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B. Halbedel, U. Krieger

Modification of iron oxide containing glass melts and their crystallization behaviour under an inhomogeneous, low AC magnetic field

7 - ELECTRO-PROCESSING TECHNOLOGIES

Abstract

In terms of electromagnetic processing of materials the interactions of high magnetic fields (>> 1 T) with solidified structures of metals, alloys and ceramics are well known and applied for crystal orientation and phase transformation, e. g. [1], [2] and [3]. In contrast the influence of an inhomogeneous low magnetic field on melts with a high content of paramagnetic ions is rarely investigated.

In this study an inhomogeneous AC magnetic field with a low flux density (up to 55 mT) was imposed on a melt containing 33.84 wt% iron oxide. The changes in the material properties of the solidified melts were investigated due to the interaction with the magnetic field gradient. The outcome of this is the effect of the magnetic gradient force acting on the ions in such melts. It enables the feasibility to influence the phase segregation and the valence of the iron ions in the melt as well as the following crystallization – without any mechanical contact and independent on other process parameters. That creates new innovative possibilities of electromagnetic processing of magnetic materials in order to adjust their properties.

1 Introduction

Melts with a high content of iron oxide are qualified for the synthesis of ferrites, particularly for the fabrication of single crystalline ferrite powders by the glass crystallization technique, [4-6]. The optimization of the production process and the modification of such powders requires the realisation of additional parameters which must be independent of the conventional process control. In order to realise this we use an inhomogeneous magnetic field during the melting [7]. The application of an inhomogeneous magnetic field to the melt results in a gradient force acting on the iron

ions (also known as magnetic interfacial force).

The magnetic gradient force $\vec{F}_\nabla$ is determined by Eq. (1)

$$\vec{F}_\nabla = \frac{\chi_m}{\mu_0} \cdot C \cdot (\vec{B} \cdot \nabla)\vec{B} \qquad (1)$$

where χ_m is the magnetic susceptibility of the electromagnetic modifiable regions in the material, μ_0 the absolute permeability, B the magnetic flux density and C the concentration of paramagnetic ions.

For the estimation of the magnetic gradient force we assume only one paramagnetic ion with the volume V_I and the magnetic moments $n^*\mu_B$ located in the melt, with the permeability of its vicinity μ_0 and a magnetic field which is inhomogeneous only in the z-direction (see Fig. 1). We get Eq. (2)

$$\vec{f}_\nabla = \frac{n \cdot \mu_B}{\mu_0 \cdot V_I} \cdot \frac{dB}{dz} \qquad (2)$$

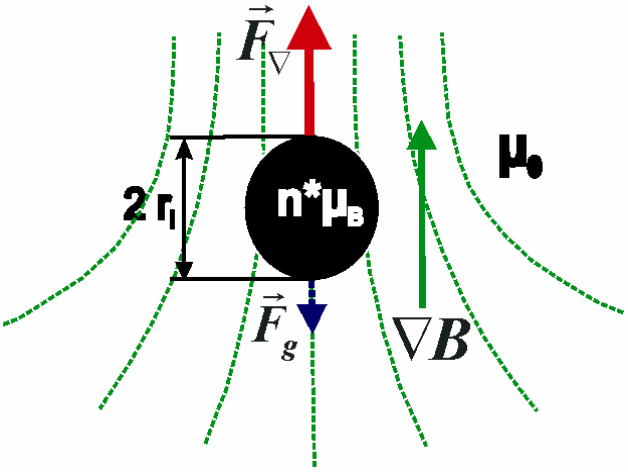

Fig. 1: Magnetic gradient force $\vec{F}_\nabla$ and gravitational force $\vec{F}_g$ in a glass melt acting on one paramagnetic ion with the ion radius $\mathbf{r_i}$ and magnetic moments $\mathbf{n^*\mu_B}$, which is located in an inhomogeneous magnetic field with the field gradient $\nabla \boldsymbol{B}$ [7].

μ_B =9,27·10^{-24} Am^2 (Bohr Magneton)
μ_0 = 4π·10^{-7} Vs/Am (absolute permeability)

It is readily identified that the magnetic gradient force density $\vec{f}_\nabla$ is generally dependent on the density of the magnetic moments of the ions in the melt ($n \cdot \mu_B/V_I$) as well as on the value of the magnetic field gradient $\nabla \boldsymbol{B}$. The direction of $\vec{f}_\nabla$ is determined by the direction of $\nabla \boldsymbol{B}$.

