JOURNAL OF MATERIALS SCIENCE 9 (1974) 1705–1709

An *in situ* grown eutectic magnetoelectric composite material

Part I Composition and unidirectional solidification

J. VAN DEN BOOMGAARD, D. R. TERRELL, R. A. J. BORN,
H. F. J. I. GILLER
Philips Research Laboratories, Eindhoven, The Netherlands

The phase diagram of the quinary system Fe–Co–Ti–Ba–O contains a region of compositions with the property that unidirectional solidification of liquids with these compositions results in an aligned two phase composite material. One of the phases is a piezomagnetic spinel and the other one a piezoelectric perovskite. The resulting composite is a magnetoelectric material, which can convert magnetic fields into electric fields and vice versa. This paper deals with the determination of the above-mentioned composition region and with the unidirectional solidification process. Some results of magnetoelectric measurements are reported.

1. Introduction

In his paper on "Product Properties: A New Application of Composite Materials" Van Suchtelen [1] mentioned a magneto electric composite material being obtained by unidirectional solidification of a $BaTiO_3$–$CoFe_2O_4$ eutectic liquid.

In this paper it will be shown that in the quinary system Fe–Co–Ti–Ba–O a curved three-dimensional space exists which gives liquid compositions that solidify into two solid phases, a piezomagnetic spinel phase S and a piezoelectric perovskite phase P (Section 2). Because one of the components (oxygen) is volatile and always present in the gas phase at the solidification temperature, the influence of this phase on the solidification process and on the properties of the samples has to be taken into account.

The experimental section deals with the determination of those liquid compositions that give rise to eutectic structures upon solidification (Section 3.1) and with the unidirectional solidification experiments (Section 3.2). In Section 4 the experimental results are considered.

2. The quinary system Fe–Co–Ti–Ba–O

Among the phases of the quinary system Fe–Co–Ti–Ba–O there are three, besides the liquid phase, that are important for our purpose. These are the perovskite phase $BaTiO_3$(P), the spinel phase, $(CoFe_2O_4)_{1-x}(Co_2TiO_4)_x$(S) and the magneto plumbite phase $BaFe_{12-2y}Co_yTi_yO_{19}$(M). Blasse [2] has shown that $CoFe_2O_4$ and Co_2TiO_4 are completely miscible in the solid state. The same holds for $BaFe_{12}O_{19}$ and $BaCo_6Ti_6O_{19}$ [3]. Although this latter phase (M) does not enter into our considerations, there are some indications that it plays a role in the composite materials with the greatest magnetoelectric effect.

We first consider the solidification reaction

$$L \rightarrow S + P$$

in the presence of a gas phase consisting of O_2 and in particular the question whether a eutectic-like equilibrium exists between L, S and P in the presence of O_2 in the gas phase, G, has to be answered.

According to Gibbs phase rule, such an equilibrium must have three degrees of freedom and thus the compositions of the liquids in equilibrium with the solid phases S and P and the gas phase are situated in a curved three-dimensional composition space which is a part of the six-dimensional pressure-temperature: composition space of the system. These equilibria cannot be represented in a simple drawing of the phase diagram. However, if we look at the equilibria at a constant oxygen pressure P_{O_2}, then the number of degrees of freedom is reduced by two because not only is the pressure fixed but because oxygen is the only component present in the gas phase, so also is the chemical potential of the oxygen. The equilibrium between L, P, S and G has now only one degree of freedom, and the composition in the quinary system is determined by the ratio between the elements Fe, Co, Ti and Ba. This enables xs to represent the equilibrium under discussion in a three-dimensional composition tetrahedron.

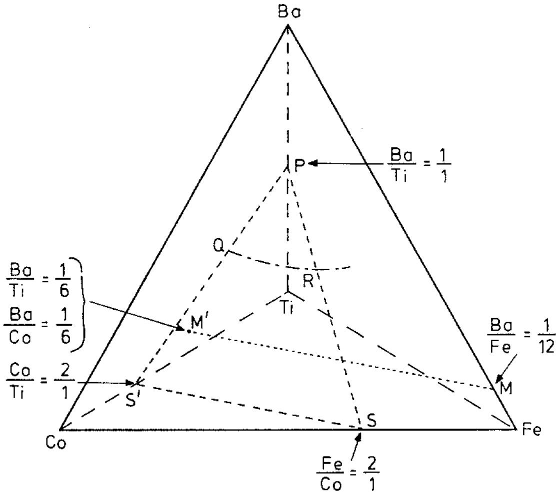

Figure 1 Simplified diagram of the quinary system giving the ratio of the metallic components.

