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# Crystallization behaviour of glass-ceramic sealant for solid oxide fuel cells

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ABSTRACT

The crystallization behaviour of a glass-ceramic suitable as SOFCs sealant has been investigated using differential thermal analysis (DTA). Glass powders of two different particle sizes ($< 38 \mu m$ and $38–75 \mu m$) have been considered. The exothermic peak in DTA thermographs has been associated with the crystallization of the diopside phase, as revealed by X-ray diffraction analysis (XRD). Avrami exponents ($n$) have been calculated for both particle sizes using the Ozawa equation, while Matusita and Sakka equation has been used to calculate the activation energy for the crystallization ($E_c$). The values found for n are 2.6 ($< 38 \mu m$) and 2.1 ($38–75 \mu m$). The obtained values for $E_c$ are 403 kJ/mol and 262 kJ/mol for the finest and the coarsest glass powders, respectively. As a comparison, the activation energies for the viscous flow ($E_\eta$) have been also evaluated: 349 kJ/mol for powders sized $< 38 \mu m$ and 265 kJ/mol for those sized $38–75 \mu m$.

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## 1. Introduction

In the modern challenge to developing a competitive way to produce "clean" energy, solid oxide fuel cells (SOFCs) can occupy a decisive role. SOFCs are devices able to convert chemical energy into electrical energy by red-ox reactions between a fuel and an oxidant. In order to obtain a satisfying output power it is necessary to build a SOFC stack [1,2]. Some of the stack elements (i.e. metallic interconnect and ceramic cell) are joined by a sealant. Recently many studies have pointed out glass-ceramic sealants among the most promising materials for this application [3–8]. This is mainly due to the possibility of tailoring their proprieties by changing their composition or thermal treatments. Glass-ceramics are materials in which a residual glass phase and a crystalline phase deriving from a devitrification process coexist together. In general, they have superior mechanical proprieties compared to their parent glasses. A reliable glass-ceramic sealant for SOFCs should have an excellent gas tightness, a high resistance to relevant SOFC operating conditions (i.e. reducing and oxidizing atmospheres) and a thermal expansion coefficient (TEC) as much as possible closest to that of materials to which they are in contact with [4]. The activation energy for the crystallization and the Avrami exponent ($n$) are the most important parameters in order to evaluate the crystallisation mechanism of glass-ceramic materials. They can be obtained from differential thermal analysis (DTA)

conducted at different heating rates. Many studies have been carried out on different glass systems (also for different applications) in order to evaluate these parameters and how they could affect the crystallization mechanisms [9–13]. A better understanding of these factors, including the effect of the mean particle size on crystallization kinetics, could lead to improved knowledge in varying glass-ceramic properties.

In this study, Kissinger [9], Matusita and Sakka [5] and Ozawa [10] equations were used to determine the crystallization mechanism and the activation energy values for the crystallization of a glass-ceramic composition designed and preliminary tested as SOFC sealant elsewhere [14].

## 2. Experimental

The composition of the glass in wt% was: 54.39% $SiO_2$, 13.78% $Na_2O$, 9.02% $CaO$, 8.37% $MgO$, 11.26% $Al_2O_3$, 1.67% $K_2O$, 0.9% $B_2O_3$ and 0.61% $Y_2O_3$. This glass was labelled as KMBY. The sealant was produced as glass by melting the appropriate oxides and carbonates raw materials in different proportions (as reported above) and by heating at 1500 °C for 1 h in a platinum-rhodium crucible. The melt was cast on a brass plate and the transparent glass was ground for differential thermal analysis. The resulting powders were sieved, obtaining two different particle sizes: $< 38 \mu m$ and $38–75 \mu m$. DTA analyses (Netzsch DTA 404 PC) have been carried out on both particle sizes, using $Al_2O_3$ as reference, at different heating rates (10 °C/min, 20 °C/min, 40 °C/min) from room

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temperature to 1200 °C. The distribution of sizes (vol % vs particle diameter) has been obtained by a particle size analyser (LS230, Coulter Corporation, USA) on two different particle sizes ($<$ 38 μm and 38–75 μm respectively). SEM (JEOL 5700) and EDS analyses have been carried out on the KMBY glass-ceramic obtained after sintering at 850 °C for 30 min in air atmosphere. The sintering behaviour (shrinkage %) has been determined by heating stage microscopy (Expert System Solutions, Italy) at heating rate of 20 °C/min.

## 3. Results and discussion

The DTA thermographs of the KMBY powder ($<$ 38 μm) are reported in Fig. 1, together with the glass transition temperature ($T_g$). The DTA analyses of the glass powder (size $<$ 38 μm and 38–75 μm) show that the crystallization peak ($T_p$) shifts to higher values with increasing the heating rate.

In a previous study [14] we observed that the crystallization peak is also affected by the particle size; the peak shifted to lower temperatures with decreasing particle size, suggesting an effect associated with the surface nucleation of the glass. According to XRD analyses, $Ca_{0.89}Mg_{1.11}Si_2O_6$ (diopside) was found as the dominant crystalline phase, potassium containing nepheline ($Na_3K$ $(Al_{0.44}Si0.56)_8O_{16}$) and traces of akermanite ($Ca_2MgSi_2O_7$) were also detected, as reported in reference [14], after a heat treatment at 850 °C for 30 min; the shaped DTA exothermic crystallization peak can be assigned to the diopside.

