

The magnetic properties of glass-ceramics in the $\text{CoO-Fe}_2\text{O}_3\text{-B}_2\text{O}_3$ system

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The preparation of glasses in the $\text{CoO-Fe}_2\text{O}_3\text{-B}_2\text{O}_3$ system is described and it is shown that the magnetic spinel cobalt ferrite (CoFe_2O_4) can be obtained in precipitate when the glasses are heat-treated. The identity of the crystalline phase is established by means of Mössbauer spectroscopy. It is shown that the magnetic properties of the glass-ceramics can be controlled by means of the heat-treatment schedule and intrinsic coercivities as high as 1900 Oe are recorded. The magnetic properties of the as-cast and heat-treated material are discussed generally in terms of superparamagnetic, single domain and multi-domain behaviour. The highest values of the intrinsic coercivity and remanence are compared to those calculated for an assembly of non-interacting single domain particles with positive cubic magnetocrystalline anisotropy.

1. Introduction

In recent years several investigations have been made of glass-ceramics containing a crystalline ferrimagnetic phase [1-6] both for reasons of scientific interest and also because the glass-ceramic route offers a possible alternative to the conventional manufacture of ferrite. Some magnetic properties of materials, particularly the coercivity, are known to be profoundly influenced by the grain size and so it may be anticipated that the small grain size and fine control of the crystallite growth offered by glass-ceramic techniques can be exploited to achieve interesting magnetic properties. The work of Shirk and Buessem [2] is a good example of this idea and in their paper the authors show how higher values of the intrinsic coercivity can be achieved with barium hexaferrite glass-ceramic than are obtained in the conventional manufacture of isotropic barium hexaferrite.

Previous work concerned with glass-ceramics containing ferrites of technical importance has fallen into two areas according to the application of the ferrite: (a) glass-ceramics containing lithium ferrite, which in its sintered form is used as a temperature stable square loop memory element material and (b) glass-ceramics containing barium hexaferrite, which in its sintered form is used as a permanent magnet material.

The present work is an investigation of the magnetic properties of cobalt ferrite glass-ceramic. Cobalt ferrite is a magnetic spinel falling into category (b) and was formerly used as a permanent magnet material although barium and strontium hexaferrites are now the only ferrites currently employed for this purpose. In common with these materials cobalt ferrite has a high magnetocrystalline anisotropy and a high intensity of magnetization per unit mass.

2. Experimental procedure

Initially attempts were made to prepare cobalt ferrite glass-ceramics from silicate, borate and phosphate glasses. These melts were all successful in that the desired phase CoFe_2O_4 was obtained in precipitate, but since the highest coercivities were obtained with borate glasses attention was concentrated on this system. The region of the $\text{CoO-Fe}_2\text{O}_3\text{-B}_2\text{O}_3$ compositional diagram explored is shown in Fig. 1. The batches were melted, cast in the form of a glass and then heat-treated to develop the ferrimagnetic crystalline phase. Cobalt ferrite was found to be the only crystalline phase present in the heat-treated material in all the compositions investigated.

In the as-cast condition the glasses were invariably partially devitrified but the devitrification was kept to a minimum by employing a fast quenching technique. The as-cast material

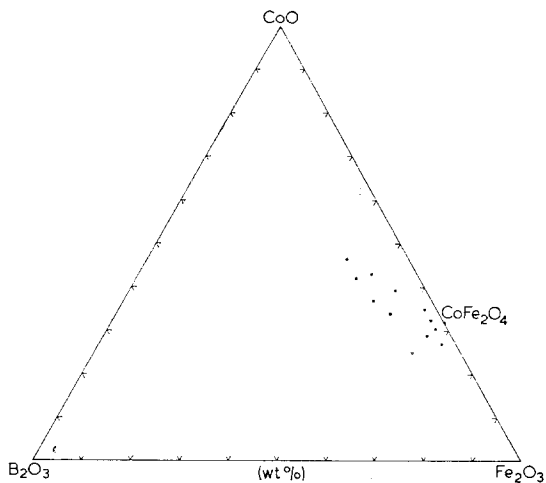


Figure 1 Compositions studied in the CoO-Fe₂O₃-B₂O₃ system.

responded sensitively to heat-treatment and both the percentage crystallinity and the grain size of the resulting glass-ceramic could be controlled by means of the heat-treatment schedule. The magnetic properties of the material were measured and relatively high values of the remanence and coercivity were obtained in some samples.

