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Electron/Ion Microscopy of Low-temperature Sintered Y-TZP Ceramics with Additive of Lithium Disilicate Glass for Dental Restorations

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The research of all-ceramic dental restorations has received much attention in recent years due to their unique characteristic, such as good mechanical properties, excellent biocompatibility, and aesthetic performance [1]. Owing to the effect of transformation-toughening phenomena associated with the tetragonal-monoclinic phase transition, zirconia has much higher fracture toughness than other ceramics used in dentistry [2]. Y-TZP (yttria stabilized tetragonal zirconia polycrystal) has been considered as one of the most advantageous candidates for dental restorations. However, the high cost of high temperature (1500 ^{o}C) sintered Y-TZP restorations inevitably limits commercial applications. To reduce production costs, a sintering additive is used to lower the sintering temperature. Lithium disilicate glass ceramics (LDGC) have been widely used for dental restorations, including inlays, crowns, and bridges [3]. LDGC fabricated by sol-gel method has also been introduced into Y-TZP to optimize its mechanical and optical properties. This study presents the role and influence of LDGC addition on the microstructure of Y-TZP using TEM and FIB/SEM.

Tetraethyl, triethyl phosphate, lithium nitrate, zirconium nitrate pentahydrate, potassium nitrate and aluminum nitrate nonahydrate were used as precursors of Si, P, Li, Zr, K, Al, respectively. The molar ratio of the glass components was designed according to $66.3SiO_2$-$27Li_2O$-$2.0Al_2O_3$-$1.8K_2O$-$1.7ZrO_2$-$1.2P_2O_5$ system (see [4] for details). Y-TZP and the prepared LDGC powders were ball-milling mixed in ethanol for 3 hrs. and the mixture was dried and screened. The compacts with a dimension of $30 \times 40 \times 6$ mm^3 were pressed by a cold isostatic pressing at 250 MPa, and then sintered at 900-1100 °C for 2 hrs. in air with a heating rate of 5 °C/min. TEM samples were prepared using a FIB/SEM (Tescan) equipped with ToF-SIMS and characterized with a FEG TEM/STEM (JEOL 2100F) equipped with Bruker EDS system. Additional XRD, TG/DSC analysis and other properties measurements were also carried out using standard methods [4].

TEM micrograph of sintered Y-TZP/LDGC mixture shows small granular particles distributed around large grains and filling in pore spaces (Fig. 1). Although both large and small grains contain Zr and O based on EDS results, the electron diffraction reveals a diverse crystallographic structure. While large grains are monoclinic, small granular particles are cubic (dark arrow in Fig. 1b and inset in Fig. 1c). Amorphous materials filling the pore space at triple junctions were confirmed as Li-Si-O glass phase by HRTEM (Fig. 1c) and EDS analysis. ToF-SIMS analysis (spectrum and elemental mapping) of Y-TZP/LDGC ceramic grains (Fig. 2) clearly depicts that Y is rich in grains of the Li-Si phase where the concentration of Zr is rather low. Both ToF-SIMS and TEM results indicate that the escaped yttrium atoms diffused into the intergranular glass phase. In addition, yttrium atoms could also be released from the ZrO_2 solid solution due to the addition of LDGC, which induced the tetragonal-monoclinic phase transition of zirconia and abnormal growth of monoclinic grains. During cooling, a considerable amount of localized stress (strain contrast shown by white arrows in Fig. 1a), and microstructural change occurred due to the recrystallization of the inhomogeneous intergranular glass phase and the CET (coefficient of thermal expansion) mismatch between the glass phase and zirconia matrix [5]. Furthermore, at grain boundary the melt-out of LDGC additive could have facilitated atom diffusion and promoted the densification of Y-TZP ceramic during low temperature liquid sintering. At the same time, the temperature increase reduced the viscosity of glass phase, which could have also promoted atom diffusion and thus facilitated the densification. This research reveals that the Y-TZP/LDGC ceramics possess a great potential for all-ceramic restorations [6].

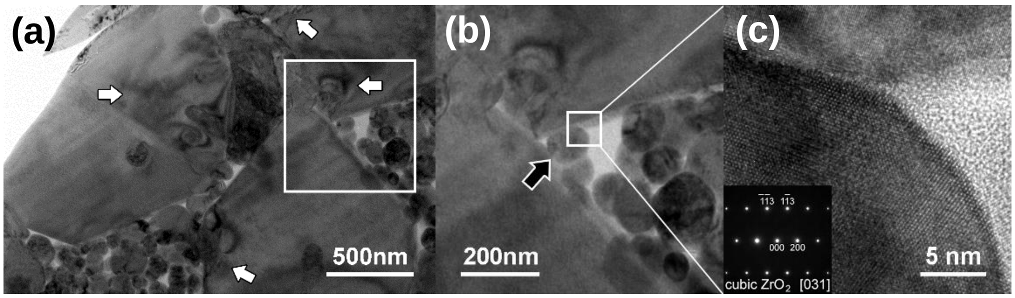

Figure 1. TEM images of sintered Y-TZP/LDGC reveals mixture of large grains and small granular particles and strain contrast due to recrystallization (white arrows) (a). Despite the same composition (ZrO_2) different crystallographic structure, monoclinic (large grain) and cubic (small granular particles) were found (b/c). HRTEM depicts amorphous Li-Si-O glass phases filling gaps in triple junctions (c).

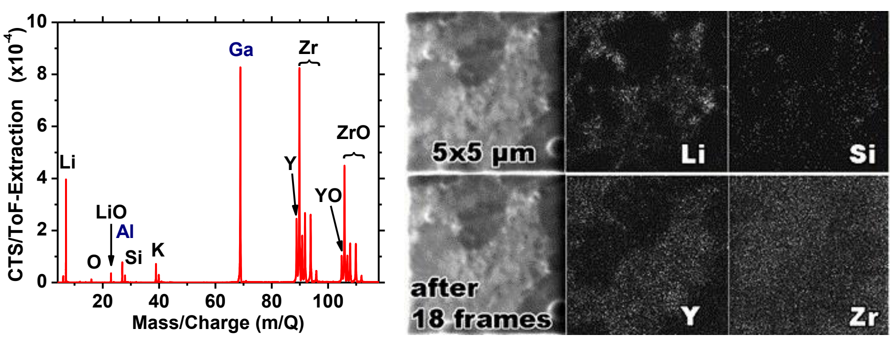

Figure 2. ToF-SIMS spectrum and elemental mapping of Y-TZP/LDGC ceramics illustrates the rich Y and poor Zr in grains of Li-Si phase.

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