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Hopkinson Effect in Soft and Hard Magnetic Ferrites

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The dependences of the susceptibility of selected spinel and hexagonal ferrites on temperature are analyzed. The susceptibility shows a peak just below the Curie temperature T_C due to the Hopkinson effect during the heating. The appearance of this effect is associated with a transition from the region of stable magnetization state to superparamagnetic relaxations of the magnetic particles. It is in contrast to other explanations of the Hopkinson effect. These results are compared with measured particles size and with scanning electron microscope micrographs of both types of ferrites.

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1. Introduction

The Hopkinson effect means the phenomenon that an initial susceptibility χ (permeability μ) of a magnetic material increases with increase of temperature and exhibits a sharp maximum at temperature slightly below the Curie temperature (T_C). Thus, a peculiar susceptibility peak (maximum) is usually observed below the T_C in a thermo-magnetic curve. This effect has been observed in many soft and hard magnetic materials, in hard one with fine grain structure [1–9]. Explanation of the Hopkinson effect is based on several ideas, mainly on domain–wall motion. Our experimental data demonstrate that the peaks are due to the effect of superparamagnetic relaxations of a system randomly oriented, single domain, interacting magnetic particles. The explanation of experimentally observed Hopkinson peak based on superparamagnetic state at a blocking temperature T_b just below T_C is proposed. This peak turns out to be associated with the transition from the region of stable magnetization to superparamagnetic state with connection of drastic fall of magnetic anisotropy.

2. Experimental results and discussion

The samples of nanosized NiZn ferrites having a structural formula $Ni_{0.33}Zn_{0.67}Fe_2O_4$ were prepared by auto-combustion method based on glycine precursor, sintered at various temperatures T_s [6]. The magnetic susceptibility χ for all T_s were measured in alternating magnetic field of $H = 421$ A/m at 920 Hz by means of balanced alternating current bridge method (thermomagnetic analysis). Figure 1 shows the temperature dependences of susceptibility $\chi(T)$ of $Ni_{0.33}Zn_{0.67}Fe_2O_4$ sintered at $T_s = 750$, 800, and 850 °C during 6 h. No other crystalline phases were detected by X-ray diffraction presented in [5], however thermomagnetic analysis (Fig. 1) suggest presence of a small amount of second phase of the samples sintered at 750 °C. The size of crystallite was changed from about 95.9 nm to 157 nm within the given temperature range (Table I). Dependences of the average size of crystallites D and the T_C on the sintering temperature are given there. T_C of samples was determined from the $\chi(T)$ dependences. It can be concluded from all curves that the low-temperature susceptibility χ increases with temperature T_s, and the samples with higher grain-size have higher value of χ. It is due to the particles size rise with T_s and the samples with higher particles size have higher susceptibility value according to D-law. All $\chi(T)$ curves exhibit sharp pronounced Hopkinson peaks just below T_C in Fig. 1. At increase of T_s, the Hopkinson peaks become higher, which is an evidence of particle growth in Table I.

All samples with presented $\chi(T)$ in Fig. 1 are small enough to be single-domain particles, see Table I.

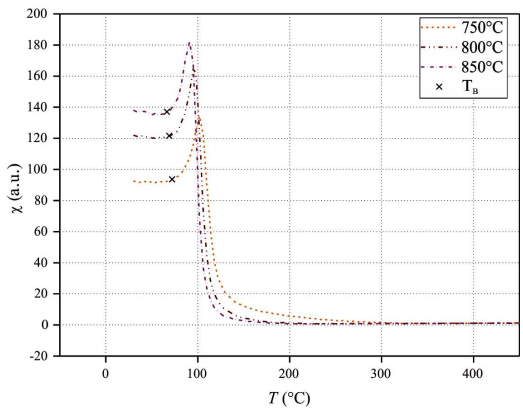

Fig. 1. Temperature dependences of the susceptibility of soft magnetic $Ni_{0.33}Zn_{0.67}Fe_2O_4$ ferrite for $T_s = 750$, 800, and 850 °C.

TABLE I

Size of crystallines D and Curie temperature T_C as a function of sintering temperature T_s

T_s [°C]	D [nm]	T_C [°C]
750	95.9	110.5
800	134.4	103.8
850	157	99.1

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The KV (K — anisotropy constant, V — volume of each particle) would become so small that energy fluctuations could overcome the anisotropy forces and spontaneously reverse the magnetization M_s of particle from one easy direction to the other, even in the absence of an applied field H. Following that, the particles of the samples turn into superparamagnetic state above a blocking temperature T_b just below T_C. When an external field H is applied, it will tend to align the moments of the particles, despite thermal energy and the Hopkinson peak occurs. The blocking temperature T_b (below which the magnetization is stable) of the $Ni_{0.33}Zn_{0.67}$ ferrites was found slightly decreasing with increase of particles size (Fig. 1).

