Influence of Co_3O_4, Fe_2O_3 and SiC on microstructure and properties of glass foam from waste cathode ray tube display panel (CRT)

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In the present study, the effect of temperature and oxidising agents such as Fe_2O_3 and Co_3O_4 on physical and mechanical properties of glass foam is investigated. The glass foam is made of panel glass from dismantled cathode ray tubes and SiC as a foaming agent. In the process, powdered waste glass (mean particle size below 63 μm) in addition to 4 wt-% SiC powder (mean particle size below 45 μm) are combined with Fe_2O_3 and Co_3O_4 (0·4, 0·8 and 1·2 wt-%) have been sintered at 950 and 1050°C. The glass foamed containing 1·2 wt-% Co_3O_4 has good physical properties, with porosity more than 80% and bending strength more than $1{\cdot}57 \pm 0{\cdot}12$ MPa. However, by adding different amounts of Fe_2O_3 in comparison with samples without iron oxide, little changes in porosity and strength are obtained.

Keywords: Glass foam, SiC, CRT, Fe_2O_3, Co_3O_4, Porosity

Introduction

The amount of waste electrical and electronic equipment or e-waste generated in the world is growing rapidly. In the European Union, waste electrical and electronic equipment represents about 7·5 million tons each year, where computer monitors and TV sets containing cathode ray tubes (CRTs) represent about 80% of the total electronic waste.[1,2] There are two kinds of CRTs: black and white (or monochrome) and colour. These two types of CRTs are made of different glasses, the neck (1 wt-%) and funnel (33 wt-%) glass constitute the back part of the CRT (hidden inside the monitor or TV set). The front part, usually known as the panel (66 wt-%), is made of a barium–strontium glass that has been free of lead since 1995 and is very homogeneous and thick. These three components are usually joined together with a solder glass called frit, which is 85% lead.[2,3] Cathode ray tube glasses contain significant amounts of heavy metals, so that they are practically banned from usage in the glass industry. Furthermore, the progressive replacement of old CRT TV and PC screen with LCD or plasma equipments is going to cause huge amounts of glasses to be landfilled.[4] Also the reuse of this glass due to high percentage of toxic substances such as lead and barium and strontium oxides is very difficult. Therefore, if the CRT glass was crushed and mixed together, recycling of these glasses in glass industry would have been impossible. Production of glass foam provides an effective solution of the cullet utilisation problem, since the colour of glass has no significant effect on the glass foam quality. However, the differences in the chemical composition and, accordingly, the different properties of the cullet of black, white and colour of CRT have an effect on the formation of the porosity and pore size distribution in foam glass batches prepared from the particular types of glass.[2,5–7] Foams are a special class of porous materials comprised of large voids (open or closed cells), with linear dimensions approximately ranging from a few micrometres to few millimetres (10 μm–5 mm).[8,9]

Glass foams are a porous heat insulating and sound proof materials, with porosity, apparent density and compressive strength values of about 80–95 vol.-%, 0·1–0·3 g cm^{-3} and 0·4–6 MPa respectively.[10] These materials possess a generally higher mechanical, chemical and thermal stability than the polymeric foams currently employed.[11] For instance, in the case of a fire, polymeric foams are known to be largely damaged with the evolution of potentially toxic gases; glass foams, on the contrary, due to their inorganic nature, are uninflammable.[12] Second, glass foams, have high mechanical strength and are suitable for building.[13] Another advantage of these materials, light weight, flexibility in design to production of building and resistance on the rodent species, because not used any fibre in it.[14]

Glass foams are currently produced by the powder method. The basis of this method consists in sintering a mixture of glass powders and special additives facilitating the formation of a gaseous phase upon heating.[15] It is generally accepted that foaming agents are of two types: redox and neutralisation agents. The redox agent

