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Glass–Ceramic from Fly Ash with Added MgO and TiO_2

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Abstract

The effects of the addition of MgO and TiO_2 to fly ash on the nucleation and crystal growth mechanisms of the derived glass are investigated with the aid of differential thermal analysis, dilatometry, X-ray diffraction and scanning electron microscopy (SEM). Phase separation occurs on heating the investigated glass. The glass–ceramic materials obtained contain anorthite ($CaOAl_2O_32SiO_2$) and cordierite ($2MgO2Al_2O_35SiO_2$) as the main crystalline phases. The morphology of the glass–ceramic material was investigated by SEM and it was consistent with the double-framework structure of the phase-separated glass and it was constituted by a low viscosity phase almost completely crystallised and high viscosity phase scarcely or not crystallised, depending on the heat-treatment.

Der Einfluß von MgO und TiO_2 auf die Keimbildung und die Kristallwachstumsmechanismen eines aus Flugasche hergestellten Glases wurde mittels Differentialthermoanalyse, Dilatometrie, Röntgenbeugung und Rasterelektronenmikroskopie (SEM) untersucht. Beim Erwärmen des Glases konnte eine Trennung der Phasen beobachtet werden. Die dabei entstandenen Glas–Keramik-Materialien enthalten Anorthit ($CaOAl_2O_32SiO_2$) und Cordierit ($2MgO . 2Al_2O_35SiO_2$) als Hauptbestandteile. Die Untersuchung der Morphologie der Glas–Keramik-Materialien erfolgte mittels SEM und entsprach der Doppelrahmenstruktur der Glasphase, die in Abhängigkeit von der Wärmebehandlung aus einer nahezu kristallisierten Phase mit niedriger Viskosität und einer hochviskosen, kaum oder nicht kristalliserten Phase bestand.

On a étudié l'effet d'addition de MgO et TiO_2 aux cendres de vitrification sur la nucléation et la croissance de cristaux dans le verre correspondant. Les outils ont été l'analyse thermique différentielle, la dilatométrie, la diffraction X et microscopie électronique à balayage (SEM). Lorsqu'on chauffe le verre, une séparation des phases se produit. Les nitrocéramiques obtenues contiennent de l'anorthite ($CaOAl_2O_32SiO_2$) et de la cordiérite ($2MgO . 2Al_2O_35SiO_2$) principalement. La microstructure de la nitrocéramique a été étudiée au SEM; elle s'accorde avec l'idée d'un double réseau composé par les phases dissociées du verre; elle est composée d'une phase peu visqueuse presque entièrement cristallisée, et d'une phase a forte viscosité à peine ou pas du tout cristallisée en fonction du traitement thermique.

1 Introduction

The processing of ores and fuels leaves large quantities of waste (ashes, slag, etc.), only part of which can be utilised by the cement industry. As regards fly ash, the amount utilised in Italy is about 1% of the cement production.[1] As a consequence, new uses of fly ash have to be searched for in order to meet requirements arising from the large production and the greater attention of the community towards an adequate disposal in terms of environmental safeguard.[2] Hence there is a considerable interest for their utilisation as starting materials for glass–ceramic production.[3,4] Moreover, coal fly ashes are much more convenient than steel slag: they are available in a fine powder form; they are ready for mixing with other ingredients in batch, and in greater quantities than slag.

This work is part of a more general study having the ultimate technological objective of maximising the amount of ashes in the batch to make the production economically profitable.

In a previous paper[5] the devitrification of fly ash derived glass without the addition of any

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other ingredient was studied. The results of this study have shown that the fly ash derived glass exhibits internal nucleation without the addition of any nucleating agent. A fine grained glass–ceramic was obtained but the viscosity of the melted glass was too high making difficult the product formability.