Fig. 1 shows a simplified composition tetrahedron with the chemical symbols of Fe, Co, Ti and Ba at the corners. At the temperatures and oxygen pressures used in our experiments, irrespective of whether there is a deficiency or a surplus of oxygen in the oxide phases, the BaO phase will be stable in the Ba apex, the TiO_2 phase in the Ti apex and the CoO phase in the Co apex of the tetrahedron. In the Fe apex, however, either the FeO phase, or the $FeO_{3/4}(=Fe_3O_4)$ phase or the $FeO_{3/2}(=Fe_2O_3)$ phase may be found, depending on the chosen oxygen pressure. At S and S'the spinel phases with the composition $CoFe_2O_4$ and Co_2TiO_4, respectively, will be present. As these two phases exhibit a complete mutual solid solubility [2] the spinel phase extends from S' to S. Of course this spinel phase will not be restricted to this line but will form a long-drawn sausage around it, the exact form of which will depend on the chosen values of the temperature and the P_{O_2}.

At P the perovskite phase $BaTiO_3$ is present. This phase will have an existence region within the tetrahedron the form of which will again depend on the temperature and the P_{O_2}. If the existence region of the S phase were only given by the line SS' and that of the P phase by the point P, the compositions of the liquid (if any) in equilibrium with the applied P_{O_2} and the solid phases P and S would be situated on a curve in the plane through SS' and P, e.g. a curve starting at Q and intersecting the line PS at R (Fig. 1). This curve is the projection of a temperature/composition curve at a constant P_{O_2} on the composition tetrahedron giving the ratio between the amounts of Fe, Co, Ti and Ba in liquids, in equilibrium with the P and S phase at a constant P_{O_2}. It may be compared with the projection of the ternary liquidus curve in ternary systems [4]. In practice, however, because the S phase is not restricted to compositions on the line SS' and the P phase is not restricted to the point P, this curve of compositions of the liquids will be situated on a regulated surface between the two solid phases. In our case this curve seems to be situated rather close to the plane through SS' and P.

With this curve an effective ternary solidus is associated, in the same way as effective ternary solidus curve is associated with a ternary liquidus curve in a ternary system [4]. This curve has to be known in order to be able to obtain regular eutectic structures upon solidification under steady state conditions (i.e. without primary precipitates [4]). This curve has to be determined for each P_{O_2}. So far we have not observed much influence of the P_{O_2} on the position of this curve of coupled growth. Therefore, only the curve for $P_{O_2} = 1$ atm has been determined to some extent by means of the Bridgman technique (Section 3)*.

3. Experimental

3.1. Determination of the curve of coupled growth at $P_{O_2} = 1$ atm

Small samples of different compositions were solidified unidirectionally in thin walled Pt tubes by means of the Bridgman technique. The ambient was 1 atm O_2 and the growth rate 50 cm h^{-1}.

The solidified samples were examined microscopically and by X-ray analysis. Only those

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*Because, depending on the value of G/R (temperature gradient/solidification rate) not only samples with compositions situated on the curve of the coupled growth will exhibit regular eutectic structures, but also compositions in the neighbourhood of that curve [5, 4]. The compositions determined will not exactly be situated on a single curve.

samples that did not contain a third phase or primary precipitates were used to determine the curve of coupled growth.

The starting materials were $BaCO_3$, $CoCO_3$, TiO_2 and Fe_2O_3. The purity of the $BaCO_3$ was 99% the other materials having a purity of 99.9%.

3.2. Unidirectional solidification experiments

Unidirectionally solidified samples were made using the edge-defined film-fed growth technique of Labelle and Mlavski [6, 7]. As the average composition of the solid differs from that of the liquid, concentration gradients are built up at the solidification front [4]. Therefore, a multichannel capillary had to be used [8] in order to avoid radial concentration gradients in the solidified bars. A schematic drawing of the crucible and the capillary used in our experiments is given in Fig. 2. The crucible and capillary material used was Pt with 20 to 30 wt % Rh. This was chosen because it was wetted very well by the melt but did not react with it. In order to obtain highly homogeneous melts the crucible with contents was kept for 2 h above the melting temperature in the desired atmosphere before the unidirectional solidification process was started. Then a Pt 20% Rh wire was lowered to the top of the capillary until it was wetted by the melt. After that it was withdrawn at the desired speed and the temperature was regulated such that the film thickness, had the maximum value for the growth of a rod with a stable (= constant) diameter. This was done as an extra measure to ensure the homogeneity of the growing bar.

