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Synthesis of dense NiZn ferrites by spark plasma sintering

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Abstract

Dense NiZn ferrites were fabricated by spark plasma sintering (SPS) at 900 °C and 20 MPa in short periods. The powder was densified to ⩾98% of the theoretical density by the SPS process. The SPS disks exhibited a higher saturation magnetization (Ms), up to 272 emu/cm^3, than did the disks sintered by the conventional process. A higher coercivity (Hci) was obtained when the green bodies were sintered by the SPS process for 5 min. A modest holding time is essential to obtain fine grain and uniformity in the SPS process. Secondary crystallization, inhomogeneous microstructure and intragranular pores were found as a result of the rapid sintering and relatively longer holding time in the SPS process. Infrared (IR) spectra were also measured in the range from 350 to 700 cm^{-1} to study the efforts of the SPS process on NiZn ferrites.

Keywords: A. Sintering (spark plasma sintering, SPS); D. Ferrites

1. Introduction

The spark plasma sintering (SPS) method is a relative new technology for manufacturing materials which utilizes the high energy of a high-temperature plasma (discharge plasma) generated when a pulse of electric energy is applied to the space among particles [1]. In the SPS process, the precursor powders are pressed uniaxially in a graphite die, and an on-off pulsed dc voltage is simultaneously applied. The current passes through the die as well as the sample, indicating that the samples are heated from both the outside and the inside. SPS promotes the material transfer and enables the manufacture of dense materials in a short time at low sintering temperatures compared with current methods.

Although its sintering mechanism is not yet well understood, SPS has been employed to study many kinds of materials, such as metals and alloys [2,3], ceramics [4–7], dielectrics [8,9], thermoelectric materials [10], solid oxide fuel cells [11], and biomaterials [12]. However, there are few reports on the application of this technique to produce dense soft magnetic materials such as ferrites, except for Ken Hirota [13].

In the present study, we attempted to fabricate dense NiZn ferrites by the SPS process. The densities, microstructure, magnetic properties, and the infrared spectra of the SPS samples were observed and compared with those of conventional sintered samples.

2. Experimental procedure

Green compacts of (NiZn)Fe_2O_4 were prepared from commercial ferrite powders, and then they were subsequently sintered under vacuum by SPS (Dr. Sinter., Model: SPS-1050T, Sumitomo Coal Mining Company, Ltd.) or by conventional sintering in an electric furnace.

(NiZn)Fe_2O_4 powder (≈3 g) was poured into a graphite die (20 mm in diameter), and an electric current of ≈600 A was applied under a pressure of 20 MPa. During this procedure, the temperature increased to 900 °C at a rate of ≈30 °C/min (controlled by the applied current). The temperature was measured by means of an optical pyrometer focused on to the sintered sample through a small hole in the die. After it was kept at 900 °C for 0, 3, or 5 min, the applied electric current was stopped, pressure was released, and the sample was cooled to room temperature (it took ≈10 min for cooling from 900 to 600 °C). The sintered SPS disks (about

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20 mm in diameter and 2 mm in thickness) were annealed in air at 800 °C for 2 h (SPS disks). For the conventional heating process, (NiZn)Fe_2O_4 powders were pressed into disks under a pressure of 2 MPa and sintered in air between 950 and 1250 °C for 4 h, at a heating rate of 4 °C/min and a cooling rate of 3 °C/min (CS disks).

The sintered densities of SPS and CS pellets were measured by the Archimedes method in distilled water. Phase purity and composition of the disks were checked by X-ray diffraction, using CuK_α radiation. The microstructure was investigated by SEM (JSM-6301F). Thermogravimetry was employed to monitor weight change on reoxidation of the disks prepared by SPS method.

Magnetization measurements on the samples were carried out with a vibrating sample magnetometer (model VSM-7307). The infrared spectra were recorded at room temperature in the range of $350 \sim 700 cm^{-1}$ by an infrared spectrometer (model SPECTRUM-GX).

3. Results and discussion

The XRD patterns of different parts of as-sintered SPS samples are given in Fig. 1, showing that all products contained only spinel phase and the sintering process did not induce any secondary phases. It should be noted that the edge parts of SPS disks showed the graphite contamination ($2\theta \approx 26°$) due to the graphite die, which can be eliminated after annealing at 800 °C for 2 h. However the central parts of SPS disks showed no XRD peaks attributed to graphite. The DTA and TGA results further confirmed the absence of graphite in SPS disks central parts before annealing as well as the removal of that in the edge parts after annealing. This phenomenon indicates that the graphite contamination produced by SPS is heterogeneous in samples. The densities of SPS disks after annealing and those of CS disks are listed in Table 1. Relatively high-density disks [more than 98% of the theoretical density (TD = 5.3 g/cm^3)] were obtained to all the SPS disks sintered at 900 °C with a short holding time, and the density increased with holding time. In contrast, the CS disks required 4 h at 1150 °C to attain 95% TD.

