A STUDY ON THE WEAR BEHAVIOUR OF MONOLITHIC MULLITE MATERIALS FOR DENTAL APPLICATIONS

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ABSTRACT

The aim of this study is to evaluate the potential use of the monolithic mullite samples for the dental applications. For this purpose, at first the monolithic mullite samples obtained by the powder metallurgy method have been characterized by the scanning electron microscopy (SEM) together with the EDS analysis. The pin-on-disk tribometer has been used to conduct the wear test in order to determine the volumetric loss. After the wear tests, the worn surfaces of the sintered mullite samples have been studied. The presence of the $3Al_2O_3.2SiO_2$ structure has been confirmed by the FT-IR spectroscopy through the observation of the characteristic Al-O-Si linkages at the spectra. The wear rate results derived from the volumetric losses have been measured to be around 2.42×10^{-6} mm³/Nm. This value has been found to be lower than those of alumina and alumina-mullite composites in the previous studies, which explains the higher wear resistance of these mullite materials. The room temperature friction coefficients of AS-1 and AS-2 samples have been determined to be 0.88 and 0.80, respectively. The wear behaviour of the samples has been correlated to the sintering temperature and the resultant relative density of the samples. The mullite samples obtained in this study have indicated better wear performance than the other materials (alumina and alumina-mullite composites) in spite of the usage of monolithic material. Therefore, this study suggests that the monolithic mullite materials have a potential to be exploited for the replacement of the previous ceramic-based dental materials. Further studies might contribute to the improvement of these materials to be utilized in the oral environment.

KEYWORDS: wear, mullite, dental material, implant

1. Introduction

Dental crowns are typically made out of porcelain veneer and alumina core. A three-layer dental structure with porcelain-mullite-alumina was produced against the risk of fracture [1]. Mullite is still an attractive material for its optical properties, such as adequate transparency. Mullite products are conventionally-processed by a shape-forming step followed by the sintering. A solid-solid reaction or a transient liquid-phase reaction can produce the mullitization process through the interdiffusion of the present atoms. The mullitization is carried out around 1600 °C during solid-state reaction [2-4]. For load bearing dental implants, poor fracture toughness is a weakening property which is the driving factor for the improvement of the dental ceramics [5, 6].

High-purity precursors are not preferred for the production of mullite ceramics for the dentistry applications due to their high costs. Instead, abundant raw materials of alumina and silica are subjected to reaction sintering to produce mullite samples with satisfactory mechanical properties at a low cost [7]. Mullite is among the oxides used for advanced ceramics with variety of optical, thermal and mechanical (strength, toughness etc) properties [8]. Besides, it exhibits some attractive properties for the field of dental implants such as thermal expansion coefficient, environmental durability.

The densification of mullite and alumina was accomplished using the additives such as La_2O_3, B_2O_3

and the final mechanical properties were improved. Also, with the addition of Y_2O_3, a full density was achieved together with mullitization [9-13]. A number of these methods have a potential to produce denser dental implants that might exhibit better mechanical performance. In addition, by studying the wear properties of the dental ceramics, a better understanding of the interacting surfaces might be facilitated in the oral environment [14].

In this study, single-stage sintering has been applied to produce dense mullite ceramics. The microstructures, and the wear properties of mullite-based dental materials have been investigated.

2. Materials and methods

In the present study, the mullite samples $3Al_2O_3.2SiO_2$ have been prepared in a stoichiometric ratio. The sample preparation has been done by powder metallurgy using the raw powders of SiO_2 and Al_2O_3 after the milling in a planetary ball mill [15] for 1-3 hours, the calcined powder has been compressed to obtain the disc samples. Then, the samples have been sintered at 1670 ºC and 1700 ºC for a dwell time of 180 min as described in detail in our previous study [16].

