INFLUENCE OF A LOW AC MAGNETIC FIELD ON GLASS MELTS WITH PARAMAGNETIC IONS

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Introduction. Compositions from the ternary system BaO-B_2O_3-Fe_2O_3 are useful for the synthesis of modified single crystalline barium hexaferrite powders by the glass crystallization technique (GCT) [1]. Such special barium hexaferrite powder $BaA^{II}_xB^{IV}_xFe_{12-2x}O_{19}$ (A^{II}: Co^{2+}, Mn^{2+} e.g.; B^{IV}: Ti^{4+}, Ru^{4+} e.g.) are a very important magnetic material for different applications. Their technical applications range from high-density magnetic recording media [2], hyperthermia in the medicine [3] to chemical [4] and microwave absorbing materials [5]. Very homogeneous melts (thermal and chemical) and a defined redox ratio are required amongst other things for the manufacturing of such barium hexaferrite powder by GCT.

The melts from the system BaO-B_2O_3-Fe_2O_3 are in black. In black melts the heat transport by radiation is nearly zero. Consequently the problems of homogeneity increase. Moreover, the iron ions and the partially substituted A^{II}-ions are paramagnetic ones with a defined magnet moment $n^*\mu_B$. It is very interesting to answer the question, how a low AC magnetic field ($\ll 1$ T) which is impressed during the melting until the cooling can help to homogenize the melt and to adjust the redox ratio and therefore the crystallization – without mechanical contact, controlled and independent on other process parameters.

The influence of high static magnetic ($\gg 1$ T) fields on the crystal orientation and phase transformation in solidified structures of metals, alloys and ceramics of different magnetic permeabilities was recently researched in many cases [7, 8, 9].

In this study a low inhomogeneous AC magnetic field (up to 55 mT, 50 Hz) was imposed in the melts. They contain 33.84 wt% iron oxide. The used experimental set-up as well as the experimental procedure will be described in detail (Section 1). In Section 2 we illustrate and discuss the results by means of in-situ measured temperature distributions using a protected thermocouple and ex-situ (drilled out samples of the cooled melt) by density as well as by X-ray diffraction and vibrating sample magnetometer measurements.

1. Experimental procedures. The equipment used in the experimental investigations are shown in Fig. 1 The set-up consists of a furnace with a maximum temperature of 1500°C electrically heated by six heating elements (SiC-bifilar-rods) and an alternating current (AC) magnet system. A cylindrical melt crucible (inner diameter: 80 mm, height: 100 mm) is positioned in the center of the furnace ($x = y = 0$). It is filled with the molten material of 48.14 BaO - 18.02 B_2O_3 - 33.84 Fe_2O_3 (wt%) up to a height

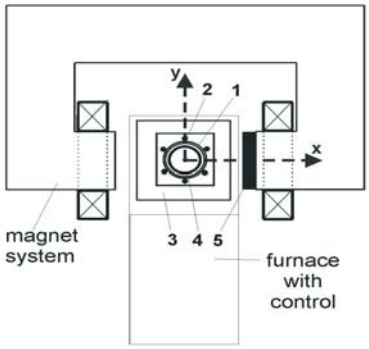

Fig. 1. Top view on the arrangement of the electrically heated furnace with the AC magnet system; 1 – mullite tube, 2 – heating rods, 3 – heat insulation, 4 – Pt crucible, 5 - additional pole shoe (MnZn-ferrite).

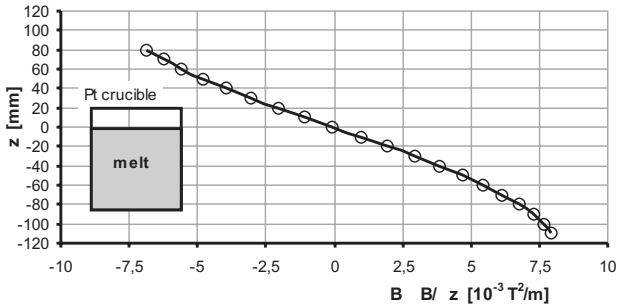

Fig. 2. Distribution of the field gradient $B \cdot \Delta B/\Delta z$ calculated from the flux density distribution $B(z)$ measured by a Hall sensor; z-positions of the Pt crucible and the melt position are plotted schematically.

of 80 mm. The crucible consists of oxide dispersion strengthened platinum (ODS-Pt) to attain a sufficiently high temperature stability and to minimize its corrosion.