In the present work MgO has been added to fly ash to lower the viscosity of melted glass. MgO was chosen in order to obtain cordierite as the crystalline phase in the glass–ceramic since its presence improves the strength. To ensure bulk crystallisation TiO_2 was also added as nucleating agent. In this paper the effects of the addition of the aforesaid oxides on the nucleation and crystal growth mechanisms of the fly ash derived glass are investigated with the aid of differential thermal analysis (DTA), thermal dilatometry (TD), X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2 Experimental Procedure

The glasses were prepared by mixing, in a Pt crucible, fly ash with analytical grade reagents MgO and TiO_2. The composition of the fly ash, obtained from the Coal Burning Power Plant (ENEL, Porto Marghera, Venezia) is reported in Table 1. The fly ash and MgO were mixed in the weight ratio 10 : 0·75 to obtain a glass whose composition approach that of the glass–ceramic materials based on the $MgO–CaO–Al_2O_3–SiO_2$ system,[6] since, as is known, the glass–ceramic materials based on this system are very hard and abrasion resistant. As regards TiO_2, it was mixed with the fly ash in several weight ratios ranging up to 10 : 1. The glasses were melted in an electric oven at 1500°C for 4 h and then quenched in a cast iron mould. The as-quenched glass, annealed for 30 min at about 100°C below the glass transition temperature, was cut by a diamond saw blade in pieces suitable for the experimental measurements.

Differential thermal analysis (DTA) curves were recorded in air at the heating rate of 10°C/min on bulk specimens of about 50 mg. Powdered Al_2O_3 was added to improve heat transfer between the bulk sample and sample holder. A Netzsch thermoanalyser High Temperature DSC 404 was used with Al_2O_3 as reference material. Thermal expansion of annealed samples were measured by means of a Netzsch dilatometer model 420E.

Table 1. Coal fly ash composition

Oxide	*wt%*
SiO_2	48·72
Al_2O_3	35·79
Fe_2O_3	3·72
CaO	8·10
MgO	1·40
K_2O	0·57
Na_2O	0·16
TiO_2	1·54

To verify the amorphous nature of the as-quenched glass and to investigate the crystalline phases grown during the heat treatments, the thermally processed samples were finely ground and then analysed in a computer-assisted X-ray (Cu*K*) powder diffractometer (XRD) using a Philips diffractometer model PW1710, with a scan speed of 1°/min. Using a built-in computer search program, the X-ray diffraction patterns were matched to JCPDS data and corresponding phases were identified.

To investigate the glass–ceramic texture and crystal morphology, a scanning electron microscope (Cambridge model S-240) was used. Samples were mounted in epoxy and surfaces were ground smooth, then polished with diamond paste. Samples were etched in 1% HF for approximately 60 s. The etched samples were coated with a thin Au film.

3 Results and Discussion

Preliminary tests indicated that at low TiO_2 contents, crystallisation started from the surface. So attention was directed to the glass obtained by mixing fly ash, MgO and TiO_2 in the weight ratio 10 : 0.75 : 1, as it seemed promising.

The DTA curve of this glass, as-quenched, trace (a) in Fig. 1, shows a slope change followed by two exothermic effects of different shape and size at temperatures of about 820° and 975°C, respectively. The slope change may be attributed to the glass transition. In this work, the inflection point of the DTA curve was taken as the glass transition temperature (T_g = 730°C). This value of T_g has been confirmed also by thermodilatometric measurements.

When a glass sample is heated to the temperature of the first DTA peak (820°C) in spite of the evident exothermic effect, it does not crystallise and its XRD pattern (trace (c) in Fig. 2) exhibits only a small broad reflection in an amorphous background that can be attributed to the main reflection of the crystalline phase $4MgOAl_2O_39TiO_2$. A small amount of crystals are formed if a glass sample is heated to the temperature of the second DTA exo-peak (975°C). The XRD pattern of this sample (trace (d) in Fig. 2) shows few broad reflections in an amorphous background that can be

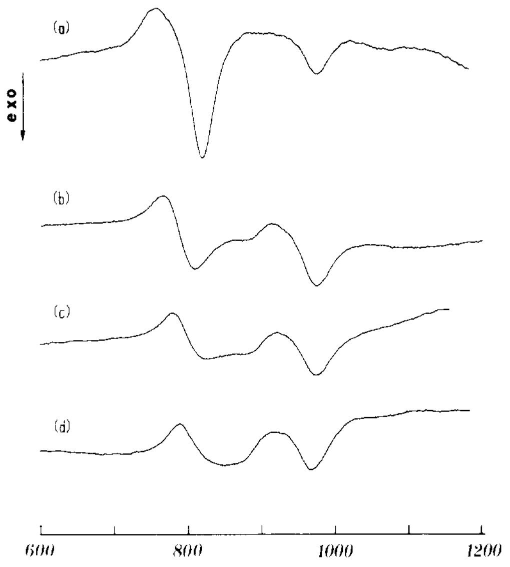


Fig. 1. DTA curves recorded in air at the heating rate of 10°C/min. (a) As-quenched glass; (b) sample heated 2 h at 730°C; (c) sample heated 4 h at 730°C; (d) sample heated 8 h at 730°C.