Fourier Transform Infrared Spectroscopy (ATR-FTIR) analysis (Perkin-Elmer) has been carried out at ambient temperature in the spectrum range of 4000-400 cm^{-1} for the qualitative analysis on the chemical bonding. Au-Pd coating unit has been utilized prior to the microstructural characterization by means of SEM (Scanning Electron Microscope), using Jeol-JSM-6060 equipped with Energy Dispersive Spectrometer (EDS).
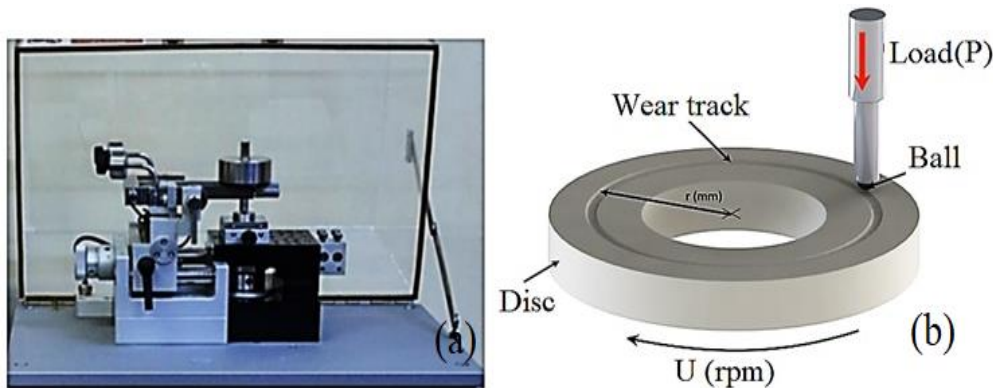

Fig. 1. *(a) Tribometer set-up and (b) design of pin-on-disk test according to ASTM-G99* [17]

The wear tests have been carried out using the tribometer set-up in Figure 1(a) (CSM Instruments). The tribometer is a pin-on-disk type set-up which applies a load of 10 N at a speed of 0.15 m/s. The test distance was 200 m and the wear test was conducted against Al_2O_3 balls as the counterpart under unlubricated wear conditions. The volumetric wear loss values for the samples AS-1 and AS-2 have been determined in cubic millimetres. After the wear test, the wear rates of the mullite samples have been calculated by Eq.1 as described in [18, 19].

$$W_{V\ (disc)} = V_{disc} / F_N .L \qquad (1)$$

where W_V is the disc wear rate (mm^3 /Nm), V_{disc} is the wear volume (mm^3), F_N-load (N), L sliding distance (m).

3. Results

According to FTIR results, as the sintering temperature changed from 1670 °C to 1700 °C, the intensities of the FTIR bands increased. Mullite is a structure of parallel chains where edge-sharing MO_6 octahedra is cross-linked with TO_4 tetrahedra [8] and at the spectra in Fig. 2 and Fig. 3, the wide bands at 3448 cm^{-1} and at 3450 cm^{-1} can be associated with the stretch vibration of OH for AS-1 and AS-2, respectively similar to those of the silicates. The stretch vibration of OH in Si-OH groups has also been observed at 3748 cm^{-1}. The bands observed at around 1150 cm^{-1} in Fig. 2 and Fig. 3 might be related to vibrational mode of asymmetric stretching of Si-O-Si and the peaks at 1137 cm^{-1} and 1140 cm^{-1} in any of the graphs which might be related to SiO_4.

Since 3/2-mullite with its formula $Al_2(Al_{2+2x}Si_{2-2x})O_{10-x}$ is an orthorhombic aluminosilicate (where x is 0.25) [8], the peaks observed at 755 cm^{-1} and 750 cm^{-1} are attributed to (Si,Al)-O-(Si,Al) bending mode for AS-1 and AS-2 samples, respectively in the mullite structure. The deformation vibration of the adsorbed water has been observed at around 1600 cm^{-1} [20].

Mullite microstructures have been given in Fig. 4 with the relevant EDS analysis results. EDS results

have indicated that the compositions are close to the mullite solid solution in the binary phase diagram. Also, the relative sintered densities have been measured to be 86-98% and the equiaxed grain morphology has been observed with grain size values of 2.5-4 μm in our previous study [16].

