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Influence of ZnO on the crystal phase and properties of lithium disilicate glass-ceramic doped with Ag_2O

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ABSTRACT

The purpose of this paper was to investigate the influence of ZnO on antibacterial properties, flexural strength and translucency of a novel dental lithium disilicate glass-ceramic doped with Ag_2O by changing crystal phase composition and microstructure. Investigations were carried out by means of differential scanning calorimetry, X-ray diffraction, scanning electron microscopy, antibacterial test, toxicity test, flexural strength and translucency test, respectively. Research showed that the introduction of ZnO increased the antibacterial activities of the lithium disilicate glass-ceramic doped with Ag_2O. But with the increasing of the ZnO content, the translucency and flexural strength reduced, because the introduction of ZnO hampered the transition from Li_2SiO_3 to $Li_2Si_2O_5$ and formed the crystal phase of $Li_3Zn_{0.5}SiO_4$. The flexural strength values of glass ceramic were above 300 MPa when the content of ZnO was below 4 wt%. The lithium disilicate glass-ceramic doped with 0.2 wt% Ag_2O and different content of ZnO had a large range of translucency. This material can be better applied to dental restoration.

1. Introduction

Lithium disilicate glass-ceramics (hereafter referred as LDGC) were first introduced into the denture restoration in 1998 by Ivoclar Vivadent due to its good biocompatibility, high strength and ideal aesthetic. However, the formation of dental plaque on dentures is easier than natural teeth because denture restoration breaks the environment of the original oral cavity [1]. The dental plaque and dental plaque toxins will lead to oral diseases, such as secondary caries, gingivitis and periodontal disease. These oral diseases are the urgent issue which need to be solved [2]. The emphasis of antibacterial materials research is adding inorganic antimicrobial into the materials in recent years [3,4].

It is well known that although Ag^+ has strong broad-spectrum antibacterial activities [5], the reduction of Ag^+ would discolor the materials [6]. Zinc, that is abundant in the earth and is cheaper than silver, also has broad-spectrum antibacterial activities [5]. Moreover, the use of binary Ag^+-Zn^{2+} is better than only using Ag^+ in the field of biomaterials because of the synergy of the antibacterials [7]. However, the high strength and ideal aesthetic are also important to the application of dentures. All of these properties depend on the crystal phase composition and microstructure of glass ceramic [8]. The content of components influences the properties of LDGC, for example, P_2O_5 promotes the whole devitrification when there is an appropriate amount of P_2O_5 as a nucleating agent in LDGC. When the content of P_2O_5 is higher, the crystal size of the $Li_2Si_2O_5$ becomes obviously small and the strength of LDGC decreases [9]. The introduction of an appropriate amount of ZrO_2 as a nucleating agent enhances the strength and translucency of LDGC, but, it doesn't have a nucleating effect with excess ZrO_2 [10]. However, when ZnO as an antibacterial agent is introduced into LDGC doped with Ag_2O, the influence on microcosmic structure and macroscopic properties of LDGC are still rarely reported at present.

In this study, the antibacterial properties of LDGC were investigated by adding appropriate amounts of ZnO and Ag_2O. We found that the antibacterial properties of LDGC doped with Ag_2O were enhanced with the increasing of the ZnO content, though the translucency and flexural strength reduced. And the influence of ZnO on the flexural strength and translucency of LDGC doped with Ag_2O were confirmed by the investigations of crystal phase composition and microstructure. Thus, the right amounts of ZnO evidently improved the practical application of LDGC.

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2. Experimental

2.1. Glass-ceramic preparation

The composition of matrix glass batch (in wt%) was as follows: 71.5 SiO_2, 13.5 Li_2O, 2.8 Al_2O_3, 3.2 K_2O, 1.5 B_2O_3, 3.0 ZrO_2, 2.0 P_2O_5 and 2.5 SrO. Different contents of antibacterial metallic oxides (Ag_2O, ZnO) were added. We found that excess Ag_2O in this glass caused an unexpected color of yellow. So the content of Ag_2O was a definite value. The matrix glass was prepared using analytic grade SiO_2, Li_2CO_3, Al_2O_3, KNO_3, H_3BO_3, ZrO_2, P_2O_5, $Sr(NO_3)_2$, $AgNO_3$ and ZnO, which were weighed by a balance with an accuracy of ± 0.01 g. The raw materials were melted in a corundum crucible at 1480 °C for 1 h. Then the glass specimens were annealed at 550 °C for 1 h and subsequently cooled to room temperature at a rate of 1–3 °C/min. The glass specimens were crystallized by keeping the glass warm for 2 h at 670 °C. Then raising the temperature to 800 °C quickly and keeping it there for 30 min.

2.2. Differential scanning calorimetry (DSC)

Thermal properties of the glass specimens doped with different antibacterial metal ions were studied by DSC to identify the optimal temperature of the heat treatment process. The powders of the glass specimens were scanned from indoor temperature to 1000 °C with a heating rate of 10 °C/min, using differential scanning calorimetry (STA409 PC, Netzsch, Selb, Germany).

2.3. Crystal phases analysis and microstructure

The type of crystal phases and their diffraction intensity of specimens doped with 0.2 wt% Ag_2O and different content of ZnO were characterized by XRD. After grinding and getting through 200 mesh sieve, the powders of each group were scanned from 10° to 80°, with a scanning rate of 4°/min, using a diffractometer (Ultima IV, Rigaku, Tokyo, Japan) at 40 kV and 20 mA.

