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Ceramics International 33 (2007) 163–168

CERAMICS INTERNATIONAL

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Magnetic characteristics of iron-containing glass originated from the mixture of various wastes

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Received 6 June 2005; received in revised form 25 June 2005; accepted 7 September 2005
Available online 5 December 2005

Abstract

The devitrification of iron oxide containing waste generated from mixing blast furnace slag and blast furnace flue dust has shown magnetic characteristics. An investigation of the room temperature *M–H* hysteresis loops and saturation magnetization has been conducted in a different composition of iron-rich glass-ceramics with grain sizes ranging from −45 to 500 μm and at different heat treatment crystallization. Analysis of hysteresis loop data for sample heat treated at 900 °C for 2 h yielded values of 0.7 emu/g and 57.6 Oe for the saturation magnetization and coercitive force, respectively. Pyroxene and magnetite were identified as two major phases after heat treatment. Results of thermal expansion and density of the crystallized glass are also reported.

Keywords: D. Glass-ceramic; Wastes; Saturation magnetization; Hysteresis; Coercitivity

1. Introduction

Disposal of inorganic waste products is an ever-increasing worldwide burden to heavy industry; their conversion to useful products would serve not only to reduce degradation of living environment, but also to contribute to the conservation of resources and to provide economically favorable solutions as well as create jobs.

The production of glass-ceramic materials based on inorganic industrial waste generated by different industries is a promising line [1–4]. It addresses the increasing shortage of raw materials for the glass industry and provides for economically effective utilization of wastes. Accordingly, the range of waste-based materials and products is extensive. The main technical problems in developing production of glass-ceramics based on such waste are the impossibility to control the chemical composition of the glass batch components and the inconvenience of transporting mineral waste from the site of their origin to the site of their use. Consequently, it is advisable to develop mixture compositions that can make use of various inorganic kinds of waste generated by a single large industrial enterprise [5].

Iron-bearing oxide glasses can be used to produce glass-ceramics with magnetic characteristics. Iron oxides contained in blast furnace flue dust act as initiators/additives for the process of transformation of glass into glass-ceramics. In this context, in order to produce glass-ceramic materials with magnetic properties, the process of crystallization of iron-bearing glasses and its effect on magnetic susceptibility and structural modifications occurring under heat treatment was investigated.

The controlled crystallization of glass is commonly employed to produce glass-ceramics with desirable properties. Among the glass compositions that precipitate a magnetic phase are B_2O_3–Al_2O_3–SiO_2–Fe_2O_3–CaO [6], Li_2O–SiO_2–Fe_2O_3 and Li_2O–SiO_2–Fe_2O_3–MnO [7], BaO–B_2O_3–Fe_2O_3 [8], SiO_2–Al_2O_3–Fe_2O_3–K_2O [9],CaO–Fe_2O_3–Al_2O_3–B_2O_3 [10] and BaO–Fe_2O_3–SiO_2 [11].

This paper presents aspects of the devitrification of a glass, generated from the intimate mixing of blast furnace slag and flue dust, whose crystallization products are magnetic. Apart from the interest in the control of magnetic properties, the magnetic changes accompanying devitrification furnish a complimentary tool for investigating the effect of heat treatment on the magnetic susceptibility of samples. A detailed

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0272-8842/$32.00
doi:10.1016/j.ceramint.2005.09.005

Table 1
Analysis of blast furnace slag and blast furnace flue dust

Materials	Egyptian slag content (%)	Egyptian blast furnace flue dust content (%)
SiO_2	36.97	6.6
Al_2O_3	14.79	3.4
Fe_2O_3	0.33	35
CaO	26.64	4.3
Mn	3.29	1.1
MgO	6.70	1.1
K_2O	0.65	0.3
Na_2O	1.43	0.38
S	1.09	0.85
BaO	6.16	1.7
P_2O_5	0.00	0.00
Fe	0.00	0.00
FeO		4.7
C		42.8
Ignition loss		45.1

investigation on the crystallization kinetics in vitrified slag/dust mixtures is the focus of an ongoing study.

