

Reactive Coating of Magnetite by a PbO–B₂O₃–SiO₂ Glass

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(Received 8 August 1995; revised version received 21 December 1995; accepted 3 January 1996)

Abstract

The wetting behaviour of a PbO–B₂O₃–SiO₂ glass on a pure magnetite substrate was studied in air and CO₂ atmosphere from room temperature to 600°C. The decrease in contact angle observed at 590°C was explained by considering the formation of an oxidized layer (~20 µm) during the wetting experiment. The final coating was proved to be free of cracks due to the small residual stress at the interface because of the low thermal expansion mismatch. © 1996 Elsevier Science Limited.

1 Introduction

Stoichiometric spinels have the general structure A[B₂]X₄, where A refers to cations in tetrahedral sites, B to cations in octahedral sites and X to anions that are essentially cubic close-packed. For example, the ferrites MFe₂O₄ — where M represents a solvent metal cation such as Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺ and Cu²⁺ — are a family of commercially important magnetic oxides. They all have magnetic spins exhibiting partial or completely inverse structures. The ferric ions on the tetrahedral sites have magnetic spins which are antiparallel to those on the octahedral sites. This arrangement gives the ferrites either antiferromagnetic or ferromagnetic properties.¹

Magnetic ceramics, most often represented by ferrites, are becoming increasingly important materials for electronic components. In recording media, ferrites are used to store information, either analogue as in music or speech recording or digital for computer and information processing. Therefore this material must be capable of being permanently magnetized locally but must be capable of being read or demagnetized without much difficulty.²

The aim of this investigation was to obtain a physically and chemically stable glass coating in

order to protect magnetite (Fe₃O₄) substrate from environmental effects and also to improve its wear resistance. Glasses from the PbO–B₂O₃–SiO₂ system have been selected for this purpose.

2 Experimental

The following starting materials were used for the glass preparation: reagent grade PbCO₃ (Merck, D), and BO₂O₃ (Merck, D) and glassy silica (Vesuvius, E) powder (99.99%, < 10 µm). Based on the PbO–B₂O₃–SiO₂ phase diagram^{3,4} (Fig. 1), as well as the data reported by Nagesh,⁵ the following composition was selected: 70 wt% PbO, 20 wt% B₂O₃ and 10 wt% SiO₂. Batches of ~50 g of glass powder were obtained using the following procedure:

- (i) dry mixing in an alumina ball mill for ~15 min;
- (ii) the mixture was then melted in a silica–alumina crucible at 1000°C for 30 min with a heating rate of 10°C min⁻¹; and
- (iii) the melt was water-cooled, then dried at 100°C for 2 h, and subsequently dry ball-milled down to 37 µm.

After this operation, wet chemical analysis performed on the glass powder by means of inductively coupled plasma analysis (ICP) found: SiO₂, 10.74; Al₂O₃, 2.40; PbO, 65.30; B₂O₃, 21.0 (in wt%).

Magnetite powder (Aldrich Chemie, D) with 5 µm average particle size was used. This powder was attrition-milled in isopropanol for 1 h, using Si₃N₄ balls. After drying at 70°C for 24 h, the powder was sieved down to 63 µm in order to eliminate agglomerates. The average particle size was determined by scanning electron microscopy (SEM) to be ~2 µm. The powder was subsequently cold-isostatically pressed at 200 MPa into a cylindrical block with ~12 mm diameter. Based on the data reported by Yamaguchi *et al.*,⁶ it was sintered at 1175°C for 2 h in a flux of CO₂ (0.4 l min⁻¹). The sintered samples were cut and polished down to 1 µm for optical

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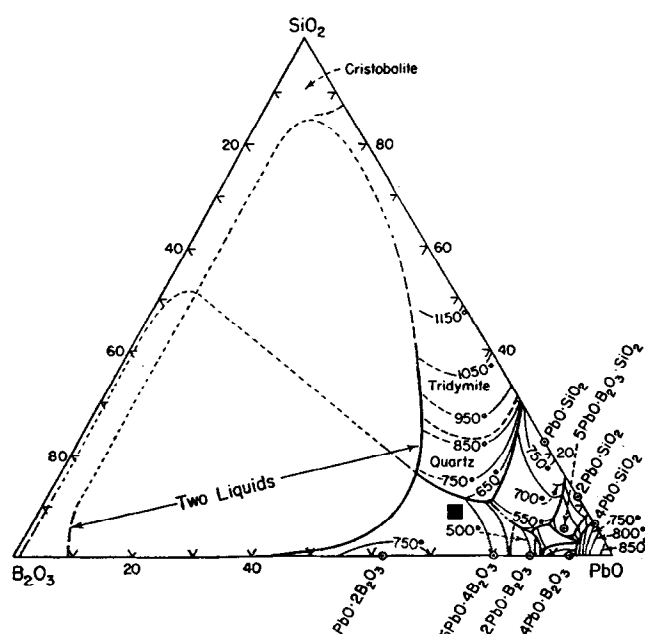


