

# Sintering of glass bonded ceramic barium hexaferrite magnetic powders

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Mixtures of low-melting glasses (glazes) and barium hexaferrite magnetic powders sinter at relatively low temperatures (800° C) and produce dense items in which excessive grain growth has been inhibited.

## 1. Introduction

Ceramic magnets made of barium hexaferrite are produced by sintering prefired mixtures of barium carbonate and iron oxide. The final firing step is necessary to obtain dense items because magnetic induction is roughly proportional to density. At the same time the mean grain size should not be larger than 1 to 2  $\mu\text{m}$ , since exaggerated grain growth could lower the coercive magnetic field. Furthermore, apart from these almost opposite needs, industry requires as short as possible firing times, which mean faster sintering rates.

The problem has been solved practically either by adding substances which should inhibit grain growth and accelerate sintering rates and/or, by using the stoichiometric ratio of barium to iron oxide equal to 1.0:5.5 [1-5]. In both cases, however, the firing temperatures were quite high, in the 1200° C range. This means large energy requirements and kiln financial investment to reach and maintain these high temperatures.

In this investigation we have tested the possibility of obtaining ceramic magnets at lower sintering temperatures by means of the introduction of a low melting glass (glaze) in the hexaferrite powders in order to promote sintering and inhibit grain growth. A similar approach had been undertaken by Arendt [6], but data on sintering rates have not been reported. It has been the aim of the present investigation to find out the most convenient hexaferrite to glaze mass ratio in order to bring the firing and sintering temperature down to values lower than those proposed by Arendt [6].

## 2. Experimental details

The barium hexaferrite powder was obtained from

a commercial source and it was of a grade suitable for rubber magnet production. Chemical analysis indicated a BaO to  $\text{Fe}_2\text{O}_3$  ratio of 1.00:5.96. The surface area was found to be about 2 square metres per gram. The low melting glazes were chosen with a softening temperature as low as 750° C and have been prepared by mixing and melting at 1000° C the pure chemical compounds. The fluid mass was fritted in water and ball milled. The resulting powder was sieved and the fraction lower than 10  $\mu\text{m}$  was used for experimental purposes.

Mixtures of the hexaferrite powder and glaze were added with 0.5 wt% zinc stearate to be mixed in a ball mill with ethanol to make up a slurry. After dehydration powders were pressed down as cylindrical pellets 5 mm high and 10 mm across under a 200 MPa pressure in a steel die.

Sintering was carried out in air under isothermal conditions by placing the samples directly into the hot zone of the kiln, set to the convenient temperature, and held there for variable periods of time.

Sintered samples were checked according to reflected light microscopy both as polished and etched sections (HF 5%) to point out their microstructure. Powdered samples were checked by X-ray diffraction analysis (XRD), according to the Guinier-de Wolff geometry camera, to find out the eventual phase separation or crystallization. Bulk densities of the sintered pellets were measured according to the mercury picnometry technique, whereas absolute density values were obtained from powdered samples according to the Archimedes' method in toluene.

The sintering process was followed also by

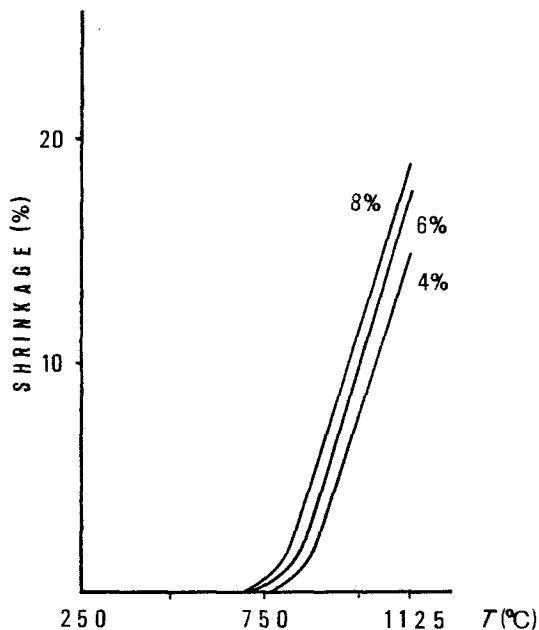


Figure 1 Dilatometric curves of samples containing 4, 6 and 8 wt % of glass type "A"; heating rate  $5^{\circ}\text{C min}^{-1}$ .

means of an electronic dilatometer (Netzsch 402-E).

Before sintering experiments were carried on, it has been considered necessary to verify the reactivity on the magnetic phase and the sintering temperature. Pressed pellet samples, containing 8 wt % of the chosen glaze, have been fired for one hour at  $1050^{\circ}\text{C}$  and then checked by reflected light microscopy and XRD analysis.

The first glazes examined did contain  $\text{B}_2\text{O}_3$ , being members of the alkaline-earth oxide, alumina, boric oxide, silica system. Boric oxide was expected to promote wetting between the glassy phase and the hexaferrite powder. It had been investigated with the aim to possibly circumvent the use of the toxic and expensive lead monoxide flux.