From calculations using Eq. (2) we have obtained, that in fluids which contains Fe^{3+}-ions (n = 5) and are penetrated with an inhomogeneous magnetic field the gradient $\boldsymbol{dB/dz}$ = +0.1 T/m creates an approximately five times larger gradient force compared to the gravitational force [7].

Until now the possible effects of such force ratios on the local chemical composition in the melt and the following crystallization are unknown. For the determination of these effects we performed comparative melt experiments without and with a defined

inhomogeneous magnetic field and measured the changes of the chemical and physical properties of the solidified melts.

The used experimental set-up as well as the experimental procedure will be described in detail (section 2). In Section 3 we illustrate and discuss the results by means of in-situ measured temperature distributions obtained with a protected thermocouple and ex-situ (drilled samples from the solidified melts) by using X-Ray diffraction, chemical analysis and vibrating sample magnetometer measurements.

2 Experimental set-up

The equipment of the experimental investigations is shown in Fig. 2. The set-up consists of an electrically heated furnace with a maximum temperature of 1500°C provided by six heating elements (SiC-bifilar-rods) and an alternating current magnet system.

In order to prevent melt flows as a result of buoyancy, the heating system generates a very homogeneous temperature field in the area of the furnace where the crucible is positioned. The crucible is cylindrical (inner diameter: 80 mm, height: 100 mm), and consists of oxide dispersion strengthened platinum (ODS-Pt) to attain a sufficiently high temperature stability and to minimize its corrosion.

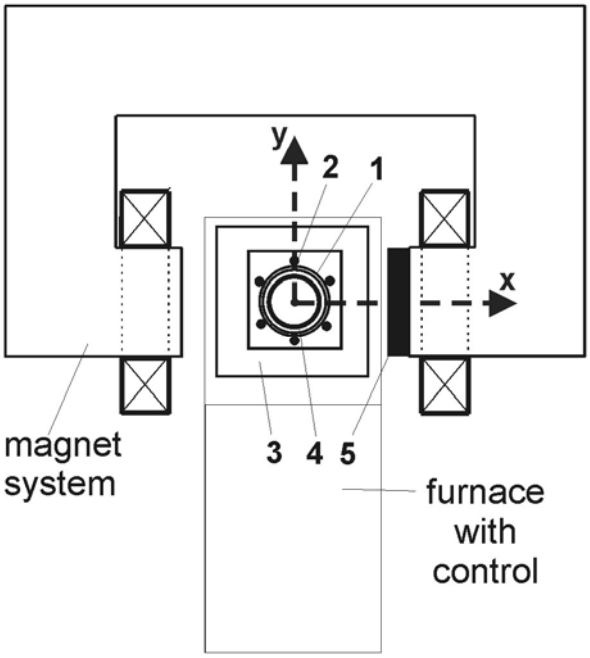

Fig 2: Top view on the arrangement of the electrically heated furnace with the AC magnet system [7].
1 - mullite tube, 2 - heating rods, 3 - heat insulation, 4 - Pt crucible, 5 - additional pole shoe (MnZn-ferrite)

The Pt-crucible contains the molten material of 48.14% BaO + 18.02% B_2O_3 + 33.84% Fe_2O_3 (wt%) up to a height of 80 mm.

Due to the location of the furnace in the air gap of the magnet system and the low frequency (50 Hz) the generated magnetic field penetrates the crucible and the melt completely. In order to obtain a larger field gradient in the z-direction, the air gap is asymmetrically deformed in z-direction with an additional pole shoe made of MnZn ferrite (see Fig. 2). The generated distribution of the flux density B_x in the air gap about z is

shown in Fig. 3.