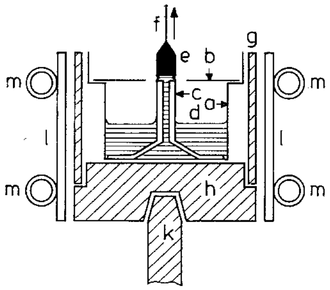

Figure 2 Schematic drawing of the crucible with capillary. a = Pt 30% Rh crucible; b = lid of the same material; c = capillary of the same material o.d. 5 mm, i.d. 0.8 mm; d = melt; e = growing composite material; f = Pt–20% Rh wire; g = ceramic ring; h = ceramic plate; k = ceramic rod; l = copper r.f. coil; m = water cooling (copper pipe).

The oxygen pressure was kept low in order to avoid oxygen bubbles, oxidation of Rh and evaporation of RhO. As in the experiments reported here, no influence of the presence of N_2 in the ambient has been found; the low oxygen pressures were obtained with mixtures of N_2 and O_2 with a total pressure of 1 atm.

Although the oxygen pressure and the ratio of the metal components were found to have some influence on the properties of the composite material, we focused our attention in the first place on small variations of the composition while keeping the growth velocity and the oxygen pressure constant.

TABLE I Compositions of melts resulting in regular eutectic two-phase structures after unidirectional solidification under steady state conditions.

Sample	Composition in mol %			
	CoO	Fe_2O_3	TiO_2	BaO
(a)	28.62	9.06	34.48	27.83
(b)	25.44	15.61	29.45	29.50
(c)	25.15	14.28	31.40	29.17
(d)	28.25	12.99	29.92	28.84
(e)	27.78	11.12	32.75	28.36
(f)	23.65	16.04	30 13	30.18
(g)	24.27	15.61	30.61	29.50
(h)	25.30	14.94	30.43	29.33
(i)	26.29	14.29	30.25	29.17
(k)	26.13	13.64	31.23	29.00

4. Results

Table I gives a number of compositions that exhibit regular eutectic two-phase structures after unidirectional solidification with the Bridgman technique. Unidirectionally solidified bars made with the Labelle and Mlavski technique were mostly prepared with composition (a) of Table I and with small variations of this composition. The growth rate was fixed at 1.8 cm h^{-1} and the P_{O_2} was also fixed (2.5% O_2 in N_2). Fig. 3 shows a transverse section of a rod with a eutectic structure. In nearly all cases the ⟨100⟩ direction of the P phase was parallel to the growth direction. The same holds for the ⟨100⟩ direction of the S phase, i.e. the ⟨100⟩ directions of both phases are parallel to each other. There are indications, that, certainly in small regions, the other cubic directions of both phases are also parallel to each other. It would appear from transverse sections of some of the solidified bars that in some cases the ⟨111⟩ directions of both phases are parallel to the growth direction, but this has not yet been confirmed by X-ray analyses.

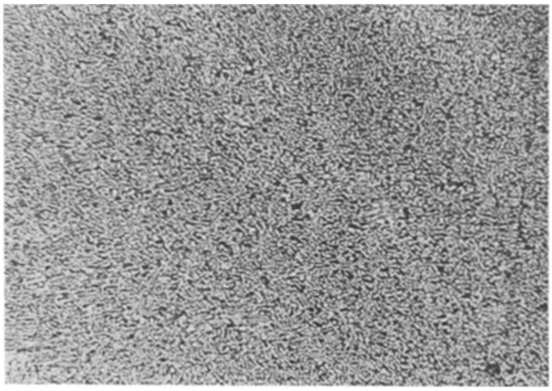

Figure 3 Micrograph of a transverse section of a unidirectionally solidified rod, with a regular eutectic structure. The dark phase is perovskite, × 20.

The magnetoelectric effects were measured by Van Run *et al.* [9]. For bars with a composition (a) in Table I, having a regular eutectic structure, they found:

$$\left(\frac{\mathrm{d}E}{\mathrm{d}H}\right)_{\max} = 1 - 4\,\mathrm{mV\,cm^{-1}\,Oe^{-1}}\,.$$

A slight excess of TiO_2 in composition (a) ($\approx$ 1.5 wt %) resulted in a much higher magnetoelectric effect. The highest value found up till now is:

$$\left(\frac{\mathrm{d}E}{\mathrm{d}H}\right)_{\max} = 50\,\mathrm{mV\,cm^{-1}\,Oe^{-1}}\,.$$

It was found that a composite with a slight excess of TiO_2 had a cellular structure as shown in Fig. 4. In the middle of the cells four-finned spinel dendrites are present surrounded by a eutectic structure of spinel and perovskite. The cell walls consist of perovskite with coarse precipitates. Finned dendrites of this type may be expected in such faceted composites [10].