Results, however, have not been encouraging because a marked reactivity between these glasses and the hexaferrite powder was found. Optical and XRD evidence indicated the formation of hematite. This phenomenon was supposed to be due to the solubilization of barium oxide into the liquid glassy phase which could leave the iron oxide to crystallize out as an independent phase.

Better results were obtained with the alkaline-earth oxide, lead monoxide, alumina, silica system. In this case the reactivity turned out to be very low. A small amount of hematite could be found

in samples which were fired up to  $1100^{\circ}\text{C}$  for 4 h.

The best results, however, have been obtained with the alkaline oxide, lead monoxide, silica system. In this case, neither the microscopy nor the XRD technique could reveal newly formed phases in the sintered samples.

On the basis of the preliminary investigation, two glasses were chosen to perform the sintering experiments. The compositions have been the following: glass "A":  $\text{Na}_2\text{O}$  16.0%,  $\text{PbO}$  43.2% and  $\text{SiO}_2$  40.8%, glass "B":  $\text{CaO}$  9.2%,  $\text{PbO}$  58.5%,  $\text{Al}_2\text{O}_3$  2.3% and  $\text{SiO}_2$  30.0% (by weight).

The amount of the glasses to be added was fixed at 4, 6 and 8 wt %. The least amount was found after preliminary tests which indicated that it was difficult to reach useful final densities with lower amounts of glass, whereas the upper amount was fixed in order not to further lower the ferri-magnetic phase concentration.

### 3. Results and discussion

Dilatometric measurements of the shrinkage progress are reported in Fig. 1. The initial sintering is placed around  $750^{\circ}\text{C}$  for samples containing the glass type "A". It is worth mentioning that pure barium hexaferrite densifies at temperatures above  $1100^{\circ}\text{C}$ .

Samples made with glass type "B" had the same behaviour as presented in Fig. 1; except for a  $50^{\circ}\text{C}$  increase of the initial shrinkage temperature. The difference was due to the softening point of the two glasses found at  $690$  and  $740^{\circ}\text{C}$  for glasses "A" and "B", respectively.

Figs. 2 and 3 report the sintering kinetics at  $1000$  and  $1050^{\circ}\text{C}$  of the two groups of samples containing 4, 6 and 8 wt % of the two glasses.

At  $1050^{\circ}\text{C}$  samples containing glass type "A" did show a very limited density increase with time. Furthermore, the 8% sample showed an overfiring behaviour which corresponds to a density lowering after long soaking times. This density decrease is supposed to be due to the loss of the glassy phase. Chemical analysis indicated that in these type of samples the  $\text{PbO}$  content could decrease down to a 20 wt % value. Microscopy evidence has ascertained that the maximum porosity was concentrated in the external part of the samples in direct contact with the surrounding atmosphere. Glass volatilization, therefore, was found to occur at elevated temperatures in samples with the higher glass concentration.

In the series made with glass type "B" this

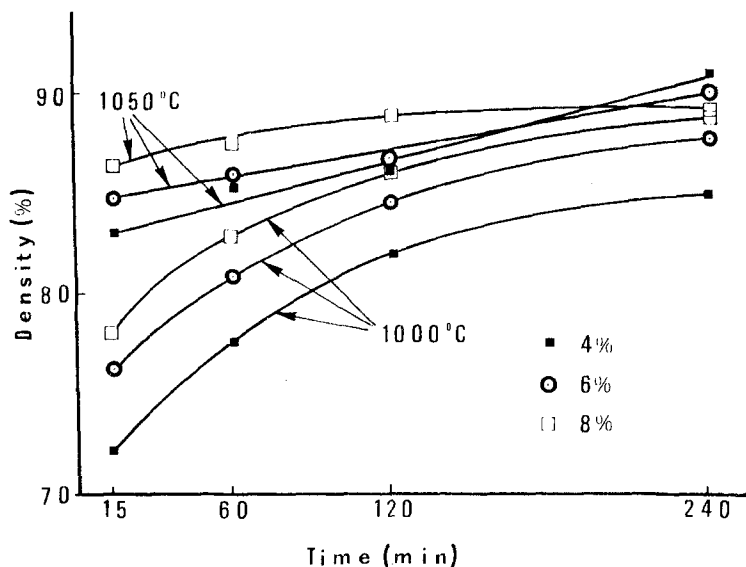


Figure 2 Densification isotherms of samples containing 4, 6 and 8 wt % of glass type "A" both at 1000 and 1050°C.

phenomenon was less evident and it was found to occur only at 1100°C or above [5, 7].

In the industrial practice, sintering of hexaferrite powders is obtained at about these temperatures; therefore, the overfiring phenomenon was not investigated in greater detail since it develops at temperatures well above the range of interest herein examined.