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mainly includes carbon; graphite and silicon carbide to produce glass foam thermal insulation are used. The latter consists of some sulphates, organic compounds and carbonates such as Na_2CO_3 and $CaCO_3$ that are decomposed during heating and gas exit as CO_2.[16] Generally, the choice of foaming agent influences the foaming process, e.g. temperature of foaming or volume of released gas. Reaction products, e.g. CaO from the $CaCO_3$ decomposition which remain in the bubble can influence the glass properties such as the glass viscosity or the crystallisation behaviour. Therefore, to avoid such an effect, reduced foaming agent such as SiC may be preferred.[17] This foaming agent produces a certain amount of carbonaceous products, which in turn are capable of foaming, and residual silicon oxide, to be incorporated in the glass. The release of silicon oxides from the foaming agent may result in partial crystallisation of the glass, with the precipitation of cristobalite, particularly pronounced in borosilicate glasses. The key feature of such foaming is the lack of a reaction with the furnace, thus avoiding the risk of a differential access of comburent oxygen to C and SiC, and resulting in a rather homogeneous microstructure and fine porous microstructure.[11]

In this study, we have tried to find out about the effects of agents such as Fe_2O_3 and Co_3O_4 on increasing the porosity, size and distribution of porosity. The effect of these factors simultaneously with SiC to produce glass foam has not been studied.

Materials

Recycled panel glass of colour CRT (HITASHI TV) was used as the base material. The chemical analysis of this glass obtained by electron microprobe analysis is 58·86 wt-% SiO_2, 0·00 wt-% PbO, 7·33 wt-% K_2O, 7·56 wt-% Na_2O, 2·21 wt-% Al_2O_3, 1·10 wt-% CaO, 0·21 wt-% MgO, 9·30 wt-% BaO, 8·19 wt-% SrO, 0·61 wt-% Sb_2O_3, 0·04 wt-% Fe_2O_3, 0·36 wt-% TiO_2, 0·01 wt-% ZnO, 2·47 wt-% ZrO_2 and 1·73 wt-% others oxide. A commercial grade of SiC powder was also used as a foaming agent, and Fe_2O_3 and Co_3O_4 powders were used as oxidation agents. The average particle size of Fe_2O_3 and Co_3O_4 is below 63 μm.

Methods

The glass fragments were ground in a dry ball-mill until reaching a particle size below 63 μm. Dried SiC based polishing waste was used as foaming agent (4 wt-%), and Fe_2O_3 and Co_3O_4 powders were added to promote the oxidation of SiC at elevated temperatures, in different amounts (0·4, 0·8 and 1·2 wt-%). Batches were obtained by wet mixing the components in a fast mill for 15 min. Polyvinyl alcohol (PVA) was added to improve the pressing of the glass powders. Uniaxial pressing was conducted at 75 bar in a laboratory press, and samples with dimensions of 13 (length) × 2·5 (width) × 1 (thickness) cm were obtained. The samples were dried in three days at room temperature.

The specimens were heated at different temperatures (in the range 850–1050°C) and at a rate of 10°C min^{-1}, and then they were cooled slowly in a furnace. The samples were characterised by measuring density, porosity and bending strength. The bulk density was measured with a helium pycnometer (Micrometrics ACCUPYC 1330) and the total porosity was obtained from the bulk density and the pycnometery density using the following equation (1)

$$\%\text{Porosity} = [1(\text{bulk density}/\text{pycnometery density})] \times 100 \quad (1)$$

Pycnometery density was obtained from equation (2). In this equation, a is weight of pycnometer, b is pycnometer weight and powdered glass, c is pycnometer weight and powdered glass and water weight, and d is weight of pycnometer and water.

$$d_p = (b-a)/(d-a)-(c-b) \quad (2)$$

Three-point bending strength was measured using an Industry Ceram machine with a crosshead speed of 20 cm min^{-1}. At least three tests were conducted for each specimen. The crystalline phases were evaluated by X-ray diffraction method (Philips model Expert) with Cu K_α radiation and the morphology of the foams was studied with a scanning electron microscope (Cam Scan, 30 000 ×, 30 kV).