For AS-1 sample, the wear rate has been measured to be 2.42×10^{-6} mm^3/Nm as it can be seen in Fig. 5. For comparison, the wear rate of alumina was determined to be 6.76×10^{-5}-1.66×10^{-4} mm^3/Nm whereas that of alumina and mullite binary composites were 4.6×10^{-5}-1.3×10^{-4} mm^3/Nm. The friction coefficient of alumina and mullite binary composites were found to be lower, which results in a higher wear resistance of these composites with the co-working of both fracture and plastic wear mechanisms [21].
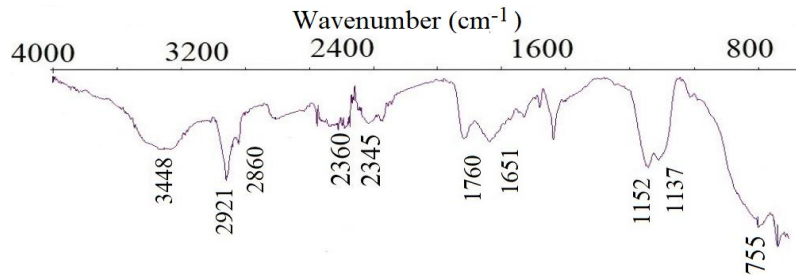

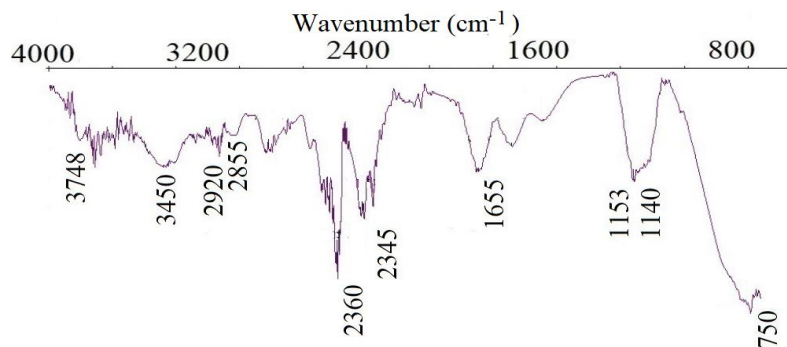***Fig. 2.*** *FTIR spectrum of AS-1 within 800-4000 cm^{-1} after heat treating*

Fig. 3 *FTIR spectrum of AS-2 within 800-4000 cm^{-1} after heat treating*

The friction coefficients of AS-1 and AS-2 samples have been measured to be 0.88 and 0.80, respectively. For some of the different mullite compositions, friction coefficients were found to be 0.75-0.9 [22]. A number of researchers investigated the wear behavior of the mullite-based materials using various temperatures [23]. The room temperature friction coefficient was measured to be 0.75-0.90, rising up to 1.0 with the temperature. The wear rate values were found to be 7×10^{-4} mm^3/Nm and 3.5×10^{-5} mm^3/Nm for mullite and alumina materials, respectively [22].
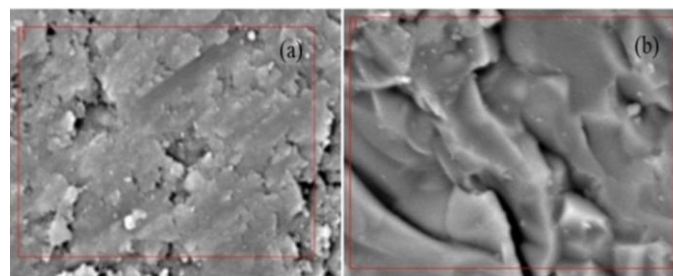
Component	Mole Conc.	Conc.		Component	Mole Conc.	Conc.	
Si	36.988	37.927	wt.%	Si	36.122	37.052	wt.%
Al	63.012	62.073	wt.%	Al	63.878	62.948	wt.%
	100.000	100.000	wt.%		100.000	100.000	wt.%

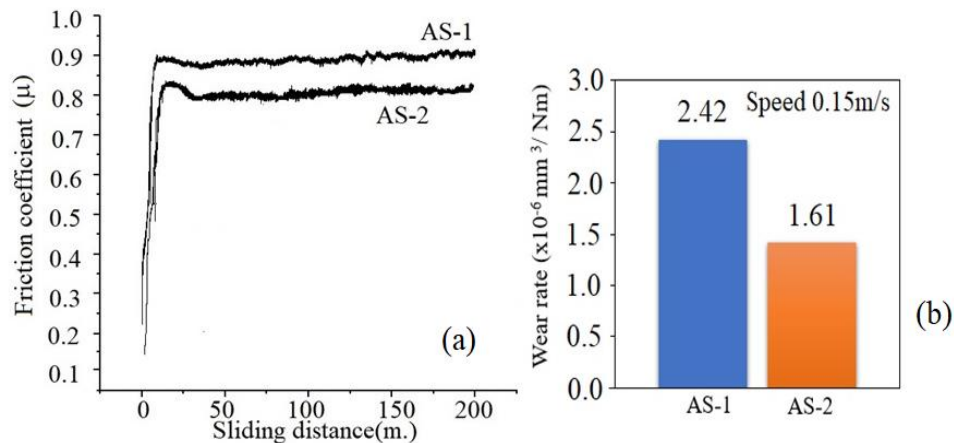***Fig. 4.*** *SEM-EDS analysis of (a) AS-1 and (b) AS-2*

