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Zirconia toughened mica glass ceramics for dental restorations

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ABSTRACT

Objective. The objective of the present study is to understand the role of yttria stabilized zirconia (YSZ) in achieving the desired spectrum of clinically relevant mechanical properties (hardness, elastic modulus, fracture toughness and brittleness index) and chemical solubility of mica glass ceramics.

Methods. The glass–zirconia mixtures with varying amounts of YSZ (0, 5, 10, 15 and 20 wt.%) were ball milled, compacted and sintered to obtain pellets of glass ceramic-YSZ composites. Phase analysis was carried out using X-ray diffraction and microstructural characterization with SEM revealed the crystal morphology of the composites. Mechanical properties such as Vickers hardness, elastic modulus, indentation fracture toughness and chemical solubility were assessed.

Results. Phase analysis of sintered pellets of glass ceramic-YSZ composites revealed the characteristic peaks of fluorophlogopite (FPP) and tetragonal zirconia. Microstructural investigation showed plate and lath-like interlocking mica crystals with embedded zirconia. Vickers hardness of 9.2 GPa, elastic modulus of 125 GPa, indentation toughness of 3.6 $\mathrm{MPa \cdot m^{1/2}}$, and chemical solubility of 30 $\mu\mathrm{g/cm^2}$ (well below the permissible limit) were recorded with mica glass ceramics containing 20 wt.% YSZ.

Significance. An increase in hardness and toughness of the glass ceramic-YSZ composites with no compromise on their brittleness index and chemical solubility has been observed. Such spectrum of properties can be utilised for developing a machinable ceramic for low stress bearing inlays, onlays and veneers.

1. Introduction

One of the global goals of oral health is to increase the number of individuals with functional dentition by the year 2020 [1]. The present global statistics demonstrate an alarming need for dental crowns and prosthetic rehabilitation. According to National Commission on Macroeconomics and Health (NCMH), the incidence of complete edentulism has been reported to be 7–69% world-wide, with developing nations, having edentulism at 11–37% in the age group of 65–75 years [2,3]. Addressing the above clinical problem of edentulism,

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dental ceramics have been popular as indirect restorative materials due to their esthetics, biocompatibility and chemical inertness. An important class of dental ceramics is glass ceramics with favourable properties such as ease of fabrication, good aesthetics, marginal fit, minimal abrasiveness with enamel and chemical durability [4–7]. Mica containing glass ceramics (SiO_2–Al_2O_3–MgO–K_2O–B_2O_3–F) are well-known materials for dental restorations due to their machinability, bioactivity and resemblance to tooth colour [8–10]. However, they are brittle in nature and have poor mechanical properties [7,11–13]. It is apparent that for optimal performance of a dental material in load bearing function *in vivo*, a desired combination of hardness, fracture toughness and flexural strength is essential.

Zirconia ceramics, despite few limitations have gained a remarkable interest amongst the metal free ceramic systems, due to their impressive mechanical properties [14,15]. The limitations of zirconia consist of an apparent moisture related low temperature degradation in the oral cavity. The associated moisture related phase transformation of t-ZrO_2 to m-ZrO_2 in the substructure of zirconia, results in 30–40% reduction of its fatigue strength [16–19]. Despite its opacity and the recent trends towards translucent zirconia ceramics, the success of cementation using air abrasion and tribochemical bonding remains a critical issue in zirconia ceramics, with no sufficient clinical evidence [20–27]. Cohesive veneer fractures of zirconia restorations reported in clinical studies further add up to its limitations [16,20–24,28]. Such fractures have been related to the low flexural strength of veneering ceramics and its vulnerable interface with zirconia [29,30]. The low thermal conductivity and its associated cooling rates and subsurface tensile stresses result in unstable cracks in ZrO_2-based veneers during firing [31,32]. Further, insufficient support of the veneer and improper core design in the prosthesis contribute to their unpredictable failure [32–36]. With advances in adhesive bonding and CAD-CAM technology, we intend to address the above clinical gap with a mica glass ceramic reinforced with yttria stabilised zirconia to increase their hardness and fracture toughness for possible applications involving monolithic ceramics for low stress bearing inlays, onlays and veneers [21,37].