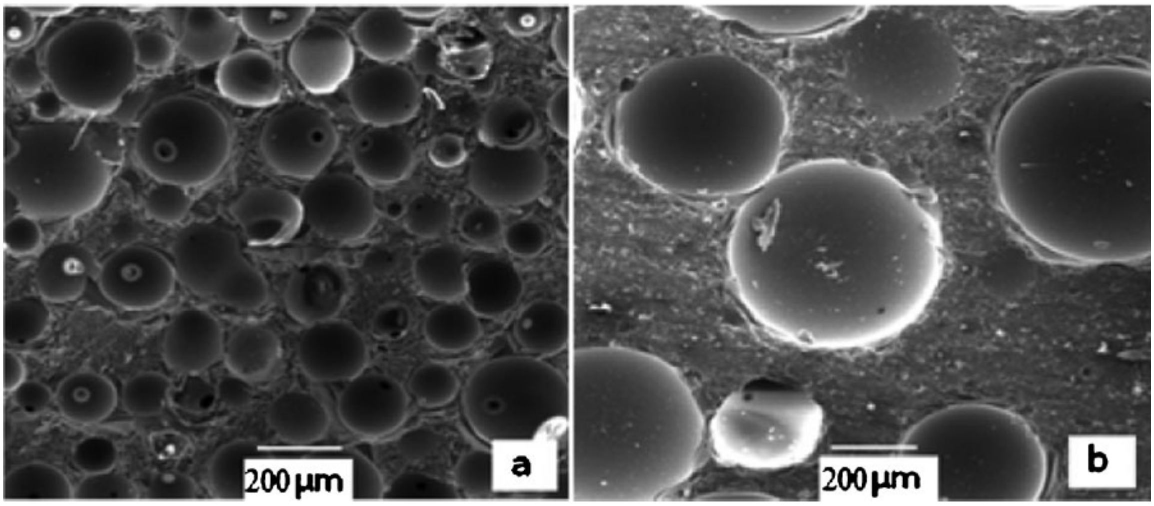
Results and discussion

It can be found that the glass foamed containing just SiC as a foaming agent, has high bending strength (12–24 MPa) and low porosity (about 50–55%). When SiC is mixed with glass particles and pressed into a pellet (at temperatures below the glass transition temperature, T_g), the oxygen necessary for carrying out the reaction diffuses via the porosity available. The amount of oxygen available inside the glass pellet, upon softening point may not be sufficient to complete the oxidation reaction. Therefore, the introduction of substances that generate oxygen at elevated temperatures, such as Fe_2O_3 and Co_3O_4, may improve the oxidation of SiC and the porosity of glass microstructure would be increased, as shown in Table 1. From the results, it is clear that sintered samples containing of 4 wt-% SiC have equal porosity at 950 and 1050°C. Moreover, samples containing 4 and 6 wt-% of SiC, show a difference of 5% at the above mentioned temperatures. In order to achieve glass foam with high properties, two tests were carried out. It means that two samples consist of 4 wt-% SiC and 0·4 wt-% Co_3O_4 (the lowest amount of oxidising agents) were sintered at both 950 and 1050°C. The purpose of adding oxidising was to help oxidation and increasing the porosity of glass foam. At 1050°C, the porosity and dimension of porosities are increased (see Table 2 and Fig. 1) although the bending strength in comparison with the sample without oxidising agent is unchanged.

Therefore, in order to study the effect of oxidising agent on bending strength, porosity and microstructure of glass foam, the samples containing different percentages of oxidising agents were added into 4 wt-% SiC and sintered at 1050°C.

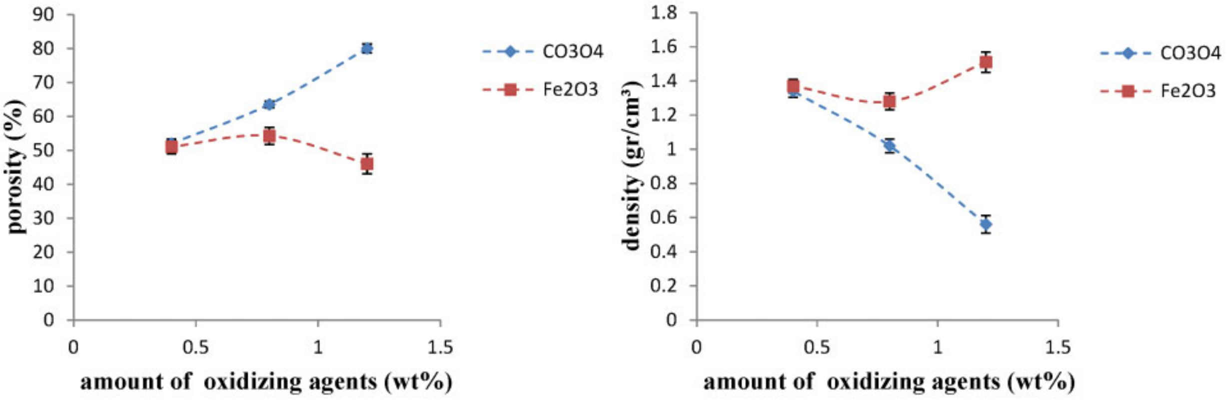
Table 1 %Porosity of samples with different amounts of SiC