2. Experimental

The parent glass was synthesized using a mixture of iron-containing waste blast furnace flue dust (BFD) and blast furnace slag (BFS). Both BFD and BFS were obtained from the Egyptian iron and steel company. Table 1 reports the chemical analysis of the BFS and BFD obtained using X-ray fluorescence (ARL 72000). The growth of the crystal phase in the vitrified sample was investigated using a SETARAM (labsys^{TM} TG-DTA16 model) in argon atmosphere at 15 °C/min. The phase of the product was identified by X-ray diffraction (XRD), using Cu Kα radiation with secondary monochromator (model-Bruker AXS D8 advance). A vibrating sample magnetometer(VSM – Model 9600) was used to measure the magnetic properties of materials by vibrating the sample at a constant frequency between a set of sensor coils. As the magnetic field is varied through a specified range the magnetic moment of the sample is measured by the sensor coils with a lock-in amplifier. A lock-in amplifier allows signals of one single distinct frequency to be measured. The use of a lock-in amplifier allows measurements of samples with very weak magnetic moments. The magnetization values were normalized by the sample weight using the magnetic moment per gram (emu/g) as magnetization unit. The density was measured by the Archimedes method using water as a medium.

3. Results and discussions

The X-ray results are shown in Figs. 1 and 2. The lack of any peak of the quenched samples using a batch composition of 50 wt.% slag and 50 wt.% dust indicates that the iron was retained in a glassy solid solution, while the XRD of the batch containing 50 wt.% slag and 70 wt.% dust shows the existence of crystallized maghemite/magnetite crystals. The DTA trace of the former composition Fig. 3 shows T_g at ∼681 °C and two exothermic peaks at 770 and 837 °C. On the basis of XRD for heat treated specimens, it was suggested that the two peaks correspond to magnetite/maghemite and pyroxene mainly of the diopside-augite composition $Ca(Mg,Fe,Al)(Si,Al)_2O_6$. The heat treatment of the latter batch composition at 1000 °C for 2 h revealed the presence of pyroxene phase besides maghemite/magnetite Fig. 2. This correlates well with the findings of other authors [12,13] regarding the formation of pyroxene and magnetite/maghemite as a major crystalline phases in the devitrification of iron-rich glass samples. The particle size of the precipitating magnetite was calculated from the line broadening using the software Topas 2 equipped with XRD. The crystallite size of magnetite was determined from the broadening of its 440 reflection peak (d = 1.48 Å). It was found equal to 58 nm for the as-quenched glass and 89.5 nm for heat-treated sample at 1000 °C.

Magnetization curves at magnetic fields up to 4000 Oe of the glass specimens heat treated at various temperatures for 2 h and

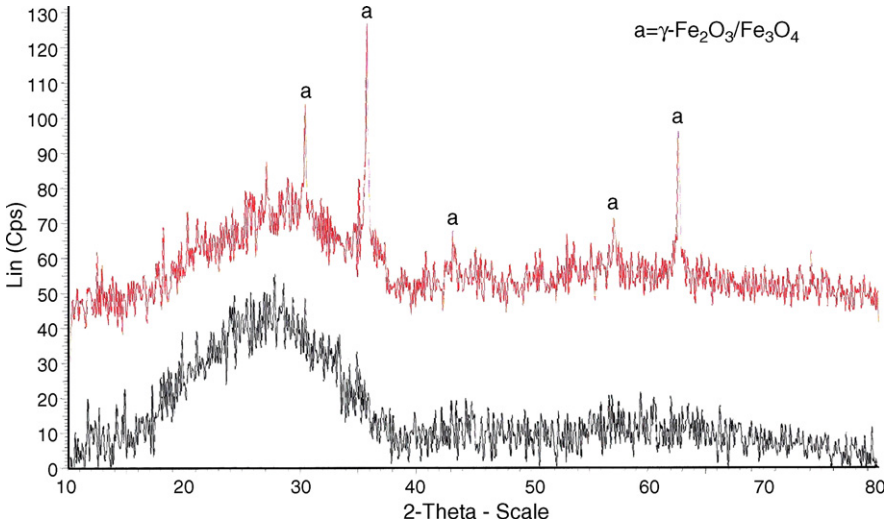

Fig. 1. XRD spectra of the as-quenched BFD/BFD samples in a 50/50 and 50/70 wt.% proportion.