The other contribution to the Hopkinson effect study is as follows. $\chi(T)$ dependences of $Ni_{0.396}Zn_{0.804}Fe_{1.8}O_4$ ferrite samples where the ratio of divalent ions Me^{2+} to trivalent ions Fe^{3+} were 1:1.5 are in Fig. 2. The samples are taken from the same batch sintered at 850 °C/6 h and 1100 °C/6 h. T_C of these samples were approximately 228.3 °C. SEM micrographs of both samples synthesized at T_s = 850 °C and 1100 °C are in Fig. 3. From both Fig. 2 and Fig. 3 one can conclude that the low temperature susceptibility χ increases with T_s due to higher grain size. The existence of the Hopkinson effect is indicated in the sample sintered at T_s = 850 °C.

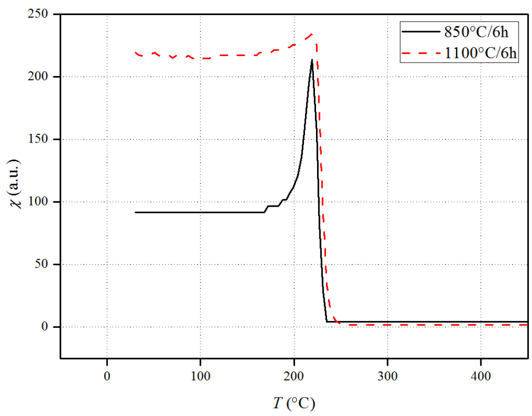

Fig. 2. Temperature dependences of the susceptibility of soft magnetic $Ni_{0.396}Zn_{0.804}Fe_{1.8}O_4$ ferrites.

It can be concluded that the Hopkinson peak appears in the sample sintered at T_s = 850 °C because the particles size D is probably lower than the upper limit D_P of superparamagnetic state, and they are unstable at $T > T_b$ = 190 °C. The main reason of the Hopkinson peak presence is again a rapid decrease of anisotropy field $H_a(T) = 2K/M_S$, yielding overcoming of the anisotropy forces by thermal energy fluctuations and spontaneous reverse of the magnetization M_s of particles. The particles turn into a superparamagnetic state above T_b.

On the contrary, for the sample sintered at 1100 °C a size of particles D is estimated as stable one. These particles are sufficiently large ($D > D_P$) so that the anisotropy is adequate and the magnetization is stable. In the sample at T_s = 1100 °C, all particles are larger than the critical size D_p, and the magnetization may be uniform up to T_C.

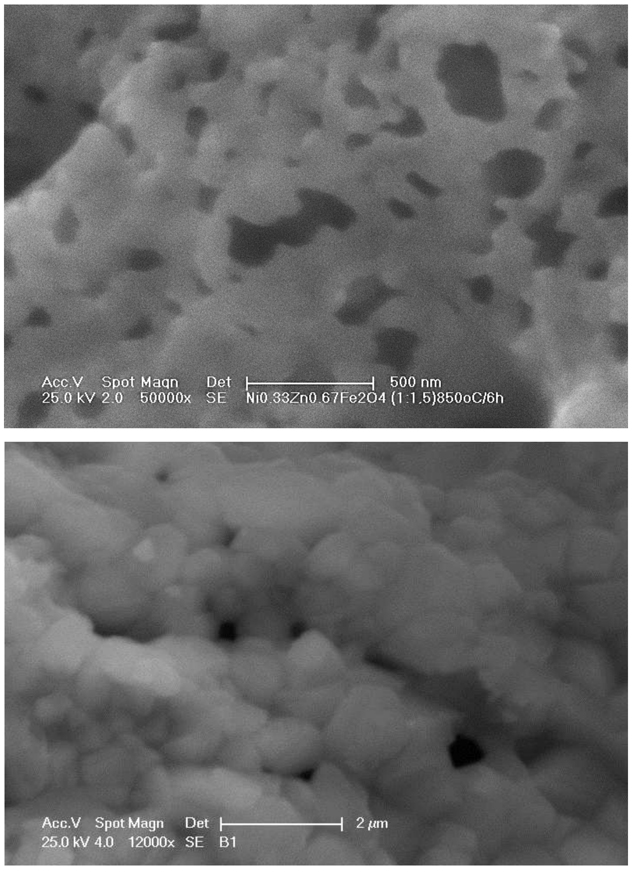

Fig. 3. SEM micrographs of $Ni_{0.396}Zn_{0.804}Fe_{1.8}O_4$ ferrite samples sintered at (top) 850 °C/6 h and (bottom) 1100 °C/6 h.

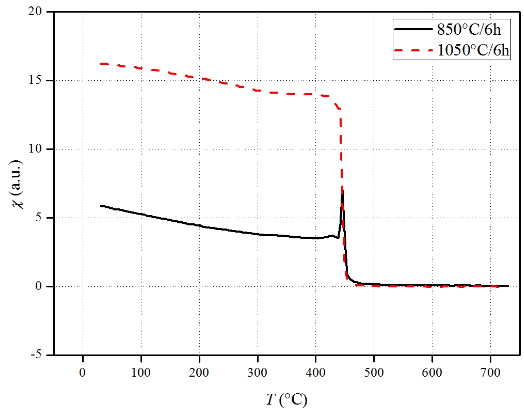

Fig. 4. Temperature dependences of hard magnetic $SrFe_{12}O_{19}$ ferrite sintered in 850 °C/6 h and 1050 °C/6 h.