SiC/wt-%		2	4	6	8
Porosity/%	850°C	34·64	43·93	48·57	50·10
	950°C	46·77	50	55	28·2
	1050°C	40·36	49·28	38·93	37·14



a 950°C; *b* 1050°C

1 Glass foams with 4 wt-% SiC sintered at different temperatures



2 Comparison of density and porosity of glass foams with 4 wt-% SiC and different amounts of Fe_2O_3 and Co_3O_4 at 1050°C

Effects of iron oxide and cobalt oxide

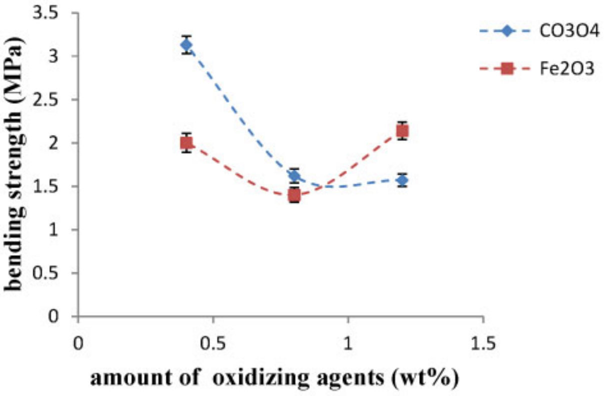
Figure 2 illustrates the density and porosity of glass foams containing 4 wt-% SiC and sintered at 1050°C when the type and amount of oxidising agents changed. Usually, the density has inverse relation with the porosity and a decrease in the porosity is due to an increase in the amounts of the porosity and the pore sizes. The amount of the porosity and the sell sizes of glass foams increased by increasing the foaming temperature (950 to 1050°C) due to increased gas pressure and lowered glass viscosity with the beginning of some coalescence.[18]

Oxidising agents (Fe_2O_3 and Co_3O_4) have different effects on the density and porosity. By increasing the amount of oxidising agent in the samples containing iron oxide, at first the density decreased and then increased. These data would seem to suggest that initially oxidisers act as an oxidising agent and cause to decrease the density and increase the porosity. After that increasing the density indicates that iron oxide acts as sintering aid and helps increasing the rate of sinter. Overcoming the rate of sinter into the rate of gases from reaction leads to a decrease in the porosity. Irrespectively, there is a definitely dependence between glass foam density and duration of heat treatment. During the period of gas releasing, the density decreases down continuously to a minimum value. After that a gradual process of destruction and foam collapse by coalescence of the pores starts. Thus, the surface energy of system is decreased due to a reduction of specific surface area of the walls of the cell. This process leads to a new stage of increasing in density.[11]

Table 2 %Porosity and bending strength of samples with 4 wt-% SiC and 0·4 wt-% Co_3O_4

Sintering temperature/°C	950	1050
Porosity/%	34·44	52
Bending strength/MPa	20±0·18	3·13±0·09

In the samples containing cobalt oxide, the density decreased continuously. This may have occurred due to the spinel structure of cobalt oxide in comparison with stable structure of iron oxide with rhombohedral crystal system. Cossee (1956) showed from magnetic measurements that Co_3O_4 processes the normal spinel structure $A[B_2]O_4$, with the Co^{2+} ions occupying the tetrahedral (or A) sites, and the Co^{3+} ions the octahedral (or B) sites.[19,20] Because of these structural defects, cobalt oxide is more willing to loss oxygen and lead to an increase in the porosity and a decrease in the bending strength of the samples.



3 Comparison of bending strength of glass foams with 4 wt-% SiC and different amounts of Fe_2O_3 and Co_3O_4 at 1050°C

Figure 3 illustrates the bending strength of the glass foam containing 4 wt-% SiC which is sintered at 1050°C. In this figure, the type and amount of oxidising agent has changed. It is observed that the strength is initially decreased by increasing both oxidising agents and then an increase in the strength is shown. The addition of different amounts of iron oxide results in the glass foams with high bending strength because of the lower porosity of these samples.