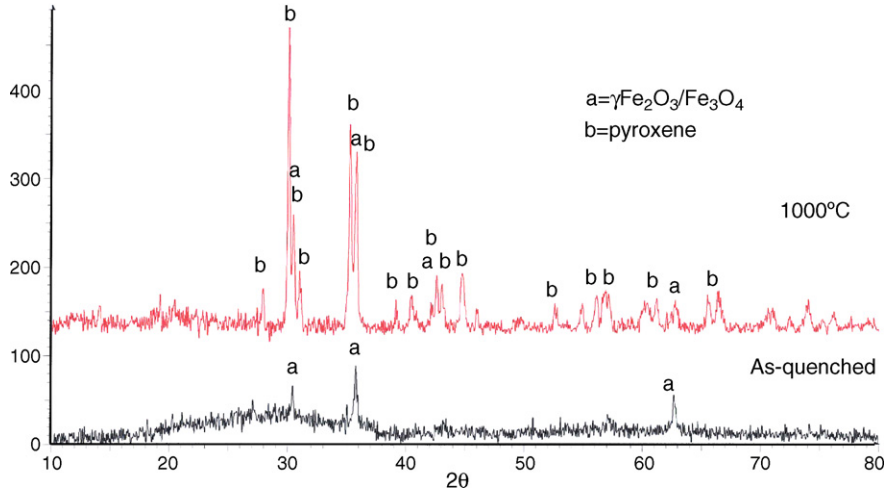

Fig. 2. XRD spectra of the as-quenched BFD/BFD sample in a 50/70 wt.% proportion and at 1000 °C.

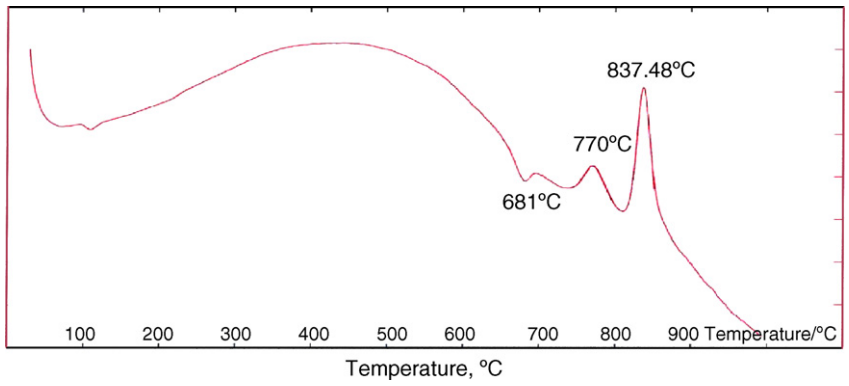

Fig. 3. DTA plot of the BFD/BFD sample in a 50/50 wt.% proportion recorded at 15 °C/min.

at constant particle size −500 + 315 μm are shown in Fig. 4. The saturation magnetization decreases from 0.7 to 0.2 emu/g with increasing heat treatment from 900 to 1050 °C. This indicates that the content of magnetite or γ-maghemite in the specimens decreased with increasing temperature. This decrease may be attributed to the formation of non-magnetic phase or to the transformation of some amount of magnetite or γ-maghemite to hematite and assimilated into the pyroxene phase. Consequently, the amount of magnetic material present is lowered, thereby reducing the saturation magnetization. The coercitive force of the glass specimens decreased also from 57.64 Oe at 900 °C to 36.3 Oe at 1050 °C. The decrease in the coercitive force and in the M_r/M_s ratio from 0.65 to 0.0618 can be interpreted in terms of magnetic multidomain structure. It

