a repeated synthesis. The effect of the annealing time is also investigated.

2 EXPERMENTAL WORK

The PVA solution was prepared by dissolving PVA powders in distilled water (10 %). It was heated at 70–80 °C until the solution became clear (5–7 h). Then, 10.59 g of cobalt nitrate, $Co(NO_3)_2 \cdot 6H_2O$, and 29.40 g of iron nitrate, $Fe(NO_3)_3 \cdot 9H_2O$ powders were mixed with the 480 mL PVA solution. The reaction mixture was stirred for a further 3 h. After that, it was heated at 80 °C for 10–12 h or until the gel was dry.

The morphology of the ferrite product was shown with scanning electron microscopy (SEM) and its structure was characterized with powder X-ray diffractometry (XRD). A copper target was used as an X-ray source (K_α, λ = 0.154058 nm) with 40 kV between the cathode and the copper target. The measurement was performed in the range of 2θ angles from 10° to 80° with each rotating step accounting for 0.02°. The crystallite size was calculated from the peak width using the Scherrer's formula:

$$d = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

where β is the broadening of the diffraction line measured at half the maximum intensity and λ is the wavelength of K_α.

To investigate the effect of the annealing time and reproducibility of sol-gel products, the time of annealing at 800 °C varied between (2, 4, 6) h and the same synthesis condition was repeated for 28 batches with the same, annealing 4 h. The magnetic properties of all the samples were characterized with vibrating sample magnetometry (VSM).

3 RESULTS AND DISCUSSION

The XRD pattern in **Figure 1** shows the cubic spinel $CoFe_2O_4$ phase [JCPDS 22-1086] with the peaks at 30.0°, 35.4°, 43.0°, 56.9°, 62.6° corresponding to the (220), (311), (400), (511) and (440) planes, respectively. Other oxides or impurity phases are not detected and the $CoFe_2O_4$ peaks are particularly sharp. The crystallite size, calculated from the line broadening of the (311) diffraction peak is approximately 45 nm. These crystallites tend to agglomerate into microscale clusters that are quite common for sol-gel-synthesized ferrites.[20] As seen in the SEM micrograph in the inset, these aggregates have flat surfaces and sharp edges. Compared to the ferrite products from the previous work,[8] the cluster size tends to increase with a reduction of PVA in the sol-gel reaction.

According to VSM hysteresis loops in **Figure 2** all the $CoFe_2O_4$ samples after varying annealing times exhibit ferrimagnetic properties. The absence of superparamagnetic behaviors is due to the particle agglome-

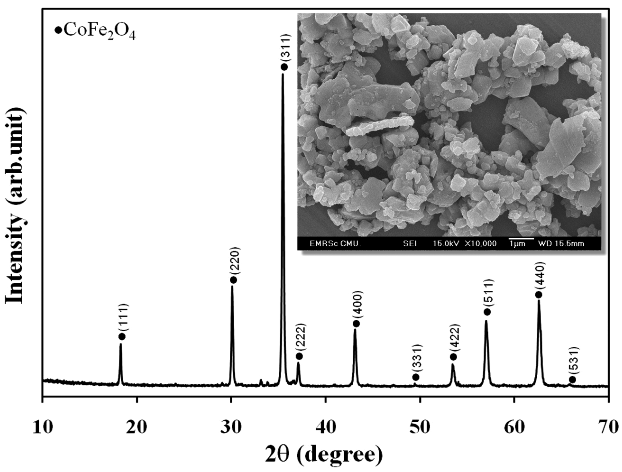

Figure 1: XRD pattern of sol-gel-synthesized ferrite products. Its SEM micrograph is shown in the inset.

Slika 1: XRD-posnetek feritnega proizvoda, sintetiziranega po sol-gel postopku. SEM-posnetek je vložen.

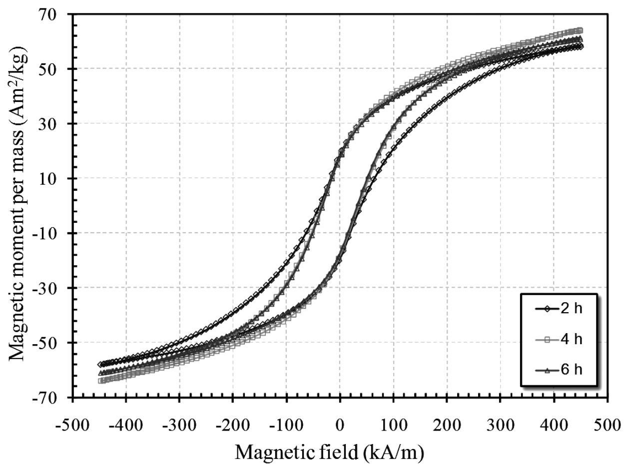

Figure 2: Hysteresis loops of $CoFe_2O_4$ from the sol-gel reaction after annealing at 800 °C for (2, 4 and 6) h

