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 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 $\chi$ (permeability $\mu$) 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 state with connection of drastic fall of magnetic anisotropy.

2. Experimental results and discussion

The samples of nanosized NiZn ferrites having a structural formula $\text{Ni}_{0.33}\text{Zn}_{0.67}\text{Fe}_2\text{O}_4$ were prepared by auto-combustion method based on glycine precursor, sintered at various temperatures $T_s$ [6]. The magnetic susceptibility $\chi$ 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 $\text{Ni}_{0.33}\text{Zn}_{0.67}\text{Fe}_2\text{O}_4$ 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 $\chi$ increases with temperature $T_s$, and the samples with higher grain-size have higher value of $\chi$. 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$_2$O$_4$ ferrite for $T_s = 750$, 800, and 850 °C.](image)

**TABLE I**

<table>
<thead>
<tr>
<th>$T_s$ [°C]</th>
<th>$D$ [nm]</th>
<th>$T_C$ [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>95.9</td>
<td>110.5</td>
</tr>
<tr>
<td>800</td>
<td>134.4</td>
<td>103.8</td>
</tr>
<tr>
<td>850</td>
<td>157</td>
<td>99.1</td>
</tr>
</tbody>
</table>

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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 $\chi$ increases with $T_s$ due to higher grain size. The existence of the Hopkinson effect is indicated in the sample sintered at $T_s = 850°C$.

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 $T_C$.

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 $\chi$ 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 are shown in Fig. 3.
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 $1\,\mu m$.

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.

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References