The identification of the crystalline phase posed something of a problem since it is difficult to differentiate between various magnetic spinels by means of X-ray diffraction techniques and consequently the possibility that magnetite, for example, might be present could not be eliminated. The problem was solved by recourse to the more powerful technique of Mössbauer spectroscopy.

2.1. The preparation of the glass-ceramics

The batch was obtained in fine powder form, intimately mixed and heated to roughly 1100°C in an alumina crucible. This temperature was then held to sinter the batch and to promote the formation of cobalt ferrite by solid state reaction.

The sintering step is advantageous since the formation of the compound CoFe₂O₄ reduces the possibility of there remaining any unreacted Fe₂O₃ which has a tendency to dissociate into Fe₃O₄ at elevated temperatures. After the sintering stage had been completed the temperature of the batch was quickly raised until the batch melted and the melt was then rapidly quenched by casting onto a liquid nitrogen cooled copper plate. A typical melting temperature was 1550°C. The fast quenching was found to be necessary in order to reduce devitrification to a minimum.

The glass was then heat-treated with a time temperature schedule chosen empirically to maximize the coercivity and remanence. In order to achieve this the magnetic properties of the material were measured during the heat-treatment by interrupting the schedule, measuring the magnetic properties at room temperature and then resuming the heat-treatment. The magnetic measurements gave information on the degree of crystallization in addition to the coercivity and remanence and thus by adjusting the temperature of heat-treatment the rate of crystallization could be controlled to any value required to maximize the coercivity and remanence in the fully crystallized material. In general the optimum heat-treatment schedule was found to be a long heat-treatment of approximately 20 h at the lowest temperature consistent with complete crystallization within this period. This temperature, *T*, varied widely with composition and ranged from 310 to 1100°C (Table I). If higher temperatures were chosen, the rate of crystallization was higher but the larger grain size of the material led to a reduction in coercivity and remanence.

2.2. Mössbauer analysis

Mössbauer analysis was undertaken principally to confirm that the phase in precipitate in the heat-treated material was in fact CoFe₂O₄. When the as-cast material was investigated by this

TABLE I Variation of magnetic properties with composition

Glass-ceramic	A	B	C	D	E	F	G	H	I	J	K	L
CoO (wt %)	30.5	29.0	27.0	32.5	35.0	25.0	34.0	37.0	42.0	46.5	39.2	43.0
Fe ₂ O ₃ (wt %)	67.0	66.0	70.0	65.0	62.5	65.0	56.0	51.0	45.0	40.7	54.4	47.6
B ₂ O ₃ (wt %)	2.5	5.0	3.0	2.5	2.5	10.0	10.0	12.0	13.0	12.8	6.4	9.4
<i>T</i> (°C)	310	380	350	380	380	500	550	500	600	930	1010	1100
<i>mH_C</i> (Oe)	1900	1650	1650	1700	1700	600	1000	1100	1000	800	400	400

