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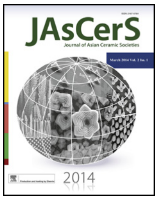

The crystallization behaviour and bioactivity of wollastonite glass-ceramic based on $Na_2O–K_2O–CaO–SiO_2–F$ glass system

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ABSTRACT

The study concerns about the crystallization behaviour and in vitro bioactivity of a glass-ceramic prepared from a series of glasses in the $Na_2O–K_2O–CaO–SiO_2–F$ system. A minor amount of cerium oxide was also added instead of calcium oxide in some selective glass batches. The main crystalline phases, formed after the appropriate heat treatments, were wollastonite solid solution and pseudo-wollastonite-like phases. There is a preferential tendency for wollastonite ($CaSiO_3$) to accommodate K, Na, F, and Ce ions in its structure forming wollastonite solid solution with variable formulas. The bioactivity of the resulting crystalline materials was examined in vitro by immersion in simulated body fluid at 37 °C. An increase of the surface bioactivity of glass-ceramic with the Na_2O/K_2O replacement was observed which is attributed to the augmentation solubility of the crystalline sample. On the other hand, the bioactivity of the crystalline sample with CeO_2/CaO replacement was improved by the crystallization of pseudo-wollastonite phase together with wollastonite solid solution phase.

1. Introduction

Glass-ceramics are produced by controlled nucleation and crystallization of glasses. The great varieties of compositions and microstructures with specific technological properties have allowed glass-ceramics to be used in a wide range of applications [1]. There is great interest in glass-ceramics that possess appropriate physical, mechanical, and biological properties for biomedical applications. These materials should be biocompatible and in most cases bioactive. Bioactivity is defined as the ability of biomaterials to promote the formation of a crystalline hydroxyl apatite (HA) layer from physiological fluid [2]. In implantology, there is considerable interest in bioactive materials to establish strong chemical bonding between the implant and bone, as well as to accelerate implant anchorage by inducing an HA layer on the implant surface [3]. Currently, several bioactive glass-ceramics are used for clinical applications as middle-ear implant for the reconstruction of the iliac crest and also as vertebral prostheses or dental implants [4].

Wollastonite ($CaSiO_3$) or calcium metasilicate is a chain silicate mineral. As it is known, calcium silicate has mainly two normal modifications, one is the low temperature phase wollastonite and the other is the high temperature phase pseudo-wollastonite [5]. By heating over 1125 °C, during the sintering, the low temperature form of wollastonite transformed reconstructively into pseudo-wollastonite [6]. Since the 1990s, wollastonite ($CaSiO_3$) ceramics have been studied as biomaterials for artificial bones and dental roots because wollastonite exhibits good bioactivity and biocompatibility. Some investigators have reported that wollastonite and pseudo-wollastonite ceramics are bioactive and observed that the formation of apatite on $CaSiO_3$ ceramics is faster than that on other bioglass and glass-ceramics in simulated body fluids (SBF) [5]. Siriphannon et al. [7] have found that the rate of hydroxyapatite (HA) formation on pure $CaSiO_3$ ceramic surface was faster than that on the biocompatible apatite wollastonite A/W glass-ceramics and some other bioactive glass-ceramics.

Fluorosilicate glass-ceramics are characterized by unique mechanical properties dependent upon highly anisotropic crystals, which assume one- or two-dimensional form. Thus, mica glass-ceramic displays mechanical machineability, whereas glass-ceramic based on amphibole and other chain silicates has shown extreme strength and toughness. Fluorosilicates-containing glass-ceramics are characterized as being less sensitive to superficial damages and exhibit higher thermal shock, erosion and fracture strength than common ceramic

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materials [8]. Several noteworthy synthetic glass-ceramics have been developed based on fluorosilicates crystalline phases: potassium fluorphlogopite ($KMg_3AlSi_3O_{10}F_2$), fluorrichterite ($KNaCaMg_5Si_8O_{22}F_2$), fluorcanasite ($(Na,K)_6Ca_5Si_{12}O_{30}F_4$), and fluor-miserite ($KCa_5\square(Si_2O_7)(Si_6O_{15})(OH)F$, where □ denotes a vacancy or "virtual site" within the structure [8]. The miserite crystalline phase, which strengthens glass-ceramic materials, has been described as a pyroxenoid (wollastonite) or hydrous pyroxenoid derivative (pectolite). It is anticipated that miserite glass-ceramic has biocompatibility, bioactivity, and excellent machineability. Thus, miserite glass-ceramic is a promising biomaterial for dental implant applications as an alternative to metallic titanium, due to its biological, mechanical and optical properties [9]. Another interesting fluorine-containing crystalline phase in glass-ceramics is cuspidine ($Ca_4Si_2O_7F_2$), a sorosilicate with isolated $(Si_2O_7)^{6-}$ double tetrahedral groups. Cuspidine is the most abundant high temperature phase in mould fluxes used in continuous casting of steel [10].

In order to enhance the capability of sensitivity of bioglass reactions in vivo, the glass could be doped with a luminescent rare earth (RE). Cerium is known to possess bacteriostatic properties and low toxicity [11]. It has been reported [12] that the activity of cerium (III) sulfadiazine against various microorganisms is comparable to that of silver sulfadiazine and cerium-doped bioactive glasses. It could be useful when implantation concerns with periodontal pockets, infected frontal sinuses, and hypersensitive teeth as a complication of periodontal treatment or tooth wear that has resulted in the exposure of dentine and dental tubules [13].