The next contribution to the Hopkinson effect study is as follows. $\chi(T)$ dependences of $SrFe_{12}O_{19}$ hexaferrite samples prepared by the combustion synthesis, and sintered at 850 °C/6 h and 1050 °C/6 h are shown in Fig. 4. The value of χ at room temperature for sample sintered at T_s = 1050 °C is approximately twice than that for T_s = 850 °C. SEM micrographs of both these ferrite samples sintered at $T_s = 850\,^{\circ}$C and $1050\,^{\circ}$C are shown in Fig. 5. All particles showed nearly hexagonal platelet shape. After the temperature treatment at $850\,^{\circ}$C, uniform particles with hexagonal structure appear, as indicated by excessive Hopkinson peak at temperature $445\,^{\circ}$C (Fig. 4). Such behavior is due to occurrence of the ordered single-phase structure with particles smaller than 1 μm.

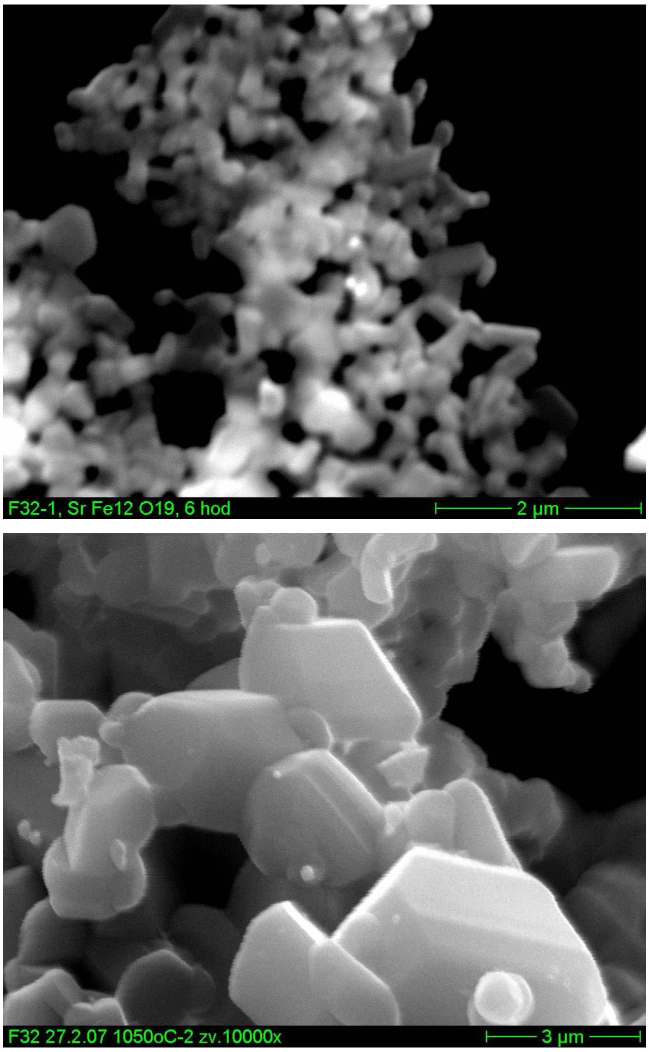

Fig. 5. SEM micrographs of $SrFe_{12}O_{19}$ hexaferrite samples sintered at (top) $850\,^{\circ}$C/6 h and (bottom) $1050\,^{\circ}$C/6 h.

The observation of the Hopkinson effect with associated ferrimagnetic behavior reveals mainly the single domain particle of size under critical volume. The Hopkinson peak at $\chi(T)$ curve appears as a consequence of superparamagnetic state in particles at $T > T_b$. We suppose that this peak can be associated with the transition from the region of stable state to superparamagnetic state of major parts of single domain grains in sintered sample. On the other hand, the Sr ferrite powders treated at $T_s = 1050\,^{\circ}$C have larger average particle size. The corresponding $D > D_p$ can be estimated as roughly stable diameter. All particles are larger than the D_p, and the magnetization may be uniform (without peak) during the transitions along the easy directions up to T_{C}.

3. Conclusion

The Hopkinson effect in a system of soft magnetic NiZn ferrite particles and hard magnetic Sr hexaferrites was experimentally studied. The recorded peaks on the thermomagnetic curves can be explained with the help of an approach developed for the superparamagnetic relaxation. The Hopkinson peak near T_{C} is related with the transition from blocked to superparamagnetic particles. The Hopkinson peak appears always close to T_{C} even for rather different sizes of the particles. It is because there are several materials with different value of T_{C}, M_S, $H_a(T)$ and different value domain wall energy of grains. Then they have disparate value of size of monodomain particles, from that follows different value of their critical size. The key to understand the role of the Hopkinson peak is to recognize that particle (grain) size is smaller than the critical size at blocking temperature with the transition from the region of stable state to superparamagnetic state. Accordingly, we are led to believe that the observed Hopkinson peaks in our synthesized samples are associated with the superparamagnetic relaxations of the particles in the samples.

Acknowledgments

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