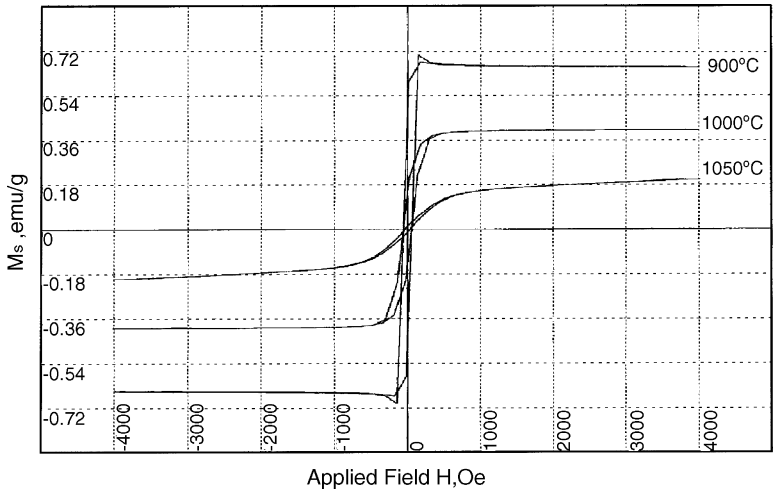

Fig. 4. Hysteresis loops for the annealed samples at different temperature for 2 h up to 4000 Oe.

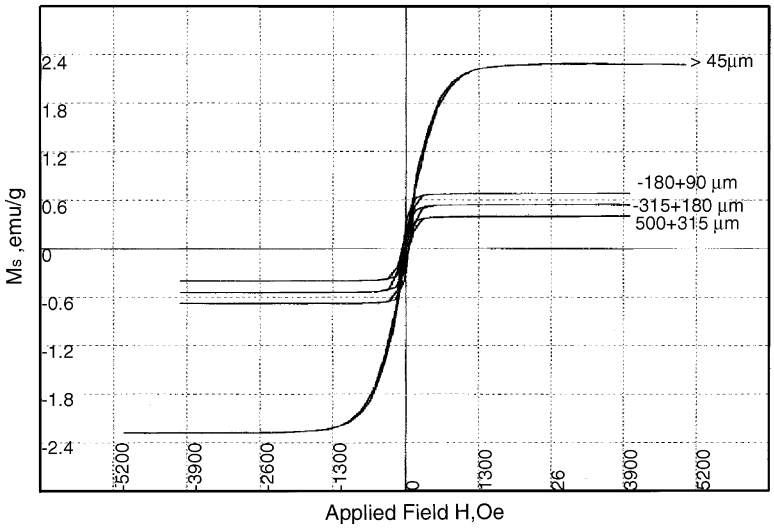

Fig. 5. Hysteresis loops for the annealed samples at 1000 °C for 2 h for different particle sizes up to 4000 Oe.

has been previously demonstrated that magnetization curves of soft magnetic materials were produced from samples containing ash and glass in a 50/50 proportion and sintered at 1500 °C for 5 h. The ash/glass sample exhibited a saturation magnetization and coercitivity of 6 emu/g and 540 Oe, respectively, which was ascribed to the presence of a ferrite-type phase [14,15]. The loops in this study appear to be consistent with soft ferromagnetic behavior. The area of the hysteresis loop is related to the amount of energy dissipation upon reversal of the field. It is known that the hysteresis properties of a sample depend in large part on its purity and quality. This means that we can engineer materials to optimize their properties for specific applications. Therefore, samples with many defects or impurities will require a large field to be magnetized but will retain much of its magnetization when the field is removed. Since the precipitating crystalline phase is a ferromagnetic spinel, devitrification changes the magnetic properties of the glass fundamentally. Moreover, the characteristics of the magnetization curve are dependent upon temperature and particle size.