Slika 2: Histerezna zanka $CoFe_2O_4$, izdelanega po sol-gel reakciji, po žarjenju (2, 4 in 6) h na 800 °C

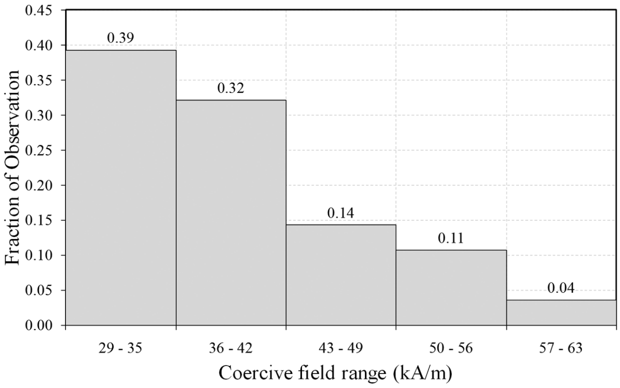

Figure 3: Distribution of the coercive field of $CoFe_2O_4$ synthesized in 28 batches
Slika 3: Razporeditev koercitivnega polja $CoFe_2O_4$, sintetiziranega v 28 ponovitvah

ration. In the applied magnetic field of 440 kA/m, the magnetization does not reach the complete saturation. The highest magnetic moment per mass is around 60 A m^2/kg, a value comparable to that of sol-gel-synthesized $CoFe_2O_4$ nanoparticles.[9–11,15] Both the coercive field and the squareness are slightly decreased with the increase in the annealing time from 2 h to 6 h. Longer annealing times apparently have a similar effect on the increase in the annealing temperature beyond 800 °C and the cluster size is, consequently, enhanced. It follows that the coercive field and the squareness are reduced.

The variation in the coercive field of $CoFe_2O_4$ is shown in the form of a histogram in **Figure 3**. Ranging from 31.2 kA/m to 63.2 kA/m, the distribution is approximately exponential with the coercive field of less than 40 kA/m in the majority of the samples. This implies that most particles are unevenly agglomerated, like those in **Figure 1**. The average coercive field of 28 batches is (39.8 ± 8.7) kA/m (compared to 34.4 kA/m in **Figure 2**). If an enhanced coercive field is aimed for, either an increase in the PVA contents or a decrease in the annealing temperature and time is recommended. In **Figure 4**, the squareness exhibits a narrower distribution, from 0.22 to 0.29. In addition to its effect on the coercive field, the particle agglomeration also results in an increase in the magnetization. However, the squareness does not exhibit a large variation, because it is the ratio between the magnetizations. With the average value of 0.26 ± 0.03, a large fraction of the samples have a squareness beyond 0.25. Interestingly, the minimum squareness of 0.22 is obtained from the batch with the smallest cluster size, signified by the maximum coercive field.

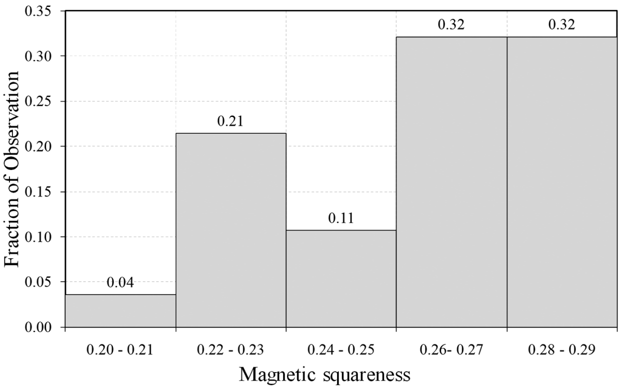

Figure 4: Distribution of the magnetic squareness of $CoFe_2O_4$ synthesized in 28 batches
Slika 4: Razporeditev magnetne četverokotne oblike $CoFe_2O_4$, sintetiziranega v 28 ponovitvah

4 CONCLUSION

The magnetic squareness and coercive field of the single-phase $CoFe_2O_4$ synthesized with a sol-gel reaction between $Co(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ exhibit a slight decrease with the increase in the annealing time from 2 h to 6 h at 800 °C. However, repeated syntheses show that the magnetic properties of $CoFe_2O_4$ obtained under the same synthetic and annealing conditions may vary due to non-uniform particle agglomerations. This must be taken into the account before implementing the sol-gel-synthesized ferrites on a large scale.

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