The activation energy for crystallisation, related to $T_p$ can be estimated by the Kissinger equation (Eq. (1)) [15]:

$$Ln\left(\frac{\alpha}{T_p^2}\right) = -\frac{E_{ck}}{RT_p} + constant \qquad (1)$$

where $\alpha$ is the heating rate, $R$ is the gas constant and $E_{ck}$ is the value of activation energy obtained by this method. The value of $E_{ck}$ can be deduced from the linear plot between $Ln(\alpha/T_p^2)$ and $1/T_p$. The $E_{ck}$ for KMBY $<$ 38 μm and 38–75 μm were found to be 233 kJ/mol and 126 kJ/mol, respectively. As stated by Matusita and Sakka [16,17], the Kissinger equation is valid only if crystallization is completely from surface sites. Otherwise, Matusita and Sakka equation should be used (Eq. (2)).

$$Ln\left(\frac{\alpha^n}{T_p^2}\right) = -\frac{mE_c}{RT_p} + constant \qquad (2)$$

where $n$ is the Avrami coefficient which depends from the mechanisms of growth, $m$ is the dimensionality of growth of the crystalline phase (i.e. rod-like, disk-like or sphere-like) and $E_c$ is

the activation energy for the crystallization; $n$ and $m$ parameters have to be calculated in order to obtain the value of $E_c$. The Avrami coefficient can be derived from the Ozawa equation (Eq. (3)) [18],

$$-n = \left(\frac{d\{ln[-ln(1-\chi)]\}}{d(ln\alpha)}\right)_T \qquad (3)$$

where $\chi$ is the volume fraction of crystallized phase at a fixed temperature T. $\chi$ was evaluated from the exothermic peak in the DTA thermographs and was calculated as the ratio between the partial area under the peak (at a chosen temperature) and the total area of the peak. The Ozawa plots $ln(-ln(1-\chi))$ versus $ln\alpha$, at different temperatures (930 °C, 940 °C, 950 °C, 970 °C) for KMBY $<$ 38 μm are reported in Fig. 2. The value of $n$ has been calculated as the mean value of the slopes of the plots and it was found to be 2.6, while for KMBY powders size $38 < $ μm $ < $ 75 the $n$ value was 2.1 (graph not reported here). Assuming that the number of nuclei is not constant with the heating rate, $n$ and $m$ are related to each other through the relation $m = n - 1$ [9–11,19]. Values of $m$ for the finest and the coarsest powders are 1.6 and 1.1, respectively, suggesting a bulk crystallization with dimensionality of crystal growth between 1 (i.e. rod like) and 2 (i.e. plate like) [11,17,20]. Fig. 3 shows the particle size distribution of the two different particle sizes batches used for the study ($<$ 38 μm and 38–75 μm). The average size for particles sieved at $<$ 38 μm was found to be 21 μm while the average size for the powder in the 38–75 μm range was 51 μm.

In Table 1, kinetics parameters, activation energies for crystallization ($E_{ck}$ and $E_c$), activation energy for viscous flow ($E_\eta$) and sintering behaviour (shrinkage %) for two different sizes of KMBY powders are reported.

In case of surface crystallization opposite results would be expected, since the lower the particle size the greater is the tendency to devitrification by growth from surface nuclei, thus leading to the
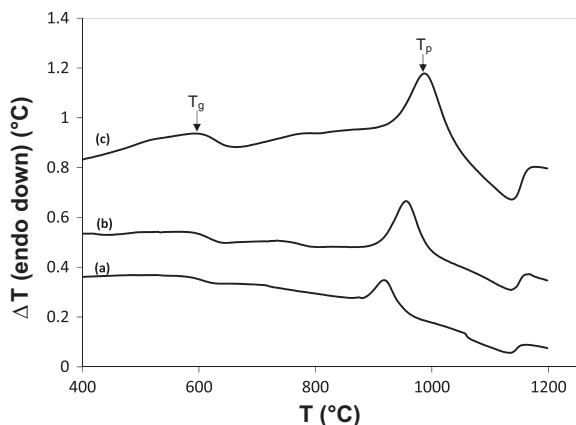


**Fig. 2.** Plots in accordance with Ozawa equation (Eq. (3)) for KMBY with powders size $<$ 38 μm.



**Fig. 3.** Particle size distribution of the two different particle sizes batches used for the study ($<$ 38 μm and 38–75 μm).



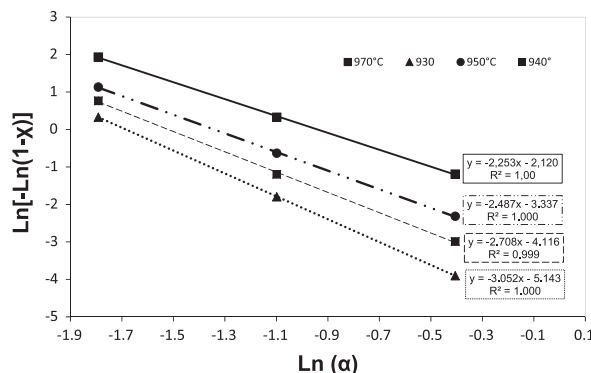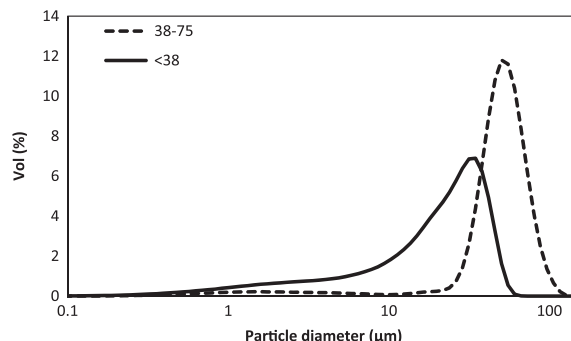**Fig. 1.** DTA thermographs of KMBY powders ($<$ 38 μm) collected at different heating rates: (a) 10 °C/min, (b) 20 °C/min, (c) 40 °C/min.