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Utilization of coal-ash minerals for technological ceramics

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Glasses synthesized from Utah bituminous coal-ash melts were crystallized to form glass ceramics to determine the feasibility of coal-ash utilization. The use of additives to promote glass formation and catalysts to serve as nucleation sites for crystallization was studied. The microstructure of the crystalline phase was investigated using X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy. The bulk glasses and glass–ceramics were evaluated by Knoop microhardness and density measurements. The crystalline phase formed has been identified as anorthite, $CaAl_2Si_2O_8$. Crystallization of the ash was possible up to a maximum of approximately 40%. The use of TiO_2 as a nucleation catalyst did little to improve the degree of crystallinity; however, the crystal phase became better defined when this catalyst was used, even in small amounts.

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1. Introduction

When coal is burned a substantial portion, typically in the range of 4–25 wt %, is converted to ash [1]. Coal ash, generally a waste product, is potentially a valuable source of minerals, including SiO_2, Al_2O_3, CaO, MgO, Fe_2O_3, K_2O and TiO_2, which are found in common glass and ceramic materials. One attractive idea based upon this readily available pre-mixed batch of materials is the preparation of glasses by melting and supercooling the ash melt. The glass may then be crystallized to form a glass–ceramic, as is well known in "Pyroceram" technology.

The composition of the ash and the prior processing history in a coal combustion plant give rise to a primarily amorphous material with some particles of crystallized silica in the form of quartz. The presence of quartz in the ash affects the ability to obtain good homogeneity in glasses. If unmelted crystalline silica regions remain in the glass, these crystalline areas would serve as nucleation sites during the bulk crystallization of the glass–ceramic and the crystal growth would be uncontrollable. Further thermal expansion differences between crystalline silica forms and vitreous silica are so large that the bulk glass or glass–ceramic will be prone to catastrophic fracture. It has been found that carbonates of lithium, sodium and potassium form a eutectic with the crystalline silica [2]. These compounds may be used to lower the transition temperature of the vitreous phase by 300 °C or more.

2. Experimental procedure

2.1 Materials

The ash used in this research was a fly ash obtained from the combustion of Utah bituminous coal. The ash composition is given in Table I [3]. The approximate liquidus temperature of the ash was found by trial and error to be 1350–1400 °C. Ashes were ultimately melted in fused silica crucibles.

2.2. Glass synthesis

To reduce the volume taken up by the ash, it was pressed into pellets. Melts of both 10 and 20g were made, all melts containing 20 wt % $CaCO_3$ to catalyse the conversion of the quartz. Later melts were made with the same composition plus 1 wt % TiO_2 to study the effect of an added nucleating agent. All melts were

TABLE I Composition of coal ash

Oxide	Wt. %
SiO_2	65.37
Al_2O_3	22.14
CaO	4.66
Fe_2O_3	3.61
MgO	1.53
K_2O	1.10
TiO_2	0.96
Na_2O	0.62

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carried out at 1400 °C for 2 h. The sample was then annealed at 400 °C for 1 h, and then allowed to cool to room temperature in the furnace. The rapid transition from 1400 to 400 °C was enough to supercool the melt to a glassy state. The annealed glass was cut into pieces ~ 1 × 1 × 0.5 cm. These pieces were ground on silicon carbide grit paper to remove any crucible material, surface bubbles and crystallization that may have occurred at the surface or at the glass–crucible interface. These pieces were then ready for either nucleation or measurement.

2.3. Glass–ceramic synthesis

Nucleation and heat-treatment temperatures were determined by trial and error, and from the results of previous researchers [3, 4]. All nucleation was done at 700 °C for either 1 or 24 h. Heat treatment was performed at temperatures of 800, 900, 1000, 1100 and 1200 °C for times of 4, 10 and 48 h. X-ray diffraction (XRD) was performed to determine the best possible combination of these variables. Samples containing TiO_2 were nucleated at 700 °C for 1 h and heat-treated at 1000, 1100 and 1200 °C for 48 h.