Usually bending strength has a direct relation with the density and a reverse one with the porosity, and this relation is always affected by the distribution and size of porosity. If the pore sizes are smaller and the porosity is uniform, the samples would be stronger.[21] Therefore, the amount and size of porosity will increase and the strength of samples would be reduced by increasing the amount of oxidising agents. Due to more uniform distribution of porosity in samples with iron oxide, the strength has been increased but in the samples containing cobalt oxide, bimodal distribution of porosity achieved and then insignificant changes occurred.

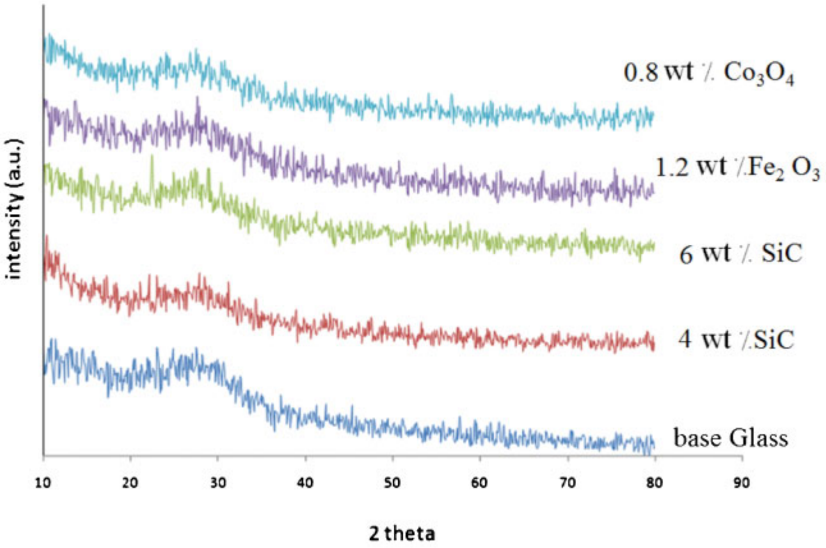
The formation of crystalline phases and the extent of crystallisation are other important factors that determine the structural evolution and the final properties of glass foams, namely the apparent density and bending strength. Figure 4 shows the X-ray diffraction spectrogram of glass foams with different compositions. As it can be seen from this picture, devitrification of the glass which would prevent the foaming of the mixture, did not happen.

