Microwave Processing of Glass

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Abstract

Microwaves at the ISM frequency of 2.45 GHz have been applied to heat the molten salt bath used for ion exchange. A commercial soda-lime silicate has been used in order to investigate the processing time and the exchange depth resulting from the microwave assisted treatment, compared to the conventional one.

Provided the molten salt, having an high electrical conductivity, does not shield the glass sample from microwave exposure, there is evidence of an increased ion mobility under microwave irradiation.

In particular, this is confirmed by the higher calculated diffusion coefficient and by the increased potassium concentration in the exchanged layers.

Introduction

Microwave radiation can be used as an alternative heating source for all those materials which present low thermal conductivity. At 2.45 GHz the electromagnetic radiation can interact with solids materials and be absorbed producing localised heating on those regions where the dielectric properties are favourable and cold areas where the materials presents poor dielectric coupling. Ceramic and refractory materials are among those solids which can be easily heated up under microwave irradiation, even though sometime are not able to get rid of the high quantity of heat generated by the coupling with the electromagnetic field and give rise to a uncontrolled thermal runaway phenomenon [1]. Nevertheless when controlled volumetric heating, faster warm-up to temperature, lower energy consumption, and improved quality and properties of the process materials can be accomplished, then these benefits made microwave heating a good process for high-temperature ceramic treatments [2-4].

In particular, microwave processing of glass has been proved to be efficient in enhancing fracture propagation in glass cullets during industrial melting process, provoking crystallisation path modification and reducing pore size during glass densification process [5-7]. Even though the ion exchange experiments on industrial glasses are well known, authors present some studies on modeling microwave/melt interaction during Na-K exchange in glass slabs under 2.45 GHz irradiation. Moreover some experimental results on sintering and crystallisation of glass ceramics are also reported.

Crystallization

It has been observed that dependently upon crystallization mechanism, microwave can induce different kinetics or different crystalline habitus [6,7].

Glasses of the Li_2O-Al_2O_3-SiO_2 (LAS) ternary compositions have been studied during the first stages of nucleation since when added of ZnO and MgO during melting, present a peculiar color change few tens degrees above the glass transition temperature that can be explained as phase separation [6]. Such phenomenon in the case of glass-ceramic production is very often sought because it is usually followed by the precipitation of crystallites. In the present case both phase separation and nucleation occurred at about 200°C above the transition temperature and left the glass transparent. The crystallites which formed during glass nucleation consisted of a mixture of isostructural Mg titanates and Zn titanates. Under microwave irradiation of the starting LAS glasses the color modifications are more rapid than during conventional treatment, as expected by the nature of microwave heating. This effect can be due to higher mobility in the microwave field of atoms such as titanium and lithium, which show themselves to be good absorbers in the microwave field [6 and references therein quoted].

As far as crystallisation process is concerned, LAS glassy compositions heated by microwave field show a larger extent and shorter times with respect to the same samples heated by conventional heating [6]. The microstructure and the growth of crystalline phases in LAS glass-ceramic was proved to be influenced by the heat treatments. In particular, it was observed a similar evolution from virgilite to β-spodumene with increasing of temperature in both treatments even if the secondary crystalline phases formed at higher temperature are quite different, since the microwave crystalline evolution based on diffusional mechanism is enhanced to purer phases through different paths. Virgilite evolution toward β-spodumene is completed at 1100°C, whereas the conventional samples do not convert completely, even after 30 min soaking time at the same temperature. Lithium oxide and alumina enter the keatite structure to produce β-spodumene crystal, the absence of the solid solution β-spodumene/$LiAlSi_3O_8$ and of the phase $LiAlSi_3O_8$ is a proof that Li^{+} has an enhanced diffusion process under microwave irradiation. Another crystalline phase evolved in LAS glass-ceramics is clinoenstatite, monoclinic polymorph of $MgSiO_3$, which never converts to enstatite, orthorhombic symmetry, during microwave heating, indicating the predominance of the lower symmetry form. These results are consistent with the very rapid heating and cooling typical of the microwave irradiation which does not allow the slow conversion of clinoenstatite. Hence, a kinetic control on the crystallisation mechanism of the major Mg-containing crystallisation mechanism is observed in microwave field.

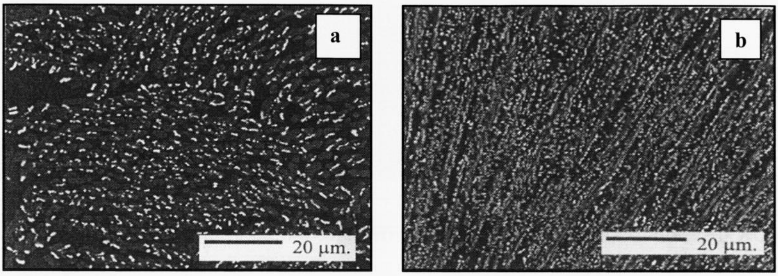

Figure 1: SEM images of conventional (a) and MW (b) heated CSZ glass ceramics.

Other glasses containing a reduced number of oxides, $CaO \cdot ZrO_2 \cdot SiO_2$ (CZS), have been tested. From optical microscope observation the microwave treated samples show both surface and bulk crystallization. Such compositions separate an interesting microstructure where small needle-like ZrO2 crystals grow on wollastonite long shaped crystals surrounded by amorphous phase [7]. Crystalline phase distribution in the samples differs passing from conventional to microwave heating. This effect is particularly relevant in the Na_2O added formulations. The conventionally treated material presents roundish wollastonite-2M crystals embedded in an amorphous matrix, while in the microwave heated specimens oriented long shaped wollastonite-1A crystals were seen (Figure 1).