2.4. Characterization of glass and glass–ceramic

Determination of the crystalline phase was done by XRD at a scan rate of 2 ° min^{-1}. Further identification of the phase was done using energy-dispersive X-ray spectroscopy (EDS) to determine the chemical composition of the crystalline phase and the number of crystalline phases present. The morphology of this phase was determined using scanning electron microscopy (SEM). Samples for this characterization were prepared by fracturing the glass–ceramic and etching with 12% HF for 20 s. The samples were then cleaned with acetone and methanol, and placed under vacuum to prevent the formation of any surface contamination. The specimens were mounted using colloidal graphite paint and sputtered with a 22.0-nm Au/Pd coating to prevent charging. The degree of crystallization was determined by using a method of internal standards. The standard used was pure copper. Samples for Knoop microhardness testing were prepared by casting polished pieces of glass and glass–ceramic in a polyester resin to assure a flat surface and even load distribution. Indentations were made with a constant load of 300 g and a dwell time of 10 s. Density measurements were made by weighing the sample in air and then in water.

3. Results and discussion

3.1. Glass synthesis

Fig. 1 shows the original, untreated ash sample, the major crystalline phase being quartz. K_2CO_3, Na_2CO_3, and $CaCO_3$ gave an amorphous glass as expected. $CaCO_3$, a cheaper and more readily available alternative to the other carbonates, was used in all melts and gave a fully amorphous glass (Fig. 2). Homogeneity was obtained at a minimum melting temperature of 1400 °C for a time of 2 h.

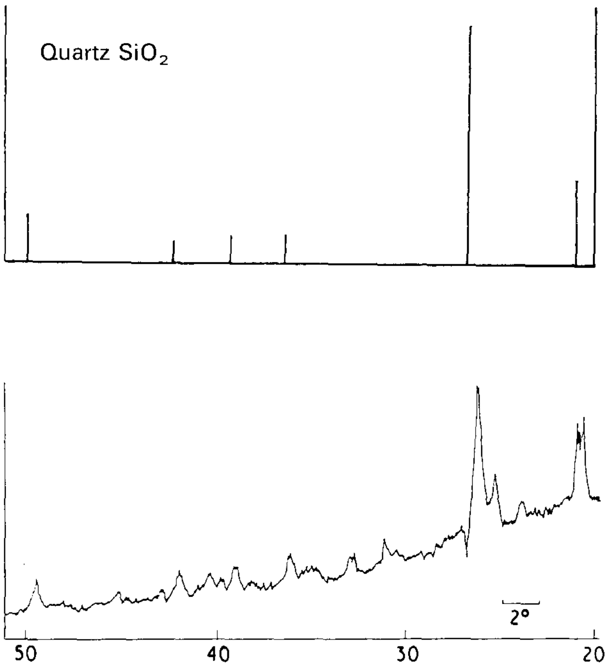

Figure 1 XRD trace of untreated ash.

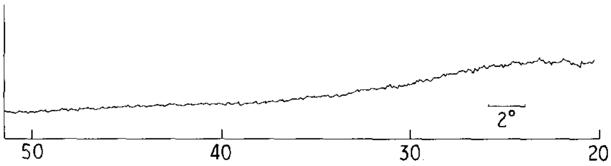

Figure 2 XRD trace of glass with 20% $CaCO_3$ additive.

3.2. Glass–ceramic synthesis

The nucleation and heat-treatment temperatures were estimated based on previous studies [3, 4]. A nucleation temperture of 700 °C was chosen, and it was found that there was little difference between nucleating for 1 or 24 h, so all nucleation was done for 1 h. Table II shows that the optimum heat-treatment temperature appears to be 1000 °C. Also, as the heat-treatment temperature increases, the degree of crystallinity decreases. These results were calculated using the method of internal standards. Both observations are true of melts with and without the nucleating agent, TiO_2.

Decreasing crystallinity with increasing temperature is an unexpected result. Two possible explanations are that this increase in temperature approaches a phase-transition temperature with either an amorphous phase, or a second crystalline phase. Since no other XRD peaks increased in intensity as the temperature increased, the latter is doubtful; therefore, it is suspected that a second metastable glass is forming.