Microstructure of samples containing of Fe_2O_3 and Co_3O_4

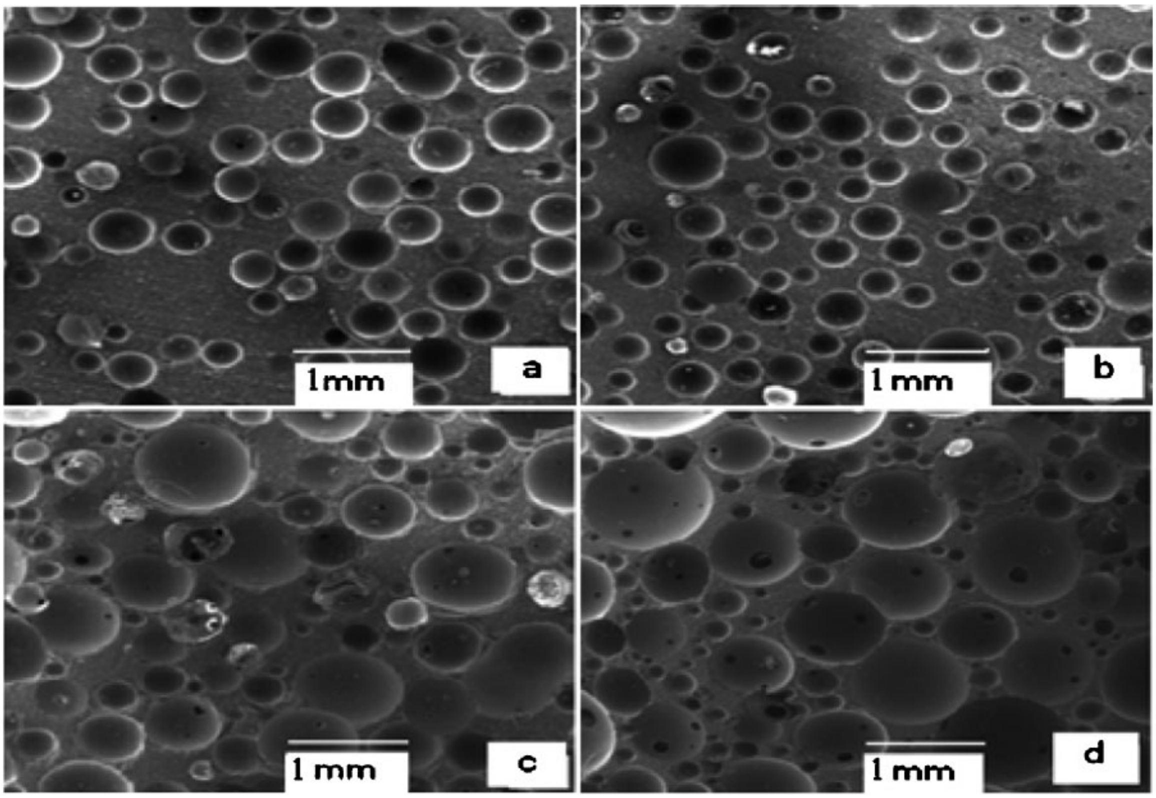
As can be seen from Fig. 5*a–d*, pore sizes of glass foamed changed by increasing the amount of cobalt oxide in the samples. By adding 0·4 wt-% Co_3O_4 to samples in comparison with the basic sample (with 4 wt-% SiC and without oxidising agent), porosity distribution is more uniform. Probably when Co_3O_4 was added to formulation of glass foam, more oxygen would be placed around the SiC particles. Therefore, due to constant heat rate (10°C min^{-1}) and adequate time (105 min) for gas exiting, pore size distribution was almost uniform. By increasing the cobalt oxide content, coalescence or coarsening phenomena occurred and smaller pores likely dissolved in larger pores which are favoured by a decrease in the surface energy of the system. These phenomena were widely reported in the literature.[21–23] The different distribution of pore size formed by increasing the amount of cobalt oxide. The porosity is bimodal, some of the pores are large and others are fine.

An increase in the amount of oxygen in the compound results in a rise in gas exhausting and pressure within the pores, which explains the growth in number of interconnection windows and the tearing of the walls of the pores. Probably because of high sinter temperature, some of the porosities restored, and some of the smaller ones became contiguous, and cause to increase the size of porosities.

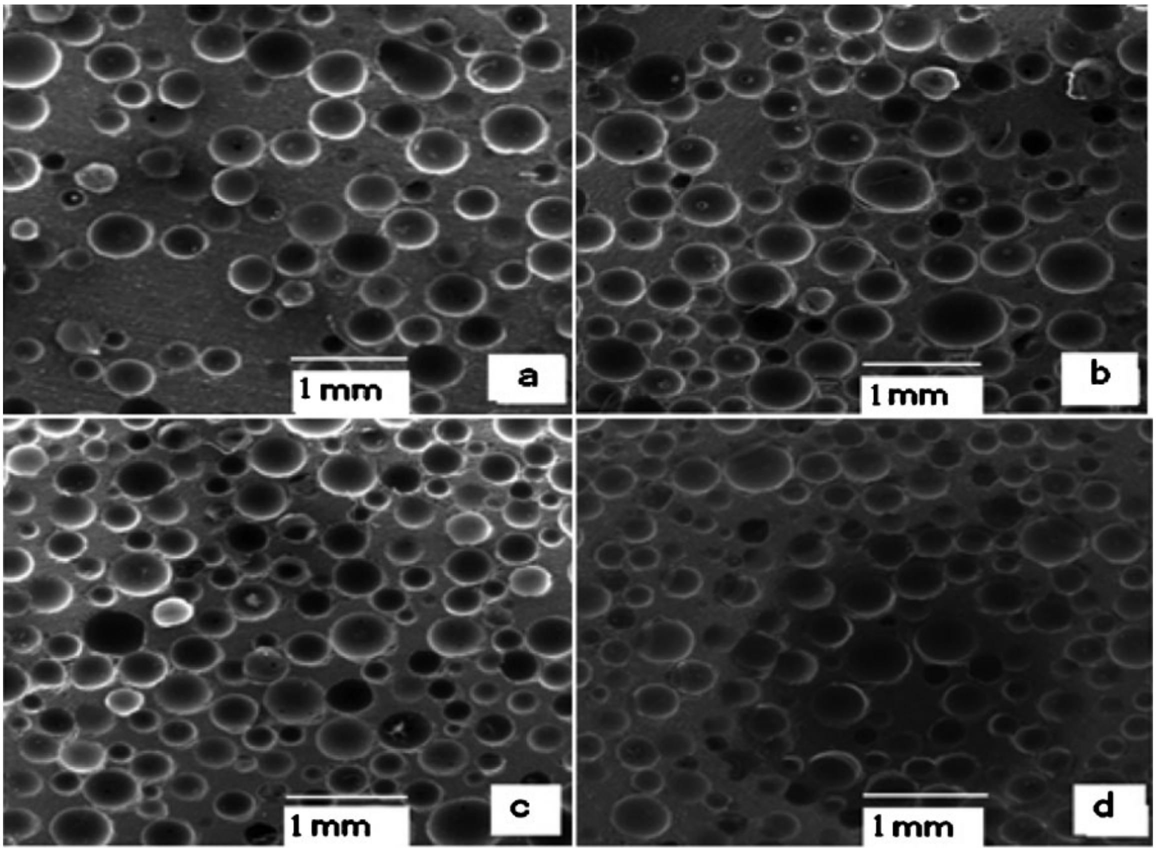
By comparing images in Fig. 6, it is seen that the pore sizes did not change with increasing iron oxide. By adding small amounts of iron oxide into the glass foam with 4wt-% SiC, non-uniformity in microstructure is observed. Figure 6*b* represents large and small porosities with empty of porosity spaces. However, in comparison with the base glass sample, the effect of iron oxide and increasing the amount of oxygen in the glass causes to fill the empty places by porosity and the porosities are