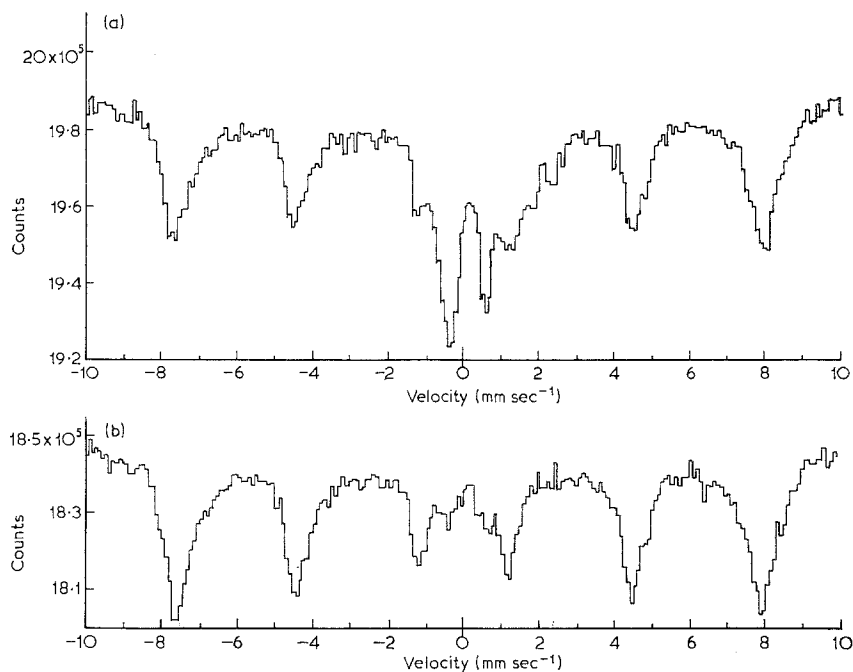


Figure 2 Mössbauer spectra from (a) as-cast and (b) heat-treated cobalt ferrite glass ceramic.

technique the spectra were found to consist of a characteristic six-line splitting together with pronounced central peaks (Fig. 2a). After heat-treatment the central peaks vanished and the six-line splitting became reinforced (Fig. 2b). In order to explain the central peaks in the spectrum from the as-cast material it is necessary first to consider the phenomenon of superparamagnetism.

Superparamagnetism is a magnetic effect occurring in very small grains of magnetic material where the grain size is lower than a certain critical value depending on the magnetic constants of the material. The energy required to rotate the magnetization vector against such anisotropies as may be present in the grain is a volume energy and at sufficiently small grain sizes this energy can fall to a value comparable with the thermal energy kT where k is Boltzmann's constant and T is the temperature. When this occurs the magnetization vector is rotated by the thermal fluctuations and no longer assumes a permanent direction within the grain. In this state the material is said to be superparamagnetic at that temperature.

The characteristic time of observation in Mössbauer spectroscopy is the precessional period of an Fe^{57} nucleus, τ_0 , which is approxi-

mately 10^{-8} sec in this case. Thus if the magnetization vector in superparamagnetic cobalt ferrite rotates in a time τ short compared with τ_0 the effective magnetic field will be zero leading to a central peak in the spectrum. Conversely, if the material is superparamagnetic but with the magnetization vector rotating in a time longer than τ_0 the six-line splitting will occur. Thus superparamagnetic behaviour can lead to either a central peak or to six-line splitting depending on the grain size of the crystallites. Ionic iron is also known to give rise to a central peak. Therefore, since the as-cast material is known to be superparamagnetic from the magnetic evidence presented in the next section, the central peaks in Fig. 2a can be attributed to the presence of superparamagnetic iron with $\tau < \tau_0$ together with a contribution from any ionic iron which may be present. The six-line splitting in the spectrum from the as-cast material shown in Fig. 2a can be attributed to the presence of superparamagnetic cobalt ferrite with $\tau > \tau_0$.

Comparison of the six-line splitting spectrum from the heat-treated material (Fig. 2b) with that from pure cobalt ferrite as recorded in the literature [7] indicates that the crystalline phase is indeed cobalt ferrite. The possible presence of magnetite can be excluded since the spectrum

from magnetite is known to be much more complicated [8]. The presence of crystalline material in the as-cast glass is of course due to partial devitrification which occurred on casting despite the fast-quenching technique employed.