The form of the dendrites suggests that their $\langle 100 \rangle$ direction is parallel to the growth direction of the composite. This is confirmed by X-ray analyses. These X-ray analyses also revealed that the material contained a relatively large amount of the magnetoplumbite phase (M). This is not unexpected. In the simplified diagram of Fig. 1 it can be seen that the existence region of this phase lies close behind the plane PSS′, namely, in the neighbourhood of the line MM′, which means that even small amounts of additional TiO_2 may result in relatively large amounts of this third phase.

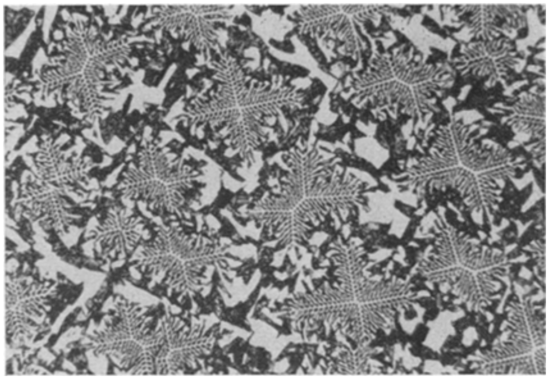

Figure 4 Micrograph of a transverse section of a unidirectionally solidified rod with an excess of TiO_2 ($\sim 1\frac{1}{2}$ wt %) showing four finned spinel dendrites in cells, × 100.

Microprobe analysis revealed that a part of the coarse precipitates in the cell walls consisted of the M phase. The other part consisted of the S phase.

Although we have not found that the oxygen pressure has a large influence on the composition of the liquids resulting in regular eutectic structures upon unidirectional solidification (see Section 2) it does have a significant influence on the ratio $Fe^{2+}:Fe^{3+}$ in the spinel phase. It is a well known fact that the electrical conductivity of this phase, and hence that of the composite material, is strongly dependent on the presence of Fe^{2+}. This conductivity will, therefore, be dependent on the oxygen pressure during unidirectional solidification. On the other hand, since $2Fe^{3+}$ may be replaced by $1\,Co^{2+} + 1\,Ti^{4+}$ in $CoFe_2O_4$, this conductivity will also depend on the Ti content of the spinel phase. Both effects were indeed found experimentally. A sample of composition (a) of Table I has a resistivity high enough to measure the *H–E* effect (magnetoelectric effect) if solidified at 1.8 cm h^{-1} in N_2 + 2.5% O_2. When the sample is solidified at the same speed in N_2 the resistivity is too low for the *H–E* effect to be measured.

A sample of composition close to the composition (f) in Table I, however, has a low electrical resistivity even though grown in N_2 + 2.5% O_2. In both cases the electrical resistivity can be increased to a sufficiently high value by firing the sample afterwards in an atmosphere of pure oxygen at 950°C.

5. Conclusions

It has been shown that the magnetoelectric composite materials can be grown in a one step process. Conversion factors higher than those of single phase magnetoelectric materials have been obtained at room temperature. The physical properties will be discussed in more detail by Van Run *et al.* [9]. A great number of questions is still to be answered such as for example the influence on the magnitude of the effect of the growth-rate, the oxygen pressure the exact composition of the phases and the presence of the spinel dendrites (Fig. 4).

Acknowledgements

The authors are greatly indebted to Mr J. Liebe for the careful preparation of the samples to Mr C. Langereis for the X-ray analysis and to Mr P. A. Paans for the electron microprobe analysis.

References

1. J. VAN SUCHTELEN, *Philips Res. Repts.* **27** (1972) 28.
2. G. BLASSE, *ibid Suppl.* **3** (1969) 1.
3. H. B. G. CASISMIR, J. SMIT, U. ENZ, J. F. FAST, H. P. J. WIJN, E. Q. GORTER, A. J. W. DRUYVESTYN, J. D. FAST and J. J. DE JONG, *J. de Phys. et le Radium* **20** (1959) 360.
4. J. VAN DEN BOOMGAARD, *Met. Trans.* **4** (1973) 1485.
5. R. M. SHARP and M. C. FLEMINGS, *ibid* **4** (1973) 997.
6. H. E. LABELLE and A. I. MLAVSKI, *Mat. Res. Bull.* **6** (1971) 571.
7. *Idem, ibid* **6** (1971) 581.
8. F. H. COCKS, J. T. A. POLLOCK and J. S. BAILEY, Proceedings of the Conference on *In Situ* Composites, September 5-8 1972. Lakeville, Connecticut, Vol. 1, pp. 141-152.
9. A. M. J. G. VAN RUN, D. R. TERRELL and J. H. SCHOLING, *J. Mater. Sci.* **9** (1974) 1710.
10. J. VAN SUCHTELEN, to be published.

Received 22 May and accepted 10 June 1974.