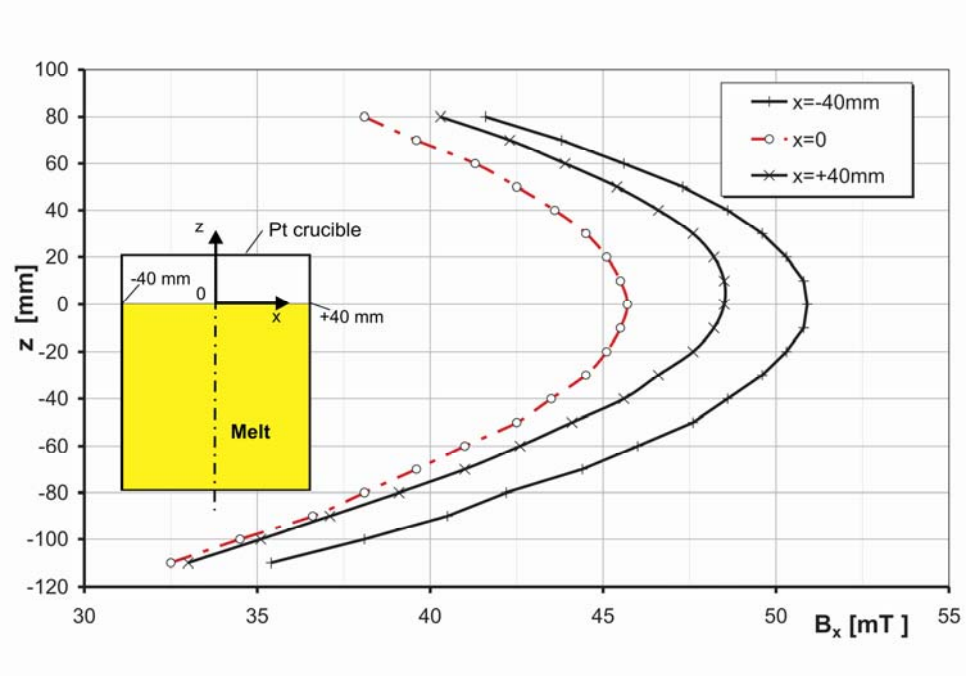

Fig. 3: Distribution of the flux density $B_x(z)$ measured by a hall probe.
z-position of the Pt-crucible and the melt are plotted schematically

The magnetic field gradient $\Delta B_x/\Delta z$ amounts approximately +0.1 T/m in the position of the melt.

The melting procedures with and without such an inhomogeneous AC magnetic field were identical. The raw materials were primarily melted in an electrically heated furnace and cast into a coquille for solidification. Afterwards the material was transferred into the described special equipment and heated up to 1300°C with a heating rate of 1.5 K/min. The residence time amounted to 420 min without magnetic field or 330 min without plus 90 min with magnetic field.

In order to quantify the influence of the magnetic field gradient we measured the temperature ϑ_M in-situ at different positions z in the melts using a protected thermocouple (diameter: 1 mm, PtRh-Pt type B, Electrotherm GmbH, Germany). Afterwards 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 the field gradient was acting on the melt, but not on the crystallized and solidified material. The viscosity of the tested melt amounted 10 dPas at 1050°C.

We drilled out several samples of the solidified melts (volume: 1 cm^3) for material investigations (ex-situ). The positions of the samples are shown in Fig. 4.

The drilled cores were split into three parts. Thus we obtained a bottom, middle and top

sample (in the z-direction) at each position. The densities of all top and bottom samples were determined by using a gas pycnometer (Typ ACCUPYC 1330, Micromeritics). After that the selected samples were filled in a vessel containing diluted acetic acid (2h / 10% CH_3COOH / 100°C). The acetic acid dissolved the soluble phases (borates), but the ferrite crystals remained. These crystals were analysed by X-ray diffraction (Bruker AXS D8 advance), by a vibrating sample magnetometer (VSM 7300 Lake Shore) and by wet chemical methods (total iron: complexometry with 0.01 M $ZnSO_4$-solution, Fe^{2+}: potentiometry with 0.01M $Ce(SO_4)_2$-solution, [8]).