Fig. 1. Phase equilibrium diagram of the $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ system (■, glass composition).

microscope- and SEM observation. The wetting behaviour of the glass on the polished magnetite surface was studied using an optical high-temperature microscope. Analysis of cross-sections was performed by energy dispersive spectroscopy in the SEM (SEM-EDS).

An ink containing glass powder ($<37\ \mu\text{m}$) was obtained by mixing it with ethylene glycol (33 wt%). The polished surfaces of magnetite sintered blocks were coated with this suspension by screen printing and heat-treated at different temperatures in air and CO_2 atmospheres.

The thermal expansion of the glass and the magnetite blocks ($5 \times 5 \times 5\ \text{mm}$) was determined

in the temperature range from room temperature to 350°C .

3 Results and Discussion

The thermal expansion coefficients of the glass and magnetite were found to be 8.1×10^{-6} and $8.3 \times 10^{-6}\ ^\circ\text{C}^{-1}$, respectively.

Figures 2 and 3 show a SEM micrograph of the fractured surface of the magnetite and the XRD pattern of the polished surface. It can be seen that the average grain size of the sintered pure magnetite block with $\sim 88\%$ theoretical density is $\sim 2\ \mu\text{m}$. Figure 4 presents high-temperature micrographs of the $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ glass on magnetite obtained at different temperatures and times, while in Fig. 5 the contact angle vs. time at 590°C in air is plotted. As observed, at this temperature a very low contact angle ($<20^\circ$) is obtained after 1 h treatment, which indicates a high wettability. A similar trend was observed in CO_2 . The main difference in the microstructure observed between both treatments (air, CO_2) was the bubble content of the glass (Fig. 6).

Figure 7 shows a SEM micrograph of the glass-magnetite cross-section, where it can be seen that the obtained glassy coating ($\sim 60\ \mu\text{m}$) is almost free of bubbles. The surface layer ($\sim 20\ \mu\text{m}$) in contact with the glassy coating was found to be haematite (Fe_2O_3) by both SEM-EDS and XRD thin film analysis. The corresponding XRD thin film analysis of a glass-free magnetite substrate after heating at 590°C for 1 h in both air and CO_2 shows the presence of a haematite layer (Fig. 8). This fact is in agreement with the $\text{FeO-Fe}_2\text{O}_3$ equilibrium diagram,⁷ i.e. at this particular temperature magnetite is stable only at

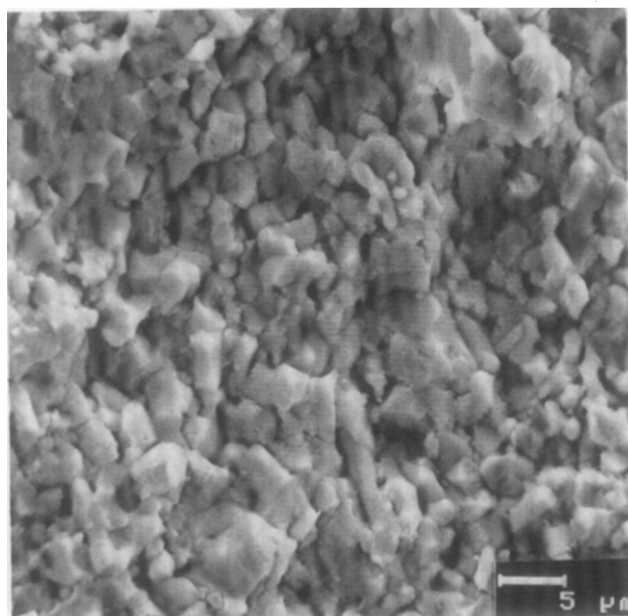


Fig. 2. SEM micrograph of the fractured surface of magnetite after sintering at 1175°C .