3. Magnetic properties

3.1. Results

The magnetic properties of the glass-ceramics were investigated in two pieces of equipment: (a) an electromagnet for measuring the intrinsic coercivity and remanence of the magnetically hard heat-treated material and (b) an M - H loop plotter working at mains frequency (50 Hz) which was used to determine the magnetic properties of the as-cast material.

M - H plots of the as-cast material were found to be linear or displaying only a small amount of hysteresis which indicates that a considerable amount of cobalt ferrite was present in superparamagnetic form. After heat-treatment, the coercivity increased at all compositions due to the increase in the average grain size. The variation in the intrinsic coercivity MH_C of the heat-treated material with composition is given in Table I. It is interesting to note that the highest value of the coercivity were obtained at those compositions requiring the lowest temperature for heat-treatment T . The highest coercivity achieved was 1900 Oe and this figure may be compared with the 2080 Oe obtained by Berkowitz and Schuele [9] for cobalt ferrite crystallites prepared by a co-precipitation technique.

The remanence also increased markedly with heat-treatment for several reasons. Firstly the higher percentage crystallinity leads to an increased remanence both directly and also because internal demagnetization is reduced at higher concentration of magnetically active phase. Secondly the remanence is increased by virtue of the higher coercivity of the heat-treated material. The greatest remanence occurred in the material of coercivity 1900 Oe and the value of the remanence was measured to be 1500 G. The ratio of the remanence to the high field magnetization was determined as 0.6. The percentage crystallinity of this sample was also determined from measurements of the high field magnetization and the value obtained was 70%. The specific gravity was measured to be 5.0.

3.2. Discussion

The high values of the coercivity and ratio of the remanence to the high field magnetization in

some samples indicate that the magnetic properties of the glass-ceramics are determined principally by the magnetocrystalline anisotropy of the cobalt ferrite. The coercivity of an assembly of small grains is known to be highly dependent on the grain size and the maximum coercivity is attained when the grains are of such a size that they are single domain particles. If the grain size is reduced below this single domain size superparamagnetism occurs yielding a remanence and coercivity of zero. Conversely, above the single domain particle size domain walls are introduced into the crystallites and the coercivity and remanence can be expected to drop since, in general, it is easier to displace a domain wall than to rotate the individual atomic spins coherently against the magnetocrystalline anisotropy. A further noteworthy point is that in multi-domain grains the mobility of the domain walls can be much reduced by the presence of intragranular inclusions. However, crystallites grown from a glassy melt would be expected to be relatively free from such inclusions and it can be anticipated that in this case the coercivity and remanence will rapidly drop when the grain size increases to bring the crystallites into the multi-domain region.

The highest values of coercivity and remanence in the heat-treated material occur, therefore, when the grain size of the cobalt ferrite crystallites approach the single domain particle size. The lower values can be attributed to the presence of multi-domain particles.

Theoretical estimates can be made of the remanent ratio and coercivity of single domain particulate cobalt ferrite. A simple model of the system is an assembly of randomly oriented non-interacting single domain particles with positive cubic magnetocrystalline anisotropy. Néel [10] has considered such an assembly and showed that the intrinsic coercivity MH_C is given by $MH_C = 0.64 K_1/M_s$ where K_1 is the magnetocrystalline anisotropy coefficient and M_s is the saturation magnetization. For cobalt ferrite this expression yields $MH_C = 3000$ Oe which may be compared with the highest experimental value for cobalt ferrite glass-ceramic of 1900 Oe. The remanence of the assembly has been calculated by Gans [11] who found that the ratio of the remanence to the saturation magnetization is 0.832. The highest experimental value for the glass-ceramic was found to be 0.6. The experimental values are thus approaching the theoretic-

cal values calculated from a single domain particle model.

4. Conclusions

Cobalt ferrite can be precipitated from glasses in the $\text{CoO-Fe}_2\text{O}_3\text{-B}_2\text{O}_3$ system and the grain size and hence magnetic properties controlled by the heat-treatment schedule. The highest values of coercivity and ratio of remanence to saturation magnetization approach those calculated from a single domain particle model.

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