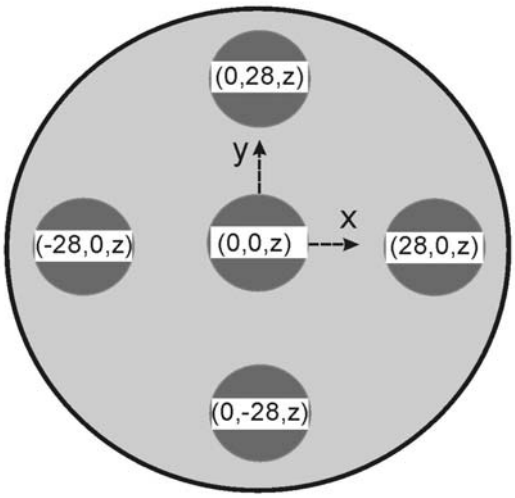

Fig. 4: Top view of the Pt crucible with the solidified melt and the position of the drilled cores.

The comparison of all analyses of the samples from the melt procedures with and without the application of the magnetic field shows the influence of the low inhomogeneous AC magnetic field on the glass melt containing iron ions.

3 Results and discussion

Fig. 5 presents the temperature distributions $\vartheta(z)$ in the melts which were measured at equal positions x = y = 0.

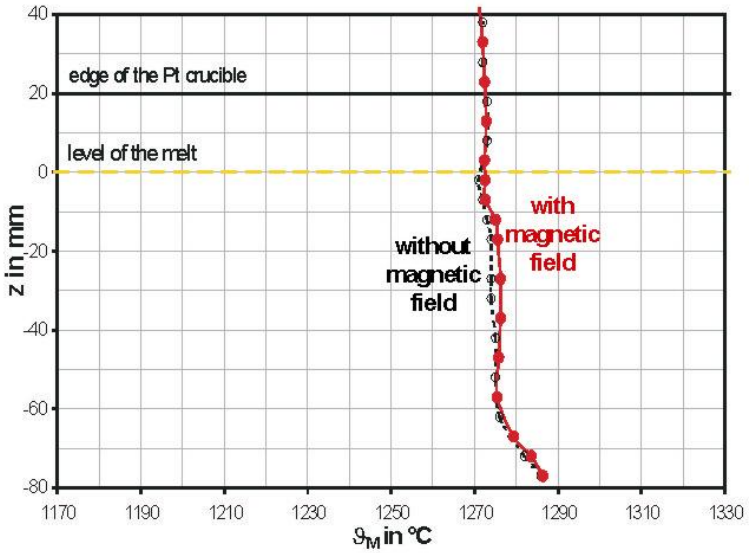

Fig. 5: Temperature distribution $\vartheta_M(z)$ in the melt - with and without the impact of the inhomogeneous magnetic field at a furnace temperature of 1300°C

The distributions are nearly constant about the melt height. Thus melt flows as a result of

the buoyancy are negligible.

Futher the interaction of the AC magnetic field shows no effect on the temperature distribution $\vartheta_M(z)$. The additional heat production in the melt resulting from the induction of eddy currents can also be disregarded. 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 too low.

In contrast to that influences on the density differences and on the magnetic properties (difference of the saturation magnetization: ΔM_S, coercivity difference: $\Delta_J H_c$) comparing the top and bottom samples are identifiable (see Tab. 1).

Tab. 1: Average differences of the densities (top – bottom) of the drilled cores (unsolved and solved samples) resulting from experiments carried out ***with*** and ***without*** the impact of the inhomogeneous magnetic field [8].

Melt experiment	**positions of the samples**	**differences of the densities [10^{-3} g/cm^3]**	
		unsolved	**solved**
without magnetic field	(28,0,z)	-19,3	10,2
	(0,0,z)	-12,7	40,5
	(-28,0,z)	-14	87,3
with magnetic field	(28,0,z)	44,8	13,8
	(0,0,z)	58,4	38,9
	(-28,0,z)	38	21,7

From these analyses we obtain that the density differences (top – bottom) of the unsolved samples at all positions are:

+ positiv in the case of the experiments ***with*** the magnetic field, i.e. the sample densities are larger at the top and increase,
+ negativ in the case of the experiments ***without*** the magnetic field, i.e. the sample densities are larger at the bottom, and are approximataly equal.

The reason for the large changes of the density distribution with the direction of z is the change of the phase content of borates and ferrites. By systematic X-ray diffraction measurements it has been found out that barium borate (β-BaB_2O_4), M-type barium hexaferrite ($BaFe_{12}O_{19}$) and W- type barium hexaferrite ($BaFe_{18}O_{27}$) exist in all unsolved samples.