attributed to $4MgOAl_2O_39TiO_2$ and $MgOAl_2O_3$. The sample heated to 975°C, although more crystallised, fully softens. So the right heat treatments that lead to a highly crystalline glass–ceramic material without dimensional instability have to be searched for. To interpret the first DTA exothermic peak that, as said, cannot be attributed to crystallisation, three glass samples were kept at 730°C for 2, 4 and 8 h respectively. A glass sample heated 8 h at 730°C is still amorphous (see trace (b) of Fig. 2). No significant difference was observed between the XRD pattern of this sample and of an as-quenched glass. The DTA curves carried out on the heat-treated glasses and the as-quenched glass are compared in Fig. 1. The heat treatment strongly affects the first exo-peak, that decreases as the time of the treatment increases and disappears for the sample heated 8 h at 730°C. The second exo-peak instead is not significantly changed by the heat treatment. On DTA curves of the treated glass samples a second glass transition appears at about 900°C (as an inflection point). This suggests that a phase separation occurs. This hypothesis was also confirmed by direct observation of a glass sample heated 8 h at 730°C as shown in the SEM photomicrograph in Fig. 3. The thermal expansion curve of the sample heat treated for 8 h at 730°C also shows a glass transition at about 900°C (see trace (b) of Fig. 4), followed by softening at the temperature of 940°C. Even this behaviour confirms the phase separation.[8]

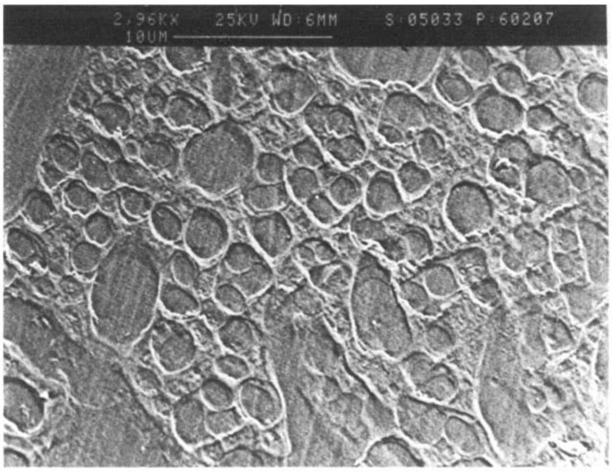


Fig. 3. SEM photomicrograph of sample heated 8 h at 730°C.

On the basis of these results, in order to change the glass into a glass–ceramic material the following three-step heat treatment was proposed:

Program 1: 730°C (8 h) → 900°C (8 h)
→ 1020°C (20 h)

The first step produces a phase separation with a morphology that permits the glass body to be heated to 900°C without softening. During the

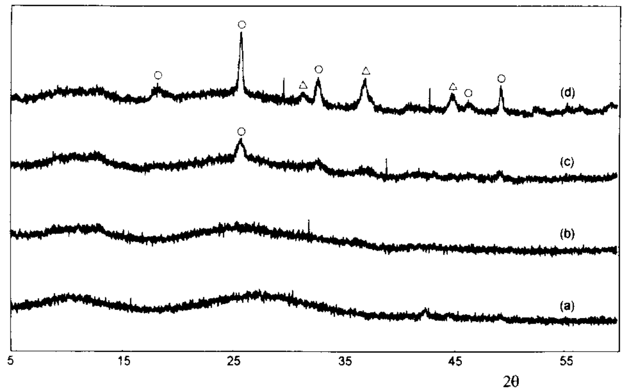


Fig. 2. X-Ray diffraction patterns. (a) As-quenched glass; (b) sample heated 8 h at 730°C; (c) sample heated up to the temperature of the first exo-peak, 820°C; (d) sample heated up to the temperature of the second exo-peak, 975°C. (Δ) $4MgOAl_2O_39TiO_2$, JCPDS Card No. 5-430; (○) $MgOAl_2O_3$, JCPDS Card No. 21-1152.