Because the furnace is located in the air gap of the magnetic system and the frequency (50 Hz) of the magnetic field is very low, the generated magnetic field can penetrate completely the crucible and the melt [10].

In order to obtain a larger field gradient, the air gap was deformed asymmetrically in z-direction with an additional pole shoe made up of MnZn ferrite (see Fig. 1).

The generated distribution of the field gradient in the air gap is shown in Fig. 2. The active field gradients amount $B \cdot \Delta B/\Delta z$ of the air gap height $\pm 8 \cdot 10^{-3}$ T^2/m and $+6,7 \cdot 10^{-3}$ T^2/m at the bottom of the crucible with a maximum flux density of 44 mT.

The melting procedures without and with such inhomogeneous AC magnetic field are identical. The raw materials were heated up to 1300°C with a heating rate of 1,5 K/min. The residence time was 240 min without magnet field or 150 min without plus 90 min with magnetic field.

In order to quantify the influence of the magnet field gradient in-situ we have measured the temperature ϑ_M at different positions z in the melts using a protected thermocouple (diameter: 1 mm, PtRh-Pt typ B, electrotherm Geraberg, Germany). After the residence times the melts were cooled down to room temperature with a defined cooling rate of 5 K/min. The magnetic field was switched off at 1050°C, so that the field gradient is acting only on the melt, but not on the crystallized and solidified structures. The viscosity of the tested melt amounts 10 dPas at 1050°C.

From the solidified melts we dilled out several samples (volume: 1 cm^3) for material investigations (ex-situ). The position of the probes are shown in Fig. 3. The drilled cores were split into three parts. Thus we obtained at each position one bottom, one middle and one top sample (in the z-direction). The densities of all top and bottom samples were determined using a gas pycnometer (Typ ACCUPYC 1330, Micromeritics). After it selected samples were filled in a vessel containing diluted acetic acid (2h/10%

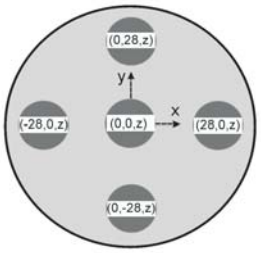

Fig. 3. Top view of the Pt crucible with the cooled melt and the drilling plan.

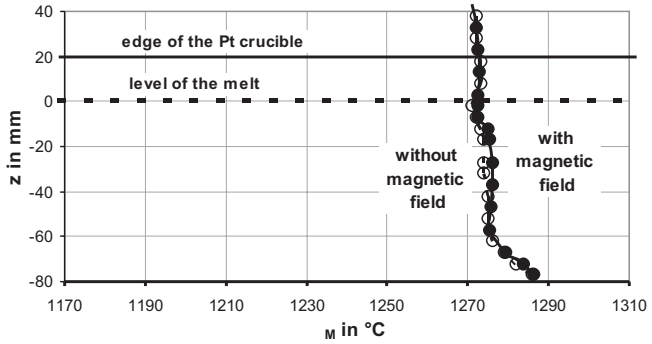

Fig. 4. Temperature distribution $\vartheta_M(z)$ in the melt – without and with the inhomogeneous AC magnet field at the furnace temperature 1300°C.