The processing strategies, such as heat treatment techniques and second phase additions to the multi component glass systems have been attempted to strengthen glass ceramics, each presenting with an array of microstructures. Heat treatment as a function of time and temperature influenced the microstructure and *in vitro* properties of mica based glasses [38]. The addition of fluoride influenced mechanical properties, microstructure, cell adhesion and antimicrobial properties of K_2O–B_2O_3–Al_2O_3–SiO_2–MgO–F glass ceramics [39–42]. TiO_2 as a nucleation agent, demonstrated improved machinability and water resistance to calcium mica apatite based glass ceramics [43]. Similarly, addition of lithium, magnesium, calcium and barium to the fluormica glass compositions affected its microstructure and properties [44,7,45].

Zirconia (YSZ) as an additive is a well-known strategy to enhance the hardness and fracture toughness in glass ceramic composites [46]. The role of YSZ in enhancing the toughness properties of ceramic due to the phenomenon of transformation toughening is apparent. The improvements in bending strength, fracture toughness and hardness were observed in mica based glass ceramic (SiO_2–Al_2O_3–MgO–K_2O–B_2O_3–F–P_2O_5) with 15 wt.% YSZ and mica apatite with 10 wt.% YSZ using uniaxial pressing [47,48]. Cold isostatic pressing of mica base glass composition of (MgF_2–Al_2O_3–B_2O_3–P_2O_5–MgO–SiO_2–K_2O) with 30 wt.% of nano zirconia resulted in significant increase in bending strength and fracture toughness [49]. Bioverit glass of mica apatite with zirconia and 20 wt.% YSZ have moderately enhanced indentation toughness [50]. ZrO_2–SiO_2 glass ceramics of 30, 35 and 40 mol% ZrO_2 produced using a sol–gel method showed sufficient transmittance, elastic modulus, hardness and indentation fracture toughness [51]. Also, 5 wt.% t-ZrO_2 toughened apatite wollastanite glass ceramics are reported to have better bending strength, fracture toughness and microhardness with increasing temperature and heat treatment time [52].

Mica glass ceramics of the phologopite type are commercially known under the trademark MACOR. Although there are strategies to improve the properties of phyllosilicate mica glass ceramics with zirconia, investigations on YSZ-MACOR based composites in particular, has not been previously attempted [45,47,49,51,53]. Herein, we present an approach to enhance the mechanical properties of mica based glass using yttria stabilizied zirconia (YSZ) as an additive, a well-known strategy to increase the fracture toughness through transformation toughening mechanism in ceramic composites [54]. In addition, the effect of YSZ on the hardness, elastic modulus, brittleness index and chemical solubility of the glass ceramic has been analysed and compared to the commercially available glass ceramics such as IPS emax Press in the present study.

2. Materials and methods

2.1. *Glass preparation and heat treatment schedule*

Precursor powders of base glass composition (47.2 SiO_2–16.7 Al_2O_3–9.5 K_2O–14.5 MgO–8.5 B_2O_3–6.3 F (wt.%)) were ball milled in an agate jar with ethanol as milling medium at 300 rpm for 6 h to ensure homogenous mixing [40]. Subsequently, the mixed powders were preheated at 950 °C for 1 h and melted at 1500 °C for 2 h in a platinum crucible. The glass melt was then quenched in deionised water to obtain the glass frit. The glass frit powder was ball milled with varying amounts of 3 mol% YSZ (0, 5, 10, 15 and 20 wt.% YSZ) ($D_{50} \approx 50$ nm) (TOSOH, Japan). The glass–zirconia mixtures were compacted in a cylindrical die (15 mm diameter) at 50 kN using a uniaxial hydraulic press to obtain green compacts. Heat treatment schedule of sintering the base glass powder for 48 h was optimised based on the results of the differential scanning calorimetry, Fig. S1 (Supplementary material) demonstrating glass transition temperature (T_g) at 740 °C and crystallisation temperature (T_c) at 1060 °C.

A two stage heat treatment sequence was followed to densify the glass ceramic–ZrO_2 powder compact. In the first stage, the green compact was heated to 800 °C with a heating rate of 25 °C/min in a muffle furnace (Carbolite, UK) and held at this temperature for 2 h to relieve thermal stresses and to initiate

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