Typical SEM micrographs of the fracture surface of annealed SPS disks are shown in Fig. 2(a)–(e). For comparison, the SEM photograph of the CS disk sintered at 1050 °C for 4 h is shown in Fig. 2(f). These results confirmed the above calculated densities, showing that the SPS process at 900 °C for several minutes was effective to obtain dense NiZn ferrites. Fig. 2 also displays that the grain size of the SPS disks depended on the holding time, the former increased with the latter. Notably, the comparison of (d) with (e) shows that the SPS disks sintered for 5 min possessed secondary crystallization (or exaggerated grain growth). This result indicates that a short holding time period is an essential factor to obtain (NiZn)Fe_2O_4 with uniform and fine grains in the SPS process. Similar phenomena have been reported previously [4,6,8]. Moreover, the inner parts of SPS disks [shown in Fig. 2(d)] were more uniform than for the outer parts [shown in Fig. 2(e)]. Such result should be attributed to the different sintering conditions, such as local sintering pressure or temperature in SPS furnace. Another interesting phenomenon can be found from Fig. 2(a)–(c) that the SPS disks were nearly porefree, with only a few pores located within grains (intragranular pores), which

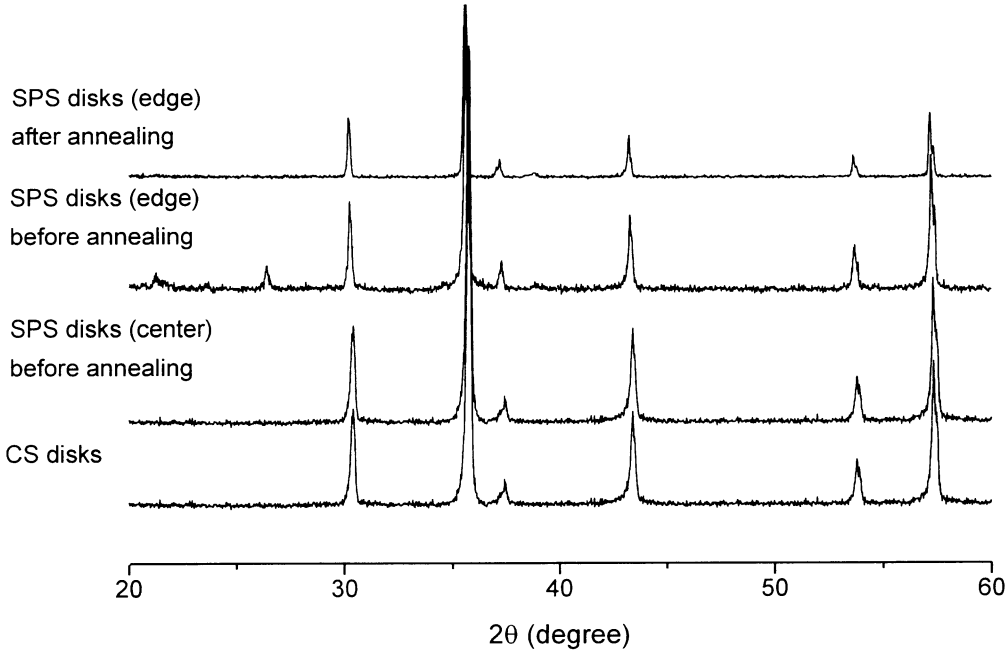

Fig. 1. X-ray diffraction patterns of SPS and CS disks.

Table 1
Sample's density, Ms, Hci, and the positions of IR absorption bands (v_1 and v_2)

Sample	CS, 1050 °C for 4 h	CS, 1150 °C for 4 h	SPS, 900 °C for 0 min	SPS, 900 °C for 2 min	SPS, 900 °C for 5 min
Density (g/cm^3)	4.8	5.0	5.2	5.27	5.3
Ms (emu/cm^3)	232	246	262	258	272
Hci (Oe)	20	41	23	31	40
v_1 (cm^{-1})	559	561	563	562	559
v_2 (cm^{-1})	393	393	394	394	395