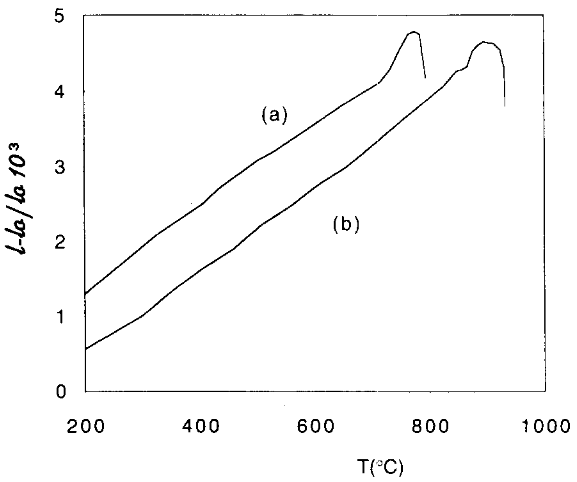
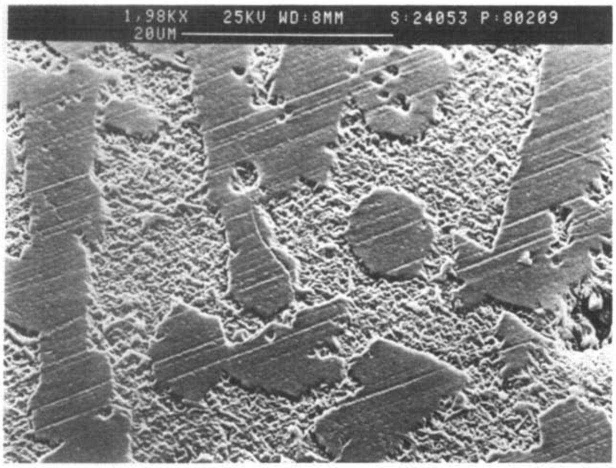
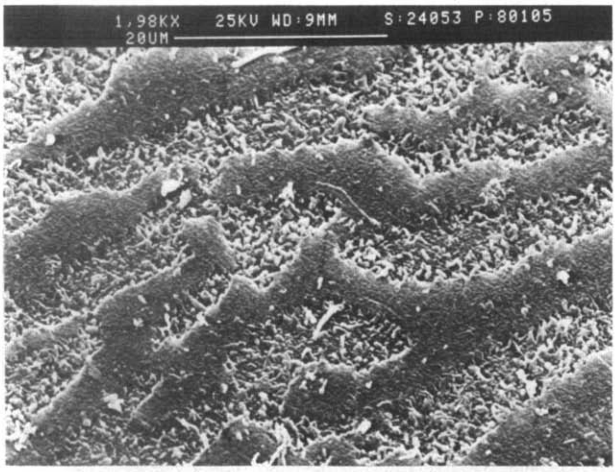


Fig. 4. Thermal expansion curves. (a) As-quenched glass; (b) sample heated 8 h at 730°C .



(a)



(b)

Fig. 5. SEM photomicrographs. (a) Sample after the heating program 1; (b) sample after the heating program 2.

Table 2. The crystallizing phases for each step of heating programs and the counts of their main peak

Time (h)	*Temperature (°C)*	*Crystallising phases*	*Counts*
Program 1			
8	730	None	—
8	900	$4MgOAl_2O_39TiO_2$ (microcrystals)	680
		$MgOAl_2O_3$ (microcrystals)	400
20	1 020	$2MgO2Al_2O_35SiO_2$ (cordierite)	3 110
		$CaOAl_2O_32SiO_2$ (anorthite)	1 500
		$4MgOAl_2O_39TiO_3$	1 600
		$MgOAl_2O_3$	240
Program 2			
4	850	$4MgOAl_2O_39TiO_2$ (microcrystals)	500
8	950	$4MgOAl_2O_39TiO_2$ (microcrystals)	1 500
		$MgOAl_2O_3$ (microcrystals)	520
20	1 020	$2MgO2Al_2O_35SiO_2$ (cordierite)	3 000
		$CaOAl_2O_32SiO_2$ (anorthite)	1 700
		$4MgOAl_2O_39TiO_2$	1 400