The main purpose of the present paper is to study the effect of compositional changes on crystallization behaviour and the in vitro bioactivity for a series of glasses based on $Na_2O–K_2O–CaO–SiO_2–F$ glass system with different Na_2O/K_2O replacement ratio. Minor amount of cerium oxide CeO_2 was introduced in the glass formula at the expense of calcium. This work is concerned with the fundamental knowledge for the type of phases, solid solutions, and the microstructure formed in the glass-ceramic materials and their biological behaviour.

2. Materials and methods

The compositions of glasses studied are listed in Table 1. Analytical grade reagents Na_2CO_3, K_2CO_3, $CaCO_3$, CaF_2, CeO_2, and Quartz (SiO_2) were used as starting materials. The homogeneous weighed batch materials (100 g), after thorough mixing, were preheated at 1000 °C for 1 h for calcination and to avoid the volatilization. The melting process was performed in a platinum crucible in a Vecstar electric furnace at 1400–1450 °C for 1.5 h. The melts were then cast into hot stainless steel moulds. The glasses were annealed at 500 °C for 1 h, and then the muffle furnace cooled to room temperature to remove the residual thermal stress.

The thermal behaviour of glasses was monitored by DTA using a differential thermal analyzer (SDTQ 600 – TA Instruments, USA) to know the glass transition (T_g) and crystallization (T_c) temperatures and to determine the optimum conditions for heat treatment processing where the temperature ranges between 25 and 1000 °C. The cast glass was crushed and sieved between 90 and 125 μm to produce glass powder suitable for DTA. About 30 mg powdered sample was placed in an alumina crucible and subjected to a heating rate of 10 °C/min from ambient temperature to 1000 °C in a flowing high purity nitrogen environment.

The progress of crystallization in the glasses was followed using double stage heat-treatment regimes. Crystallization was carried out at temperatures in the region of the main DTA exothermic peak determined for each glass. The glasses were first heated according to the DTA results at the endothermic peak temperature for 5 h, which was followed by another thermal treatment at the exothermic peak temperature for 10 h. To characterize the crystalline phases of glass-ceramic samples after controlled heat treatment, powder XRD was conducted on a diffractometer (PW1080, PANalytics, Netherlands) with Cu Kα radiation (40 kV and 30 mA source). Spectra were obtained from 10° to 80° 2θ at a step size of 0.02°. The JCPDS reference cards were used to interpret the patterns.

The microstructure observation of the glass-ceramic samples was examined using a scanning electron microscope (Quanta FEG 250, Netherlands) equipped with an energy dispersive X-ray spectroscopy (EDX) system. The fracture sample surfaces were chemically etched by immersion in a ($1\%HF + 1\%HNO_3$) aqueous solution for 60 s. After that, the samples were ultrasonically washed with distilled water and dried in the dryer. The fracture surfaces were coated with a thin layer of gold by sputtering method.

In order to estimate the in vitro bioactivity test of the selected glass-ceramic specimens, we used the SBF proposed by Kokubo et al. [14]. The Tris-buffered SBF composition is (Na^+ 142.0, K^+ 5.0, Mg^{2+} 1.5, Ca^{2+} 2.5, Cl^- 147.8, HCO^{3-} 5.0, HPO_4^{2-} 1.0 and SO_4^{2-} 0.5 mol m^{-3}). The specimens were cut by a low speed diamond disc into rectangular pieces of dimensions (10 mm × 10 mm × 5 mm). The samples were polished and sequentially ultrasonically washed in isopropyl alcohol, in acetone, and in deionized water and then air-dried. These specimens were vertically mounted on a nylon wire in polyethylene falcon test tubes containing 50 ml of SBF for 21 days at 37 ± 0.5 °C and pH = 7.2 ± 0.3, using HCl 0.1 N for pH adjustment. The ratio of the SBF volume to the area of ceramic was equal to 0.5 cm^3 mm^{-2}. After the immersion time the samples were gently rinsed with deionized water and acetone and dried in air at room temperature. The surfaces of dried samples were analyzed by (SEM–EDX) and (FTIR) to detect the appearance of HCA layer. The glass-ceramic samples were analyzed by FTIR-6100 type A machine (The Netherlands). The spectra were obtained between 400 and 1600 cm^{-1} wave number with resolution of 2 cm^{-1}.

3. Results

3.1. *Crystallization characteristics*

Typical DTA of the glass samples crystallized at the heating rate of 10 °C/min are shown in Fig. 1. The results indicate that the investigated glass has followed the typical behaviour of the vitreous materials transforming into the glass-ceramic. The DTA spectrum of each glass displays the glass transition temperature (T_g) as a shoulder endothermic peak at which the atoms begin to arrange themselves in preliminary structural elements subsequent to crystallization. The crystallization temperature of the glass (T_c), as an exothermic peak indicating crystallization reaction in the glasses, are also recorded. The base glass sample G_1 has a glass transition temperature (T_g) of 705 °C and a crystallization temperature (T_c) of 870 °C. The DTA data reveal that the addition of Na_2O instead of K_2O led to shifting the endothermic dips to lower temperatures, i.e., lower temperature is needed to start the nucleation process in the glasses. In contrast the DTA data (Fig. 1) reveal that the endothermic dips as well as the onset of crystallization were shifted to higher temperature with the addition of CeO_2 at the expense of CaO.

In order to identify the crystalline phase's assemblage in the resultant glass-ceramic formed through crystallization of the studied glasses, each glass was heat treated at its crystallization peak temperatures (extracted from the relevant DTA thermograph) for 10 h. The phases developed in glass-ceramics as indicated by the X-ray diffraction analysis (Figs. 2 and 3) are wollastonite solid solution and pseudo-wollastonite. The X-ray diffraction analysis (XRD) (Fig. 2, pattern I, Table 2) indicated that the base glass (G_1) crystallized at 705 °C/5 h–870 °C/5 h to form only monomineralic