In the Tab. 2 the densities of these phases are schown.

Tab. 2: Densities of the pure phases [8].

phase	density g/cm^3
M-type: $BaFe_{12}O_{19}$	5,351
W-type: $BaFe_{18}O_{27}$	5,318
β-BaB_2O_4	3,849

From the experiments without the magnet field we conclude that the barium borate content must be larger at the bottom and the amount of the ferrites larger at the top at the melt. These states are inverted if the inhomogeneous magnetic field penetrate the melt. Thus, the magnetic gradient forces influence the phase segregation in the melt. Furthermore, the density differences (top – bottom) of the solved samples (= ferrite powder) at all positions are

+ positiv in the cases ***with*** and ***without*** the magnetic field, i.e. the sample densities are larger at the top and
+ approximately uniform in the case of experiments ***with*** the magnetic field.

If we control the absolute values of the magnetic properties, the saturation magnetizations of the ferrite powders increase in the top position and the coercivities decrease in the middle and bottom positions by applying the inhomogeneous magnetic field, see Fig. 6 and 7.

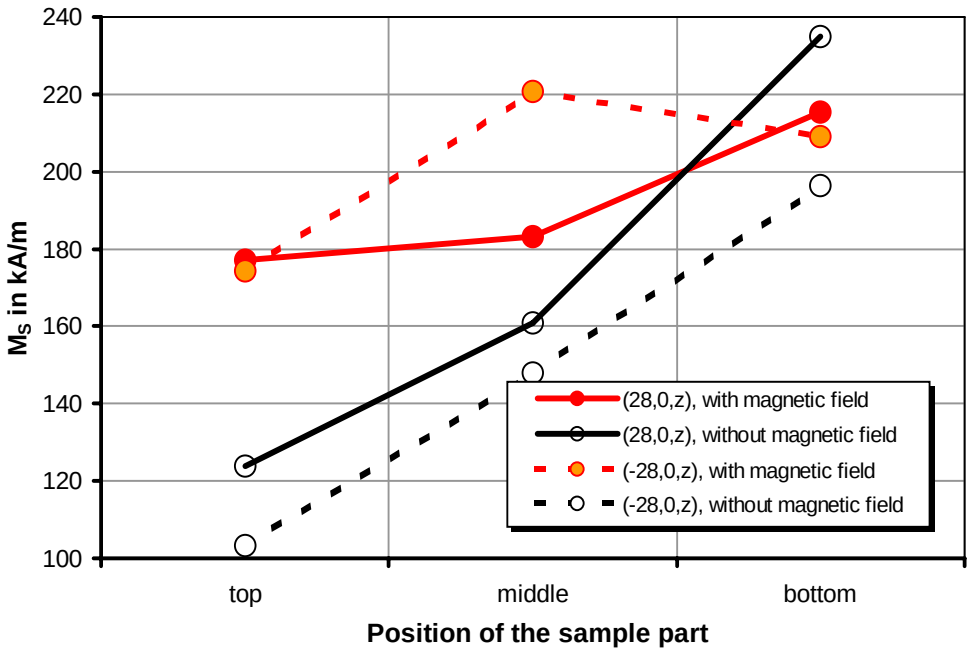

Fig. 6: Changes of the saturation magnetizations M_S in the solidified melt by applying an inhomogeneous magnetic field