Fig. 5. (a) Plot of friction coefficient vs. sliding distance and (b) wear rate values under 10 N for AS-1 and AS-2 against alumina
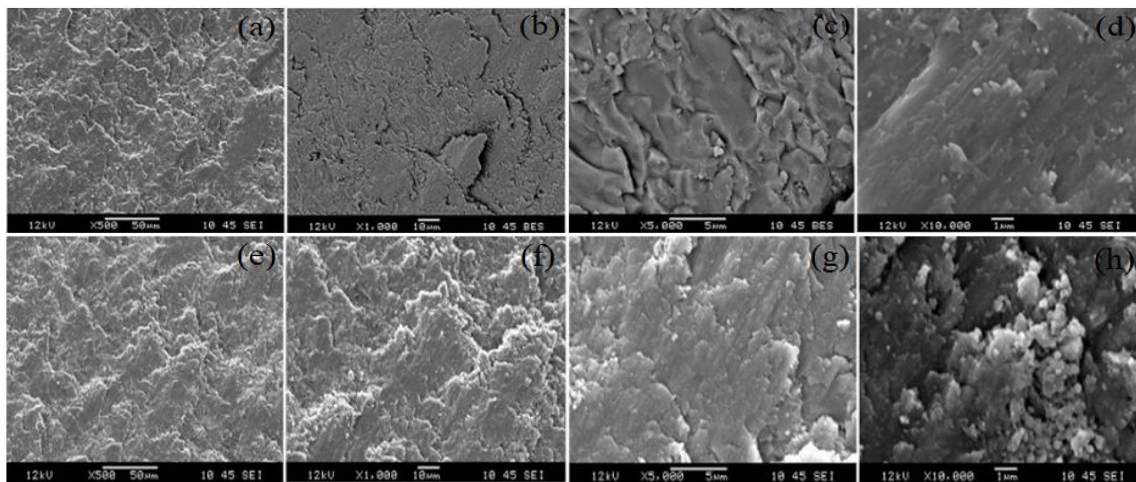

Fig. 6. The worn surfaces after the wear test of the samples (a) AS-1 and (b) AS-2

Following the wear test, worn surfaces of the two samples have been examined by SEM and the images have been given in Fig. 6. After the dry wear test of Al_2O_3-based materials, the repeated strips were observed on the worn surfaces perpendicular to sliding direction [24]. Also, the smooth regions were observed in the case of plastic deformation and the brittle fracture resulted in the pull-out of the material on the worn surface [18]. The wear rate values of the monolithic mullite samples have been found to be twenty-five times lower than the monolithic alumina materials and twenty times lower than alumina-mullite composites, showing a higher wear resistance.

The mullite phase peak intensity in the XRD pattern rises with the sintering temperature as a result of densification and the full mullitization [16]. This high wear resistance has been found to be related to the higher hardness and the densification of 98% due to sintering at 1700 °C. In addition, the uniform crystalline microstructure as described in [25] in these monolithic mullite samples has resulted in a high wear resistance.

4. Conclusions

This work presents the wear behavior of the monolithic mullite-based dental materials depending on the sintering temperature. FT-IR analysis observations have showed the characteristic Al-O-Si linkages confirming the presence of $3Al_2O_3 \cdot 2SiO_2$ structure. Under test load of 10 N, the sintering at 1700 °C has yielded a higher friction coefficient. The increase in the sintering temperature has resulted in denser mullite samples and in the improvement of the relevant wear behavior. The wear rate values of the sintered dental materials have been measured to be twenty or twenty-five times lower by comparing the results of the previously-known materials from the literature, indicating a better wear performance. This high wear resistance might be explained by higher

densification, uniform crystalline microstructure and hardness. Further studies regarding the chemical durability tests of these materials might contribute to our knowledge on their behavior in the oral environment.

Acknowledgments

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