Sintering

As far as sintering is concerned both sintering and crystallisation behaviour of a $52SiO_2$-$30CaO$-$14ZrO_2$-$2Al_2O_3$ (wt%) glass-ceramic was studied by performing a series of heat treatments in both a conventional and a multi-mode microwave furnace [8]. Temperatures chosen for both treatments were: 900, 950, 1000, 1100 and 1200°C with soaking times of 0, 5, 10 and 20 minutes and heating rate was kept at 2000°C/h. Microwave and conventional treatment were almost identical even though the conventional furnace reaches soaking temperature in a smoother way with respect to the microwave one. Although the microwave treatment results in a lower overall average pore size the difference seem to be statistically significant for the comparison for soaking times inferior to 5 minutes. Moreover the crystallization has not yet occured in the MW treated sample (Figure 2), indicating lower viscous flow, hence lower temperature.

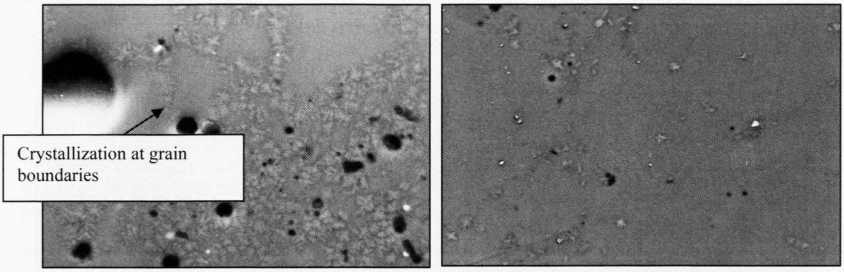

Figure 2: SEM micrographs of polished cross section of glass ceramics sintered at 900°C (a) conventionally and (b) by microwave irradiation after 5 minutes.

This result reinforces those theories [9] according to which the dielectric inhomogeneity of a porous green part, combined with the pore shape is assumed to cause an electrical field strength enhancement at convex surfaces.

Ion Exchange

Ion exchange of microscope glass slabs, 1 μm surface polishing prior to processing, were immersed in KNO_3 and $NaNO_3$ 1:4 ratio at 450°C. Since the exchange rate is a function of temperature through the interdiffusion coefficient and depends on parameters such as composition, structure, and surface condition of the glass [10], the same glass slabs were tested as comparison in conventional furnace. Temperature was controlled during the 30, 60, 120 min soaking times of exchange testing by using a stainless steel shielded and grounded K-type thermocouple. The thermocouple was inserted 20 mm deep in the ion exchange bath. Stirring of the molten salts during the treatments helped homogenising the temperature.

Interdiffusion was determined by EDS probe mounted on a SEM in a cross section of the slabs mounted in epoxy resin and polished to 0.3 μm. As clearly visible from Figure 3, the K^{+} penetration depth is high in microwave than in conventional heating also after 120 minutes, giving an higher diffusion coefficient (see slope of lines reported in Figure 4).

The reported experimental results go in the direction of sustaining the "nonthermal" effect in the form of enhanced kinetics for ion exchange. A modeling and numerical simulation of microwave-induced ion transport can be found in ref. 11 where the evaluation of the "ponderomotive force", a fundamental property of microwave irradiated interfaces that represent abrupt discontinuities in ionic mobility, is reported.

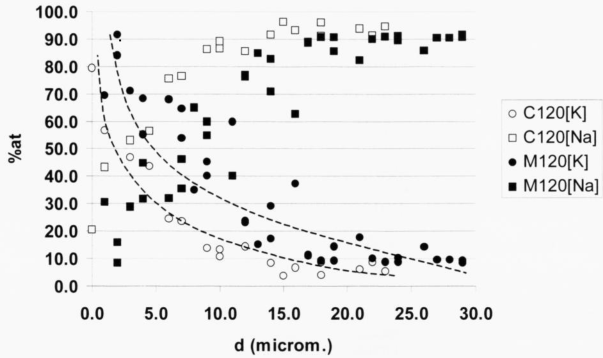

Figure 3: Exhance penetration depth, d (in μm) of sodium and potassium (concentrations expressed in atomic percent) during microwave (M) and conventional (C) treatments at 120 minutes.

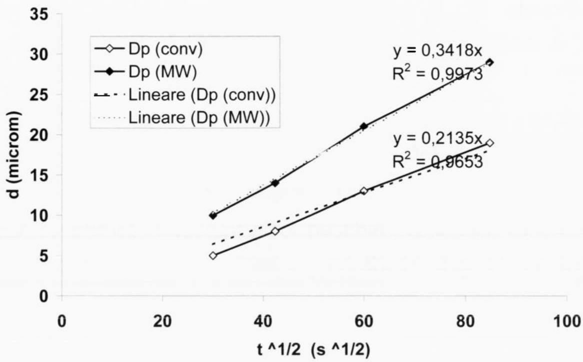

Figure 4: Exhance penetration depth, d (in μm) for microwave and conventional ion exchange treatmentsvs square root of processing time ($s^{1/2}$).

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