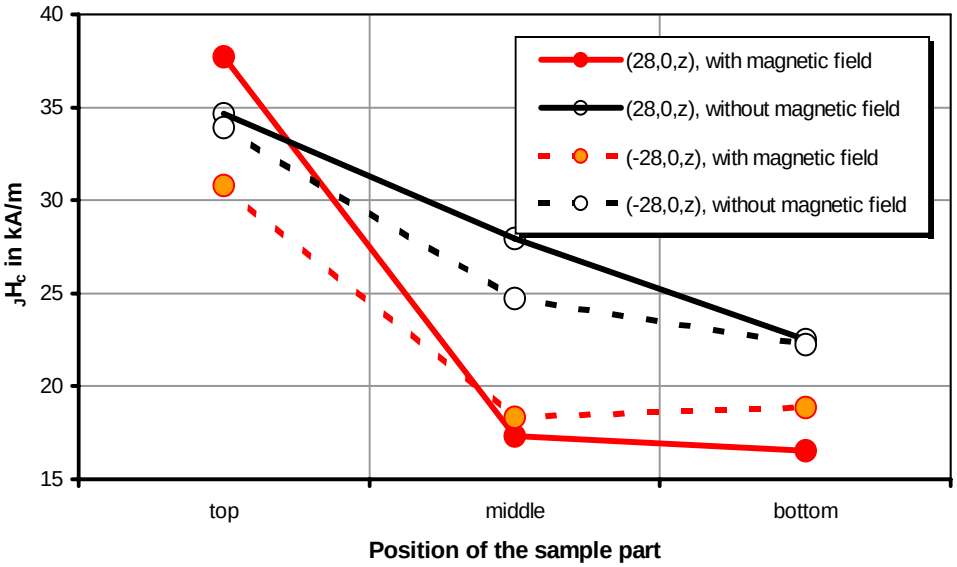

Fig. 7: Changes of the coercivities $_JH_C$ in the solidified melt by applying an inhomogeneous magnetic field

Furthermore, the bottom saturation magnetizations are higher, whereas the bottom coercivities are lower compared to the melt experiment without the magnetic field. Higher values of saturation magnetizations and lower coercivities result from decreasing amounts of hard magnetic phases and increasing amounts of the soft magnetic phases in the obtained ferrite powder. M-type barium hexaferrites are magnetically hard and W-type hexaferrite are magnetically soft.

In Tab. 3 the measured fraction of the M-type barium hexaferrite and W- type barium hexaferrite as well as the determited Fe^{2+} rates are shown in all ferrite powders.

Tab. 3: Average rates of the ferrite phases and Fe^{2+} in the ferrite powders resulting from experiments carried out ***with*** and ***without*** the impact of the inhomogeneous magnetic field [8].

melt experiment	positions of the samples	M-type [%]		W-type [%]		Fe^{2+} [%]	
		top	bottom	top	bottom	top	bottom
without magnetic field	(28,0,z)	80,6	49,7	19,4	50,3	2,4	3,0
	(0,0,z)	77,8	64,4	22,2	35,6	2,3	2,6
	(-28,0,z)	86,8	58,3	13,2	41,7	1,4	2,8
with magnetic field	(28,0,z)	73,2	45,9	26,8	54,1	1,8	3,1
	(0,0,z)	64,8	46,1	35,2	53,9	2,3	3,0
	(-28,0,z)	67,6	48,1	32,4	51,9	2,2	3,0

According to these phase compositions and their magnetic properties we conclude that the portion of the W-type hexaferrite increases and the rate of the M-type hexaferrite

decreases in the bottom range of the melt when the inhomogeneous magnetic field penetrates the melt. These changes are further associated with an increase of the Fe^{2+}-content in the bottom samples. The total amount of iron remains approximately unmodified.

The reason for the modification of the Fe^{2+} – content is the change of the redox ratio as result of the variation of the local composition in the melt.

4 Summary

The present paper demonstrates experimental results of an inhomogeneous alternating magnetic field acting on melts from the BaO-B_2O_3-Fe_2O_3 system using a frequency of 50 Hz and a field gradient $\Delta B_x/\Delta z$ of +0.1 T/m at a maximum flux density of 44 mT.

The investigations show that the temperature distribution $\vartheta_M(z)$ in the melt is not influenced by the low AC magnetic field. But the material properties like the density distribution and the valence of the iron ions about the melt height are substantially changed in the solidified material. These effects arise from the magnetic gradient force which is generated by the gradient of the inhomogeneous AC magnetic field.

Many questions are still open and will be investigated in the following research activities. Numerical simulations to calculate and design the gradient $(\vec{B}\cdot\nabla)\vec{B}$ as well as the calculation of the the magnetic gradient force distribution under consideration of real concentrations and arrangements of ions in melts are planned in near future.

Based on an improved knowledge of the associated change in the material properties the magnetic gradient forces facilitate a new application of electromagnetic processing and process control for bottom-up synthesis of special modified ferrite powders starting from fluids and melts [7].

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