Figs. 2 and 3 report the densities which could be obtained with these type of mixtures. They range at a value 90% and above of the theoretical value and meet the standard value considered acceptable for valuable commercial products.

Microscopy examination of the fired samples revealed that the use of these low melting glasses to bond hexaferrite powders did not allow any variation of the grain size. No detectable difference could be revealed between samples fired either 15 min or 4 h both at 1000 and 1050°C. Fig. 4 indicates the microstructure of a sample etched with HF 5%.

No interpretation was given to the sintering mechanism because the phenomenon in this process seemed to be too complex to allow for a simple modelling explanation. However, at least in the case of the less reactive glass type "A" the

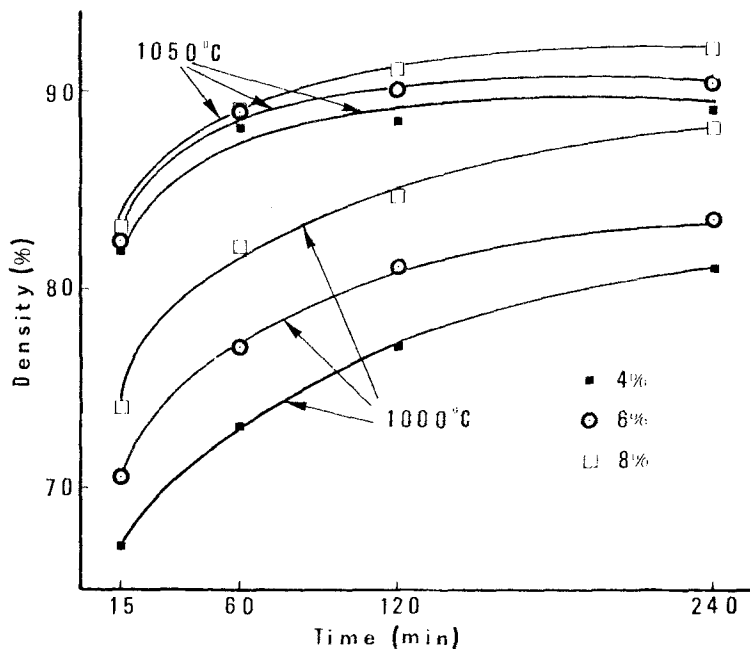


Figure 3 Densification isotherms for samples containing 4, 6 and 8 wt % of glass type "B" both at 1000 and 1050°C.

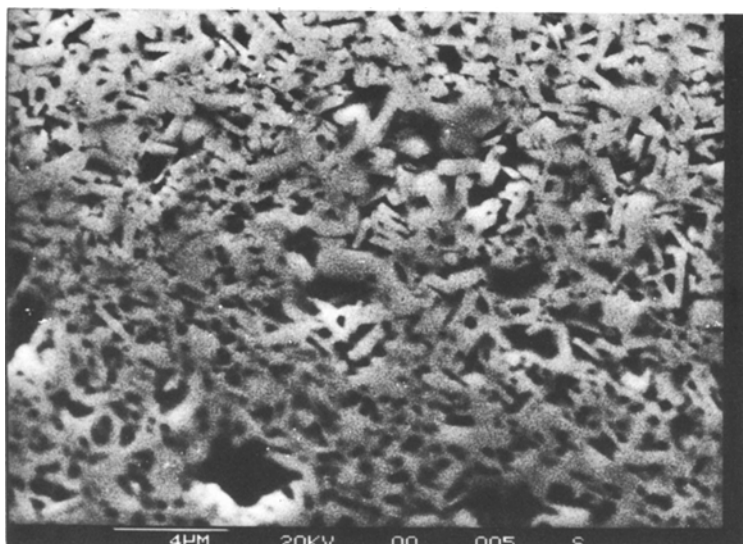


Figure 4 Scanning electron microscope image of a polished and etched (5% HF) surface of a sample containing 6 wt% of bonding glass.

determinant factor must have been its viscosity which is strongly dependent upon the glass temperature. This hypothesis has been stressed by some experiment in which the glass "A" was modified using  $K_2O$  in lieu of  $Na_2O$ . In this latter case sintering did not proceed over a discouraging 78% bulk density value. The lower viscosity of potassium oxide containing composition was blamed for the poorer performance of this modified bonding glass. The suggested composition based on sodium oxide turned out to be more apt to fulfill the sintering needs.

#### 4. Conclusions

Relatively small amounts (4 to 8 wt%) of low melting glasses, added to the hexaferrite powder, allowed one to obtain at  $1050^\circ C$  samples with a bulk density value above the 90% limit which is considered a suitable commercial grade for valuable permanent ceramic magnets.

The addition of these bonding glasses lowers the sintering temperature of about 150 to  $200^\circ C$

with respect to the industrial practice. Furthermore, the glasses maintained the grain size of the original powders throughout the final sintering process allowing for a high coercive force of the final magnetic object.

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