A comparison of a and b in Fig. 3 indicates that the addition of TiO_2 greatly enhanced the definition of the crystals, but made little difference to the degree of crystallinity, as indicated in Table II. It is important to note that, as shown by the X-ray patterns, the addition of TiO_2 had no apparent effect on the crystalline phase formed.

TABLE II Crystallinity of glass–ceramic

Description	Percentage crystallized
Glass–ceramic, nucleated 1 h, heat treated 48 h 1100 °C	28.5
Glass–ceramic (1% TiO_2), nucleated 1h, heat treated, 48h, 1000 °C	39.2
Glass–ceramic (1% TiO_2), nucleated 1h, heat treated 48h, 1100 °C	28.7
Glass–ceramic (1% TiO_2), nucleated 1h, heat treated 48h, 1200 °C	15.3

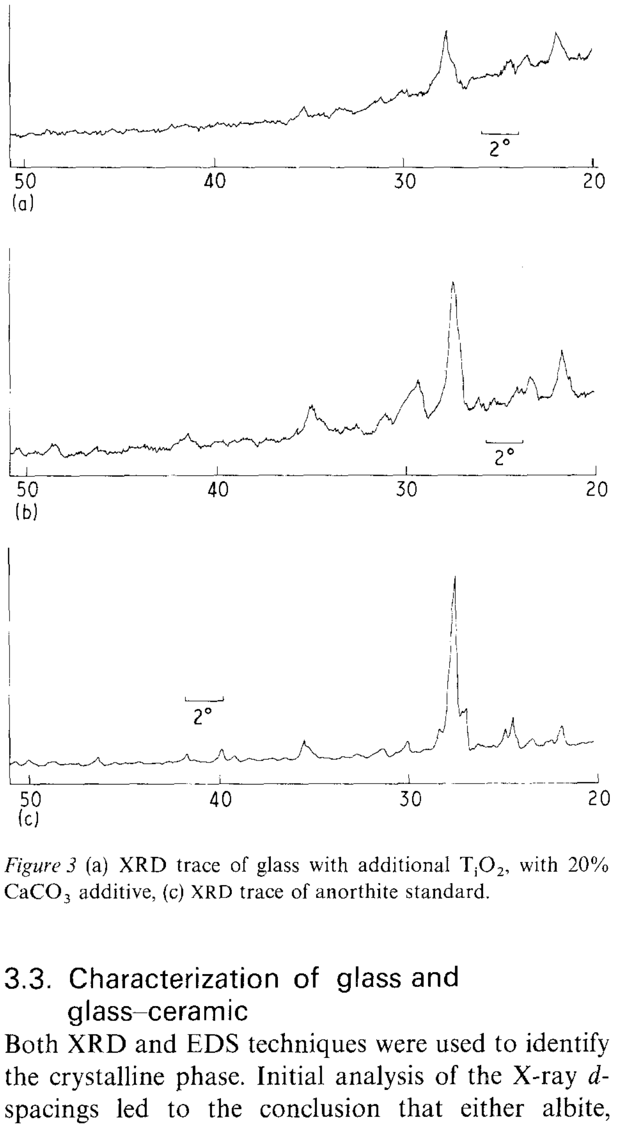

Figure 3 (a) XRD trace of glass with additional T_iO_2, with 20% $CaCO_3$ additive, (c) XRD trace of anorthite standard.

3.3. Characterization of glass and glass–ceramic

Both XRD and EDS techniques were used to identify the crystalline phase. Initial analysis of the X-ray *d*-spacings led to the conclusion that either albite, $NaAlSi_3O_8$, or anorthite, $CaAl_2Si_2O_8$, had formed. By using EDS with a low accelerating voltage to avoid including the glass matrix in the beam interaction volume, it was determined that calcium was present in the crystal growth areas and that sodium was not. This result points to the presence of anorthite as the crystal phase, and was later confirmed by obtaining an anorthite standard and comparing its X-ray pattern (Fig. 3c) with that of the glass–ceramic.