Highly polished specimens doped with 0.2 wt% Ag_2O and different content of ZnO were etched by 5% hydrofluoric acid for 60 s. Distilled water was used to clean ultrasonically for 10 min. After drying and gold sputtering, the microstructural images were produced using SEM (JSM-6701F, Jeol, Tokyo, Japan).

2.4. Flexural strength and translucency test

The flexural strength was tested according to the ISO Specification 6872 [11]. After sandblasting and polishing, the three-point flexural strength of the specimens (25.0 mm × 4.0 mm × 1.2 mm) doped with 0.2 wt% Ag_2O and different content of ZnO were tested using a universal testing apparatus (AGS-10kNG, Shimadzu, Kyoto, Japan) with a crosshead speed of 0.5 mm/min, a span was 20 mm.

After polishing, the transmittance of eight specimens (0.8 mm in thickness) doped with 0.2 wt% Ag_2O and different content of ZnO were tested by UV–visible spectrophotometer (Lambda950, PerkinElmer, Waltham, America) from 380 nm to 800 nm.

2.5. Antibacterial test

Candida albicans as a kind of common pathogenic fungus in our oral cavity was used to evaluate the antibacterial ability of LDGC doped with different antibacterial metal ions by the inhibition zone method [6,12,13]. Firstly, 100 μl of 1.5 × 10^8 CFU/ml *Candida albicans* (ATCC 10231) bacteria suspension was spread evenly on the plate of YM agar medium, then 100 μl of sterile water was added to the wafer of filter paper the diameter of which was 15 mm, the powders of 0.1 g specimens (sterilized by autoclaving) were absorbed into the filter paper. The two same specimens in the YM agar medium were to avoid the occurrence of errors. After 20 h incubation at 27 °C, the result was observed.

2.6. Toxicity test

Toxicology information that we obtain from the application of *Caenorhabditis elegans* provides a more rational basis for extrapolating the biological effects to humans. Because over 40% of *Caenorhabditis elegans* genes contain apparent human orthologs [14,15]. Therefore, *Caenorhabditis elegans* was chosen as the object of our experiment.

Firstly, 150 age-synchronized wild-type *Caenorhabditis elegans* (Bristol N2) were put averagely into three NGM agar plates that were seeded with *Escherichia coli* OP50 as a food source. Then 0.05 g specimens (sterilized by autoclaving) LDGC doped with different antibacterial metal ions was added respectively. After 24 h maintaining at 20 °C, the survival number was recorded. The above procedure was repeated and changed 0.05 g specimens to 0.00 g, 0.10 g and 0.20 g, respectively.

3. Results

3.1. Heat treatment process

DSC curves of the glass doped with different antibacterial metallic oxides shows the temperature of crystallization peaks (Fig. 1). The two obvious exothermic peaks at approximately 670 °C and 800 °C illustrated that a strong devitrification would occur at these two temperatures. The first crystallization peak of glasses were similar to the parent glass which temperature was 670 °C. The second crystallization peak temperature that LDGC doped with 0.2 wt% Ag_2O and 3 wt% ZnO was 803 °C. So the heat treatment process that kept the glass warm for 2 h at 670 °C, then raised the temperature to 800 °C quickly and kept for 30 min was confirmed.

3.2. Crystal phase composition

According to the crystallization process confirmed above, the crystal phase changes of eight groups of specimens of LDGC doped with 0.2 wt % Ag_2O and different content of ZnO were presented by the XRD patterns (Fig. 2). As we can see, all the main crystal phase in LDGC was $Li_2Si_2O_5$, the intensity of $Li_2Si_2O_5$ had a slight reduction with the increasing of ZnO content. When the content of ZnO was below 4 wt%, the intensity of Li_2SiO_3 gradually increased with the increasing of the ZnO content. And a few crystal grains of $Li_3Zn_{0.5}SiO_4$ appeared when the content of ZnO was 3 wt%. When the content of ZnO was above

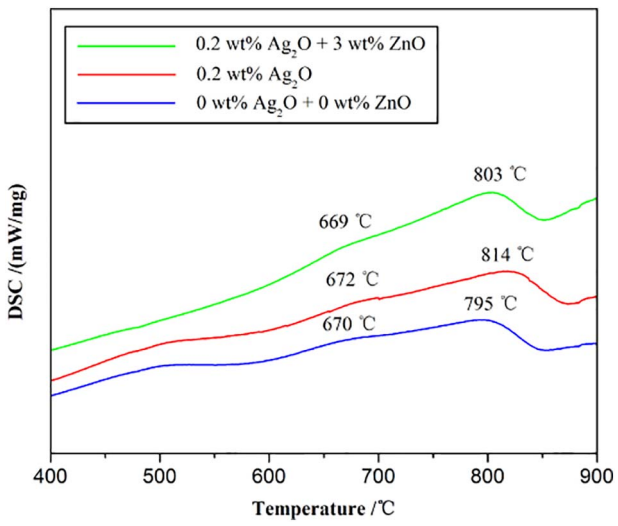

Fig. 1. DSC curves of the glass doped with different antibacterial metallic oxides.