Table 1. Average differences of the densities (top – bottom) of the drilled cores in comparison to the magnetic properties of the corresponding ferrite powder (solved drilled cores)

Melt experiment	density difference $[10^3$ g/cm$^3]$	saturation magnetization [kA/m]		coercivity [kA/m]	
	drilled cores	top	bottom	top	bottom
without magnetic field	$-7,2$	180	190	44.9	35.4
with magnetic field	$-12,8$	265	325	21.7	10.7

CH_3COOH). The acetic acid dissolves the soluble phases borates), but the contained ferrite crystals stay unsolved. These crystals were analysed by X-ray diffraction (Bruker AXS D8 advance). Their magnetic properties were characterized by a vibrating sample magnetometer (VSM 7300 Lake Shore). The comparison between the results of the same melt procedure but with and without the magnetic field shows the influence of a low AC magnetic field in a glass melt with different iron ions Fe^{2+}/Fe^{3+}.

2. Results and discussion. In Fig. 4 temperature distributions $\vartheta(z)$ for the melt are shown measured at equal positions in the melt $x = y = 0$, but without and with the inhomogeneous AC magnetic field.

The magnetic field gradient did not change the temperature distribution $\vartheta(z)$ but the density differences and the magnetic properties between the top and bottom samples (see Table 1.)

In the case of melt experiments with magnetic field the density difference between the drilled cores (top – bottom) increases. The magnetic field gradient has changed the crystallization. It is shown by the measured magnetic properties.

Applying the inhomogeneous magnetic field during the melt process the saturation magnetizations increase generally and the coercivity decrease (top and bottom) compared with the melt experiment without magnetic field. Furthermore, in both cases the bottom saturation magnetizations are higher and the bottom coercivity are lower. Higher saturation magnetizations and lower coercivity can only result by decreasing amounts of hard magnetic phases and increasing amounts of the soft magnetic phases in the obtained ferrite powder. By systematic X-ray diffraction measurements it is found that M-type barium hexaferrite ($BaFe_{12}O_{19}$), W-type barium hexaferrite ($BaFe_{18}O_{27}$) and a low rate of magnetite (Fe_3O_4) are existing in all ferrite powders. On the base of all analyses it can be only that the portion of the W-type hexaferrite increases and the rate of the M-type hexaferrite decreases if the magnetic field penetrates the melt. These changes are associated with an increased Fe^{2+}/Fe^{3+} – ratio in the samples and consequently in the melt. In order to prove this conclusions chemical analyses and further X-ray diffraction measurements are planned.

The reason for these very interesting effects is the interaction of magnetic interfacial forces [6] (known also magnetization force) at the iron ions (see Fig. 5). The magnetic interfacial forces are generally dependent on the magnetic moments of the ions in the melt (the outcome of this is the magnetic susceptibility of solidified structures) and their sizes as well as on the value of the magnetic field gradient. Its direction is determined by the direction of the field gradient.

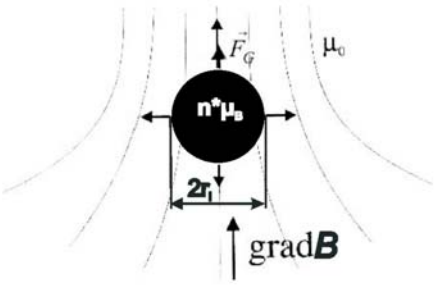

Fig. 5. Magnetic interfacial forces $\mathbf{F}_G$ in glass melts with one paramagnetic ion whose magnetic moment amounts $n^*\mu_B$, whose radius is r_i and which is located in an inhomogeneous magnetic field with the field gradient grad $\mathbf{B}$, $\mu_B = 9,27 \cdot 10^{-24}$ Am^2 (Bohr Magneton), $\mu_0 = 4\pi \cdot 10^{-7}$ Vs/Am (absolute permeability).

In contrast to the effect of strong magnetic fields [9], it can be predicted here that the changes of the enthalpy of the liquid respectively solid phases are not modified by the presence of the low AC magnetic field. Further effects as a result of the induction of eddy currents can be also disregard. The electrical conductivity of the melts (at 1300°C: 46 S/m, at 1050°C: 13 S/m) and the frequency of the magnetic field (50 Hz) are to low.