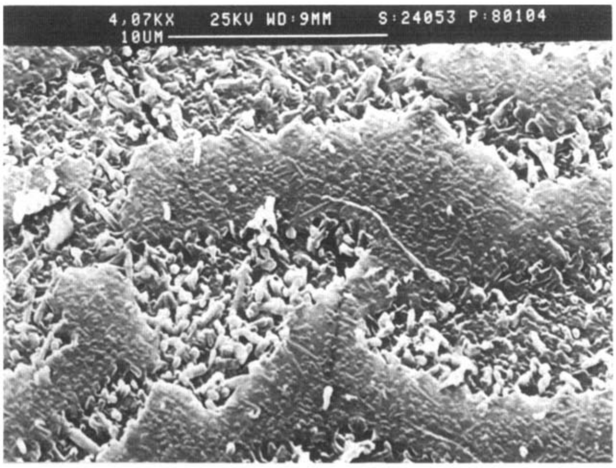


Fig. 6. SEM photomicrographs of a sample after the heating program 2.

second step crystallisation begins and the presence of a certain amount of crystalline phase allows the temperature to rise to 1020°C to produce anorthite ($CaOAl_2O_32SiO_2$) and cordierite ($2MgO . 2Al_2O_35SiO_2$) without any dimensional stability problem.

A second program was also proposed:

Program 2: 850°C (4 h) → 950°C (8 h)
→ 1020°C (20 h)

The first step is accelerated using higher temperature for less time with a second step at a higher temperature for the same time.

The phases crystallised at the end of each step of the heat treatments and the respective counts of the main peak of each phase on the XRD pattern are reported in Table 2. The two programs differ mainly for the first step in which, for program 1, no crystalline phase is produced. In the other two steps the same crystalline phases are produced even if in slightly different amounts. With both programs cordierite and anorthite are produced only in the third step at high temperature (1020°C). After 20 h almost the maximum quantity of crystalline phases are obtained. Increasing the third step duration the quantity of crystalline phases does not increase significantly.

Table 3. Thermal expansion coefficients in temperature range 200–600°C

Sample	$\alpha \times 10^7 (K^{-1})$
As-quenched glass	69
8h at 730°C	67
8h at 730°C	
8h at 900°C	59
20h at 1020°C	
4h at 850°C	
8h at 950°C	53
20h at 1020°C	

The two heat-treatment programs produce a different morphology of the glass–ceramic. In Fig. 5 SEM photomicrographs of a sample treated with program 1 (Fig. 5(a)), is compared to a sample treated with program 2, (Fig. 5(b)). In (a) the high viscosity phase is still completely amorphous whereas the other is well crystallised. In (b) even the high viscosity phase appears to some extent crystallised, see Fig. 6. In both cases the resulting glass–ceramic material morphology is a double-framework structure with the low viscosity phase completely crystallised and high viscosity phase not or scarcely crystallised.

The thermal expansion coefficients of the glass–ceramic materials can be very different from that of the original glass. It depends on the type of crystalline phase and the amount present in the glass–ceramic but can be very sensitively controlled by the heat-treatment program.

The thermal expansion coefficients, α, of the as-quenched glass and of different heat-treated samples are listed in Table 3. The α values of the glass–ceramics obtained by the two heating programs are slightly lower than those of the as-quenched glass and of the glass heated 8 h at 730°C. This should be due to the presence, in the glass–ceramics materials, of a large amount of the residual glassy phase. Moreover, the α value of the sample after the heating program 2 is slightly lower than that of the sample after the heating program 1.

4 Conclusions

From the experimental results the following conclusions can be drawn. A phase separation occurs heating the as-quenched glass. This is a preliminary step in the glass to glass–ceramic transformation process, as the high viscosity phase formed is continuous and permits the temperature to rise in the crystallisation range without softening. In addition, the phase separation determines the morphology of the glass–ceramic material, which is a double-framework structure with the low viscosity phase almost completely crystallised and high viscosity phase not crystallised, for program 1, or scarcely crystallised, for program 2.

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