SEM micrographs (Fig. 4) show that the anorthite crystals formed in a very regular shape and orientation. Their size ranges from 5 to 20 µm in length, and they have a very constant width of about 6 µm. The "holes" in the crystals are probably due to preferential etching by the HF. The results of the Knoop microhardness and density measurements are given in Table III.

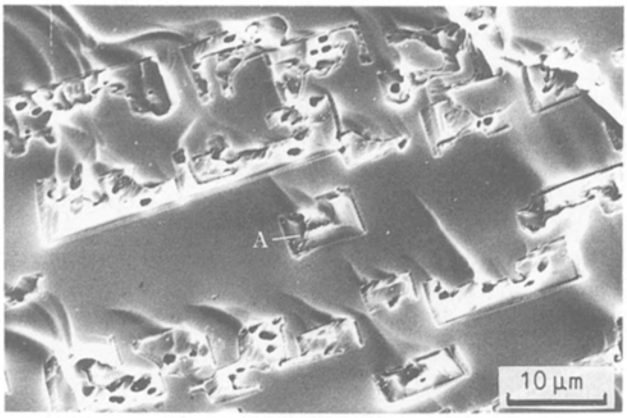

Figure 4 SEM of crystal structure (A) in glass matrix.

TABLE III Properties of glass–ceramic

Sample*	Knoop microhardness (kg mm^{-2})	Density (g cm^{-3})
1	430.0	1.61
2	498.9	1.60
3	557.6	1.61
4	579.9	1.61
5	627.2	1.69

*Samples: 1: glass with TiO_2 additive; 2: glass untreated; 3: glass–ceramic, nucleated 1 h, heat treated 48 h, 1100 °C; 4: glass–ceramic, nucleated 24 h, heat treated 48 h, 1100 °C; 5: glass–ceramic (1% TiO_2), nucleated 1 h, heat treated 48 h, 1100 °C.

The general trend in microhardness represented by these data is that, as the samples become more crystalline, their average microhardness increases. Interestingly, the untreated glass had a higher microhardness than the glass with the TiO_2 additive. Also for samples 3 and 4, an increase in nucleation time which made no noticeable difference in the XRD patterns did have a significant effect on microhardness.

Similar to the microhardness results, as the samples became more crystalline, the density increased. This result is expected as the density of the untreated glass is 1.60 g cm^{-3} and the density for anorthite is reported as 2.76 g cm^{-3}. Unlike the microhardness, the glass with the TiO_2 had a higher density than either the glass or the glass–ceramic without the additive. This result is also expected as the density of the untreated glass is 1.60 g cm^{-3} while the density of TiO_2 is reported as 4.17 g cm^{-3}.

4. Conclusions

The formation of an X-ray amorphous glass from coal ash was possible at temperatures below 1500 °C if a catalyst such as $CaCO_3$ was used. This glass could then be recrystallized into a glass–ceramic displaying several desirable properties, such as hardness and resistance to high temperatures. Due to the sluggishness with which the crystal phase precipitated from the glass, TiO_2, a nucleating catalyst, was employed in the melt. Although the use of this additive had little effect on the degree of crystallization which took place, it did improve the definition of the crystal shape and morphology, thus allowing the crystals to be seen using from SEM. The crystal phase was identified as anorthite, $CaAl_2Si_2O_8$. This identification was made on the basis of results from XRD and EDS techniques. The maximum weight fraction of crystals in the glass–ceramic was measured at approximately 40% by using the method of internal standards for XRD. Interestingly, as heat-treatment temperatures were increased, the degree of crystallization decreased. This result led to the conclusion that a second metastable glass phase was forming, as no other crystalline phase was observed. Knoop microhardness and density measurements were taken, and indicated that the glass–ceramic may have several desirable properties that would make it attractive to industry for use in high-temperature crucibles or refractory materials. The applications of this glass–ceramic are not explored here.

Acknowledgement

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