Table 2
Magnetic properties for samples heat treated at 1000 °C for 2 h at different particle sizes

Particle sizes (μm)	H_c	M_s	M_r	M_r/M_s
−500 + 315	56.05	0.4001	0.1497	0.374
−315 + 180	59.63	0.5443	0.2052	0.377
−180 + 90	50.94	0.6815	0.2824	0.414
−45	17.55	2.285	0.083	0.036

The variations of the saturation magnetization M_s for specimens heat treated at constant temperature 1000 °C for 2 h for various particle sizes was shown in Fig. 5 where a maximum M_s of 2.285 is revealed using particle size, <45 μm. The magnetic properties of the vitrified samples are listed in Table 2. Figs. 6 and 7 show the hysteresis loop of the specimens having a batch composition of 50 wt.% slag and 70 wt.% dust. The coercitive force increased from a value of 31.8 corresponding to the as-cast sample to a value of 62.3 as the heat treatment temperature reached 1000 °C, while the saturation magnetiza-

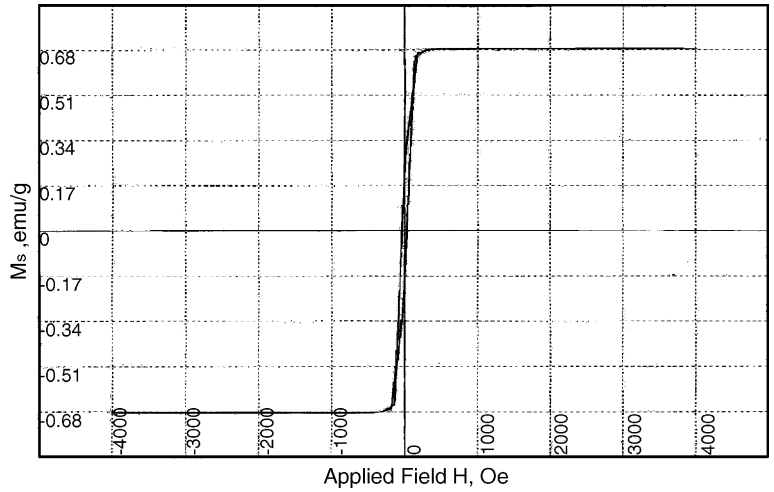

Fig. 6. Hysteresis loop for the as-quenched sample in a 50 wt.% BFS/70 wt.% BFD proportion.

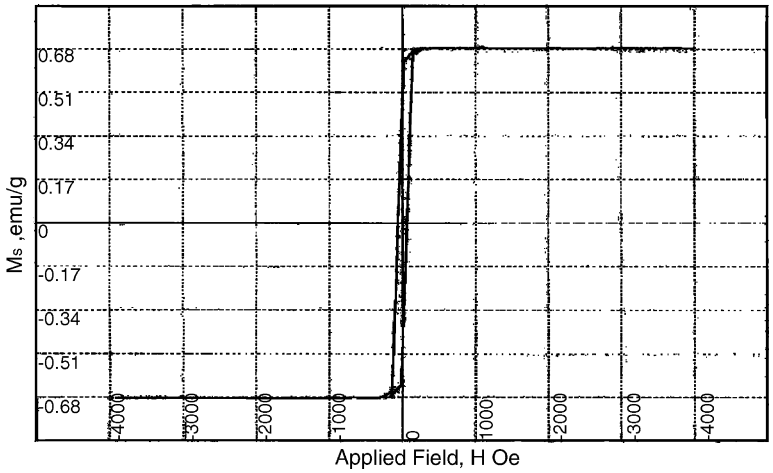

Fig. 7. Hysteresis loop for the annealed samples at 1000 °C for 2 h in a 50 wt.% BFS/70 wt.% BFD proportion up to 4000 Oe.

tion remained constant. The variation in the coercitive force can be attributed to the variation of magnetite multidomain structure where the M_r/M_s has increased to 0.72 for the heat-treated sample at 1000 °C.