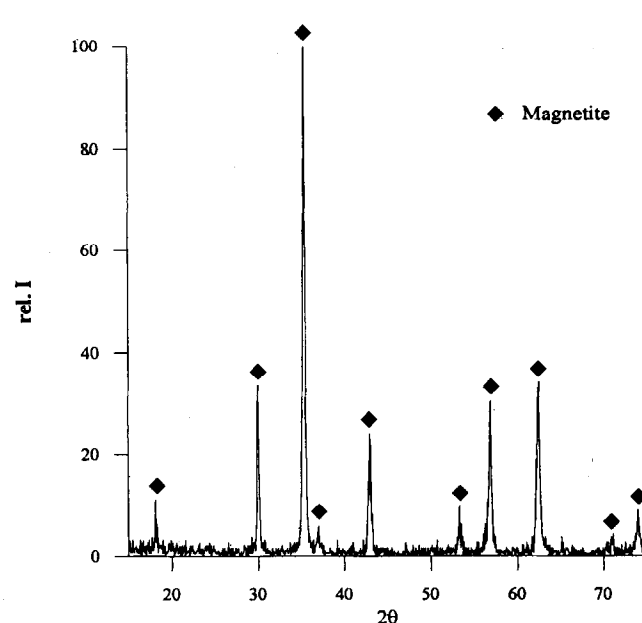


Fig. 3. XRD pattern of the polished surface of magnetite after sintering at 1175°C .