4 X-ray diffraction spectra of glass foams with different compositions at 1050°C



5 **Glass foams with *a* 4 wt-% SiC and without oxidising agent, *b* 4 wt-% SiC and 0·4 wt-% Co_3O_4, *c* 4 wt-% SiC and 0·8 wt-% Co_3O_4, and *d* 4 wt-% SiC and 1·2 wt-% Co_3O_4 (at 1050°C)**



6 **Glass foams with *a* 4 wt-% SiC and without oxidising agent, *b* 4 wt-% SiC and 0·4 wt-% Fe_2O_3, *c* 4 wt-% SiC and 0·8 wt-% Fe_2O_3, and *d* 4 wt-% SiC and 1·2 wt-% Fe_2O_3 (at 1050°C)**

greater. It is observed that the porosity distribution is almost uniform by increasing the amount of iron oxide. The sample contained 0·8 wt-% Fe_2O_3 has the best distribution in porosity. The sample also contains the highest porosity among the other samples containing iron oxide. A comparison of the two oxides in Fig. 5 and Fig. 6 showed that the amount of observed porosity in both samples is almost equal and the porosities are bimodal by adding 0·4 wt-% of oxidising agents (Co_3O_4 and Fe_2O_3). However, due to the uniform distribution of the porosity in the samples containing cobalt oxide, the bending strength of these samples is higher. It can also be clearly seen the effect of cobalt oxide is more significant than that of iron oxide on the increase in the size of porosity.

Conclusions

1. It is possible to make glass foams with appropriate physical and mechanical properties comparable with commercial samples.
2. Co_3O_4 is a suitable oxidising agent for using in glass panel of CRTs.
3. The size and amount of porosity is increased by increasing the amount of Co_3O_4.
4. Approximately 80% porosity is obtained by adding 1·2 wt-% Co_3O_4 to the glass foams. The porosity is in the range of commercial glass foams (85–95%). This increasing in porosity is very significant in comparison with the sample without Co_3O_4 (30% increase in porosity).
5. The bending strength of the samples containing 1·2 wt-% Co_3O_4 is $1{\cdot}57 \pm 0{\cdot}12$ MPa, which is higher than that of commercial glass foams (0·3–1 MPa).
6. After being added 0·4–1·2 wt-% Fe_2O_3 to glass panel CRT, the amount of porosity is unchanged.
7. Porosities are spherical and determination the dimensions of porosities are controllable with time and temperature.
8. The pore size and size distribution of glass foams are effective in bending strength.

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