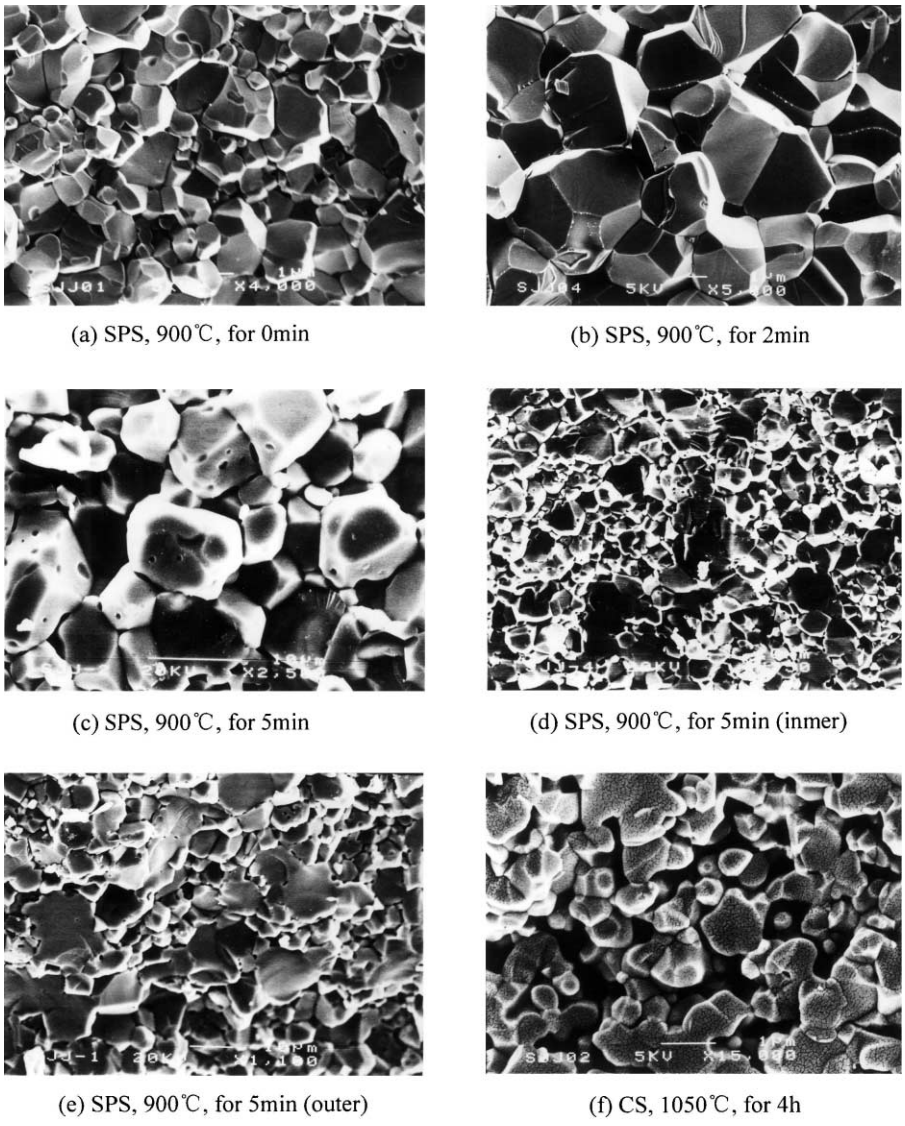

Fig. 2. SEM photomicrographs of SPS and CS disks.

partially resulted from the rapid grain boundary movement caused by the superfast sintering process of SPS.

The saturation magnetization (Ms) and coercivity (Hci) of SPS and CS pellets are illustrated in Table 1. One can note that SPS disks' saturation magnetization was higher than for the CS disks, increased in the range of 5∼17%. Because all samples have the same composition, the possible cause should be a difference in microstructure [14]. The higher saturation magnetization suggested fewer pores as well as higher density in the SPS disks. On the other hand, the maximum values of coercivity were obtained in the SPS sample sintered at 900 °C for 5 min and the CS sample sintered at 1150 °C for 4 h. It is known that coercivity decreases with increasing density [15]. So such increase in samples' coercivities should attribute to other factors. A possible cause

in our experiment is the secondary crystallization which induced higher anisotropy constant or/and intragranular pores inhibiting the motion of domain walls [16].

The IR spectra of SPS and CS disks were recorded in the range from 350 to 700 cm^{-1}. The spectra showed the presence of two absorption bands (v_1 and v_2), which is a common feature of all spinel structure. The band v_1 is attributed to the stretching vibration of Fe^{3+}–O^{2-} in the tetrahedral complexes and the band v_2 to that of octahedral complexes [17,18]. The values of the absorption band frequency are also given in Table 1. The band v_1 and v_2 remained nearly constant with increasing density. It is known that the variation in v_1 and v_2 is due to many factors such as composition, the method of preparation, grain size and porosity which influence the band position [19]. In our work, because all the samples were of the same composition, the variation of bands was slight. Furthermore, the minor change indicates a slight difference in the crystal conditions around Fe^{3+}–O^{2-}, which should be caused by the combination of lower porosity, larger gain size and lower Zn^{2+} content induced either by increasing holding time or by increasing sintering temperature in the SPS process. The above results are in agreement with that reported by Shaikh and Ravinder [19,20].

4. Conclusions

(1) We successfully employed spark plasma sintering (SPS) to obtain dense NiZn ferrites ($\geqslant$98% of theoretical density) at 900 °C and 20 MPa within several minutes. To the edge or central parts of SPS disks, the degree of graphite contamination was different, and the former could be removed by annealing at 800 °C for 2 h.

(2) A modest holding time is essential to obtain fine grain and uniformity in the SPS process. Secondary crystallization, inhomogeneous microstructure and intragranular pores were found as a result of the rapid sintering and relatively longer holding time in the SPS process.

(3) SPS disks possessed higher saturation magnetization (Ms = 272 emu/cm^3, increased by 5–17%) due to higher density. Higher coercivity (Hci) may be induced by higher anisotropy constant or/and more mntragranular pores when sintered for a longer period. Therefore, the SPS process is a promising method to produce NiZn ferrites with higher Ms or higher Hci.

(4) There was minor change of the v_1 and v_2 band in the IR spectra, indicating the SPS process did not cause significantly different crystal conditions around Fe^{3+}–O^{2-} of NiZn ferrites.

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