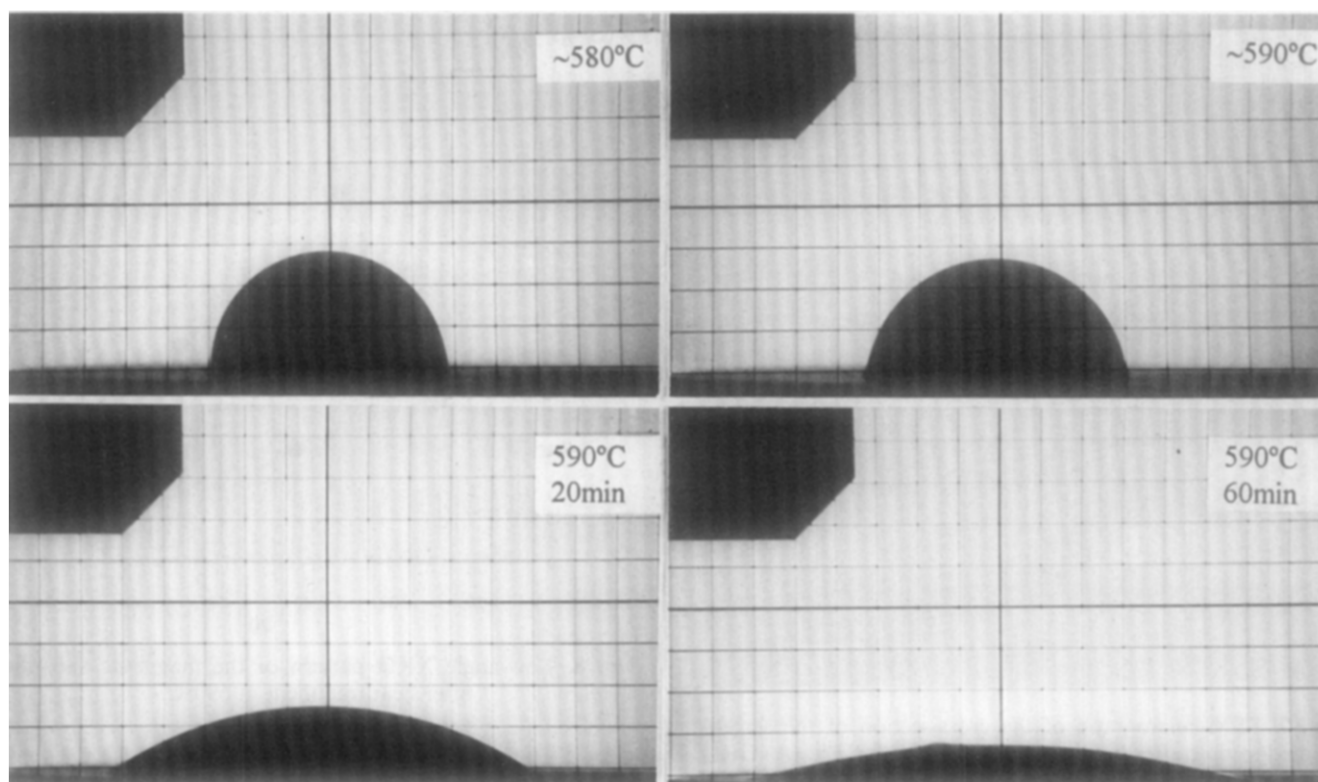


Fig. 4. Optical high-temperature micrographs of $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ -glass on magnetite.

$P_{\text{O}_2} < 10^{-20}$ atm. In a pure CO_2 atmosphere this low P_{O_2} partial pressure is not reached.

The wetting behaviour of this particular glass (Figs 4 and 5) on the magnetite substrate can be understood by considering that oxidation of the magnetite surface layer with the formation of haematite, which takes place in air and CO_2 during the wetting experiments at 590°C (Fig. 8), is the driving force for the observed reactive wetting.⁸ According to Young's equation $\gamma_{\text{SV}} - \gamma_{\text{SL}} = \gamma_{\text{LV}} \cos\theta$, where γ_{SV} and γ_{LV} are the surface free energies of the solid/vapour and liquid/vapour, γ_{SL} is the interfacial energy of the solid/liquid and θ is the contact angle, θ will tend to zero as γ_{SL} decreases. During oxidation γ_{SL} is decreasing, and consequently, decreases in the contact angle have been observed (Fig. 5). Thus, we can conclude that the oxidation of the magnetite surface was the driving force for the spreading of the glass at 590°C .

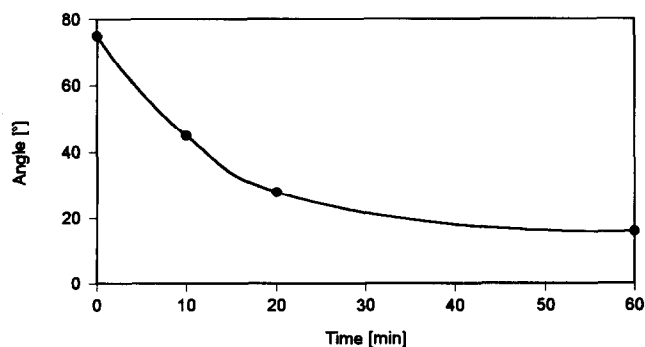


Fig. 5. Contact angle vs. time at 590°C in air.

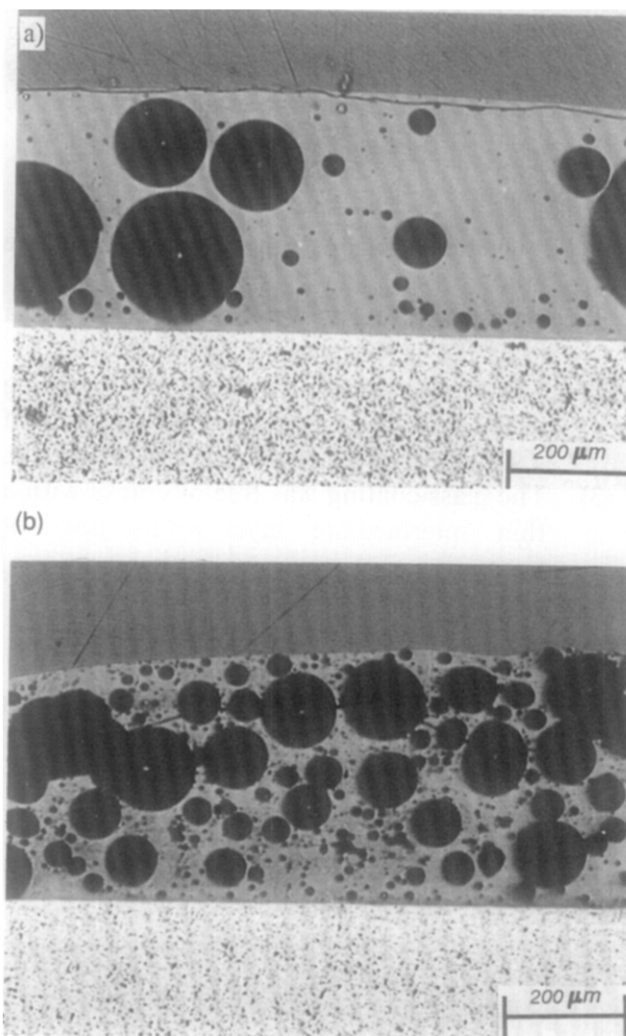


Fig. 6. Optical micrographs of the cross-sections of samples after the sessile drop experiment at 590°C for 1 h in (a) air and (b) CO_2 .