In iron-rich compositions, where the devitrification leads to the formation of pyroxene solid solution and magnetite, the degree of crystallization measured by density change coincides with XRD determination [16]. As highlighted by Fig. 8, the evolution of the crystallization phases sensibly influenced the variation of density, since the initial glass density was measured as 2.98 g/cm^3 and increased up to 3.17 at 900 °C heat treatment crystallization. In my opinion the magnetic characteristics along with density difference may be responsible for increasing H_c and M_s up to 900 °C. A typical plot of the thermal expansion of the parent sample is shown in Fig. 9, the measurement was carried out using a Linseis Model L75/L76 dilatometer in the temperature range between 100 and 700 °C at the heating rate of 10 °C/min. The mean thermal expansion coefficient at temperatures from 100 to 600 °C ranges from 7×10^{-6} °C to 7.85×10^{-6} °C which is better than the value reported by Romero et al. [17]. Due to its magnetic susceptibility, the glass-ceramic material can be used as a filler in composites absorbing high-frequency magnetic radiation and as tiles for heated floors of industrial premises [18].

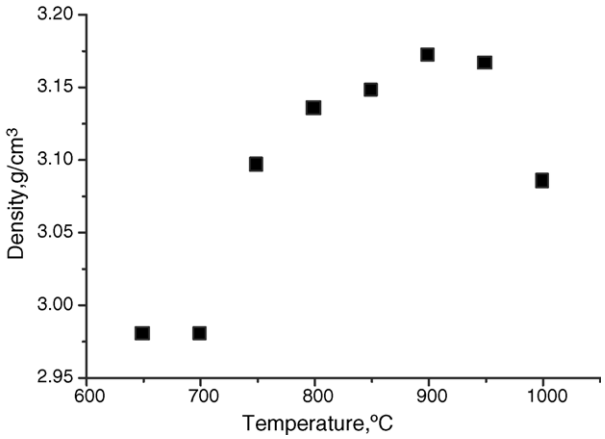

Fig. 8. Density variation of crystallized glass containing 50 wt.% BFS/50 wt.% BFD proportion as a function of heat treatment.

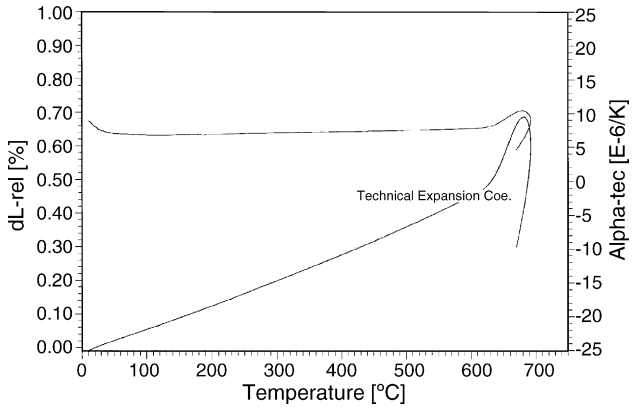

Fig. 9. Thermal expansion curve for the parent glass material containing 50 wt.%/50 wt.% proportion of BFS and BFD.

4. Conclusions

The glass-ceramic route allows the transformation of hazardous and inconvenient wastes into useful solid products with desirable properties. Magnetic glass-ceramics can be prepared using an intimate mixture of blast furnace slag and blast furnace flue dust. It was believed that the composition containing a proportion of 50/50 slag/dust would form a glass containing no crystalline phase while the one containing the proportion of 50/70 was partially crystallized. Crystals belonging to the pyroxene group $Ca(Mg,Fe,Al)(Si,Al)_2O_6$ and magnetite/maghemite were identified as the major phases. The magnetic behavior was due to ferromagnetic phases in some form that is to $Fe_3O_4/\gamma Fe_2O_3$. The variation in the coercitive force with heat treatment at different crystallization temperature was ascribed to magnetite multidomain structure. A maximum susceptibility of 2.285 emu/g was obtained using a particle size: <45 μm at crystallization temperature of 1000 °C

for 2 h. The material can be suitable for applications in floor of industrial buildings and construction or filler in composites absorbing high-frequency magnetic radiation. Further characteristics of its behavior, e.g. wear resistance and chemical durability is necessary and this is the subject of ongoing study.

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