3. Summary. The present paper demonstrates experimental results concerning the manipulation of the chemical homogeneity of indirect electrically heated melts from the $BaO - B_2O_3 - Fe_2O_3$ system using an inhomogeneous alternating magnetic field with a frequency of 50 Hz and a field gradient of $+6,710^{-3}$ T^2/m in the melt at a maximum flux density of 44 mT.

The investigations show that the temperature distribution $\vartheta(z)$ in the melt is not influenced by the low AC magnetic field. But the material properties like chemical homogeneity and density distribution are substantially changed in the solidified material. These effects arise from the magnetic interfacial force which is generated by the different magnetic moments of the iron ions Fe^{2+}/Fe^{3+} and the gradient of the AC magnetic field.

The results of the work show that the effects of magnetic interfacial force are capable to influence the chemical homogeneity in all melts, which contain paramagnetic ions, if an inhomogeneous magnetic field penetrates the melts. Many questions are still open and will be subjected by further experiments. Chemical analyses of the Fe^{2+}/Fe^{3+}-ratio, new experiments with another crucible position ($+\Delta B/\Delta z \cdot B$) and numerical simulations will complete the investigations.

REFERENCES

1. St. Belau, B. Halbedel, M. Jakob, D. Hülsenberg. Synthesis of modified single crystalline barium hexaferrite powders by glass crystallization technique. In *Proc. euromat* (Prague, Czech Republic, 5–8 September 2005).
2. P. Görnert, E. Sinn, H. Pfeiffer, W. Schüppel, M. Rösler. Glass crystallized barium ferrite powders for magnetic recording media. *J. of the Magnetic Society of Japan*, vol. 15 Supplement (1991), no. S2, pp. 669–674.
3. I. Hilger K. Frühauf, W. Andrä, R. Hiergeist *et al.* Magnetic heating as a therapeutic tool. *Thermology International*, vol. 11 (2001), pp. 130–136.
4. B. Halbedel, M. Jakob, K. Pfeifer, D. Hülsenberg. Compact, ceramic magnetic granules for applications in magnetic field supported methods and processes of chemical and biological engineering. *cfi/Ber. DKG*, vol. 81 (2004), no. 11, pp. E39–E44.
5. T. Toyoda, K. Kitagawa, K. Yamawaki *et al.* Site preference study of Ti-Mn and Ti-Co substitution for Fe3+ in Ba hexagonal ferrites by means of X-ray diffraction and absorption measurement. *J. Ceramic Society of Japan, Supplement 112-1, RacRim5 Special Issue*, vol. 112 (2004), no. 5, pp. 1455–1458.
6. B. Halbedel, U. Krieger, D. Hülsenberg *et al.* Generation and Influences of Lorentz and Magnetic Interfacial Forces on Black Glass Melts from the $BaO - B_2O_3 - Fe_2O_3 - SiO_2$ System. In *Proc. of the Asia-Euro Workshop on Electromagnetic Processing of Materials* (Shenyang, China, Sept. 6-8, 2004), pp. 61–67.
7. W. Watanabe, M. Motokawa. *Materials science in static high magnetic fields* (Springer Verlag Berlin, 2001).
8. K. Sassa, H. Morigawa, S. Asai. Controls of Precipitating Phase Aligment and Crystal Orientation Using High Magnetic Field. *J. Japan Inst. Metal*, vol. 61 (1997), no. 12, pp. 1283–1287.
9. W. Qiang, W. Eng-gang, H. Ji-eng *et al.* Effects of strong magnetic fields on solidified structures of metals with different susceptibilities. In *Proc. of the Electromagnetic Processing of Materials International Conference* (2003), pp. 464–468.
10. D. Hülsenberg, B. Halbedel, G. Conrad *et al.* Electromagnetic stirring of glass melts using Lorentz forces – Experimental resultsn. *Glass Sci. Technol.*, vol. 77 (2004), no. 4, pp. 186–192.