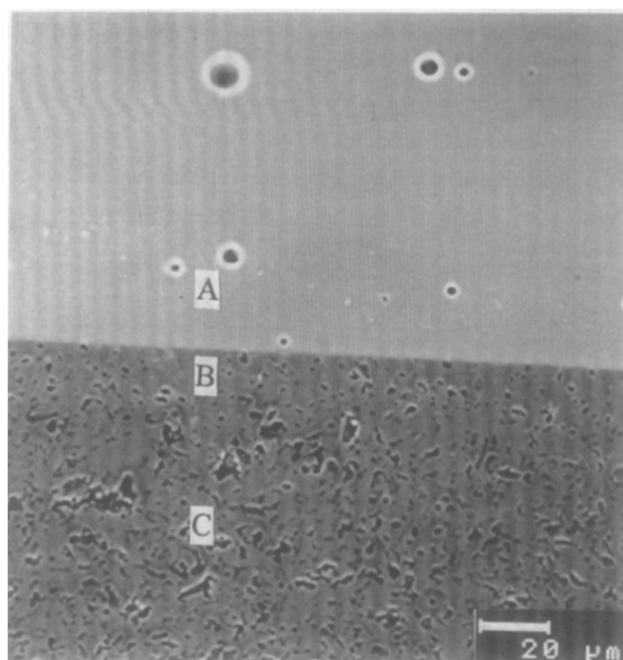


Fig. 7. SEM micrograph of the cross-section of the screen-printed sample after heating in air at 590°C for 1 h. (A) Glass coating; (B) haematite intermediate layer; (C) magnetite substrate.

Due to the small mismatch (<3%) between the thermal expansion coefficients of the glass coating and the magnetite substrate, a perfect glass coating free of cracks at the interface was obtained (Fig. 7).

4 Conclusions

The following conclusions can be drawn from the present study.

- (1) It is possible to coat magnetite by a $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ glass at 590°C in air.
- (2) The driving force for wetting and spreading of the glass was found to be the oxidation of a surface layer of magnetite into haematite.
- (3) The glass coating was free of cracks with a thin intermediate layer (<20 μm) of haematite.

Acknowledgements

This work was supported by CICYT (Spain) under contract MAT. 94-0974. F. Müller thanks COMETT

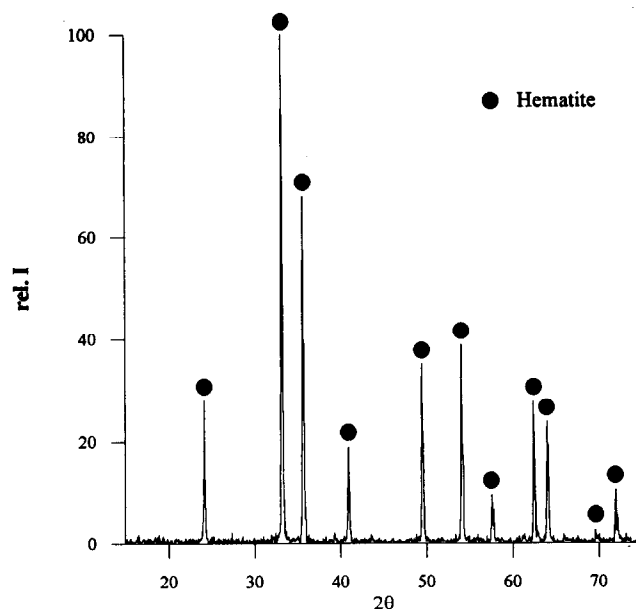


Fig. 8. Low-angle XRD pattern of the magnetite substrate after heat treatment at 590°C.

for financial support. H. P. Steier thanks the Commission of the European Communities. The authors thank A. P. Tomsia for the helpful discussion.

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