Crystal Modification on Lithium Disilicate Glass Ceramics Sintered Using Microwaves

Modificación de Cristales de Cerámicas de Vidrio
de Disilicato de Litio Sinterizadas con Microondas

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ABSTRACT: Microwaves are an interesting alternative to process dental ceramics. It is well documented that Microwave Hybrid Sintering (MHS) allows important savings in time and energy consumption. However, little is known about its effect on lithium disilicate glass ceramics, a popular material in dentistry today. We analyzed the microstructure of lithium disilicate glass ceramics sintered with MHS compared with conventional sintering. We sintered lithium disilicate glass ceramics using MHS and conventional furnaces, and we analyzed the samples using X-Ray diffraction and SEM. Samples sintered with MHS showed an increased crystalline phase, with an increased number of crystals. These crystals have larger perimeters compared with samples sintered in conventional furnaces. MHS produced a different crystallization pattern and crystal/matrix ration in lithium disilicate glass ceramics when compared to conventional sintering. This can be associated with the improved mechanical properties of these materials reported previously.

KEY WORDS: microwave sintering, glass ceramics, crystalline phase, dental ceramics.

INTRODUCTION

Lithium disilicate glass-ceramics have become an increasingly popular material in dentistry. These materials offer several advantages for all-ceramics systems, with thermal expansion coefficients more similar to zirconia ceramics used in frameworks, and improved mechanical properties, which allow a full lithium disilicate crown produced in a CAD-processing device. All these advantages are accompanied by a better translucency which resembles natural teeth more closely (Dickerson & Miyasaki, 1999; Höland *et al.*, 2006; Gonzaga *et al.*, 2009; Ivoclar Vivadent, 2009; Bergmann & Stumpf, 2013; Huang *et al.*, 2013).

As usual for dental ceramics, lithium disilicate materials require a sintering process, which is achieved by a sintering process using a conventional furnace programmed with different firing protocols, according to the material and furnace settings. Nonetheless, all the conventional sintering furnaces share a common

ground: the sample is heated by convection/diffusion or conduction from the surface to the core of the material, which usually leads to over-heating of the surface to sinter the center of the sample, or under-heating of the core to keep the surface at the proper temperature, with the subsequent thermal stresses.

Microwave hybrid sintering (MHS) has been previously proposed to sinter dental ceramics, allowing a volumetric heating of the materials. In this case, an additional heating source (susceptors) is used to heat the materials until the increased temperature allows the coupling of the ceramics to the microwaves field, leading to the heating of the material across its entire structure simultaneously, leading to a uniform heating. MHS also offers other advantages, such as reduced processing times and energy savings, when compared to conventional sintering (Oghbaei & Mirzaee, 2010).

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Microwaves have been used to sinter ceramics in the past, and other authors reported faster processing times, and improvement of the mechanical properties of the materials. Hardness and flexural strength of different ceramic materials appear improved when processed using MHS, with reduced sintering times (Kashi *et al.*, 2005). Nevertheless, little information is available about the microstructure changes produced in the material when sintered using microwaves. In this paper, we compared the microstructure differences between dental lithium disilicate glass ceramics, sintered using conventional furnaces and MHS, and attempted to relate those differences with the reported improvement in mechanical properties.

MATERIAL AND METHOD

Samples: These experiments were conducted using a lithium disilicate dental glass-ceramic (IPS e-max CAD from Ivoclar Vivadent, Amherst, NY). This material offers a high degree of homogeneity, highly convenient for scientific work (Dickerson & Miyasaki; Rahaman 2003; Ivoclar Vivadent).

Samples were obtained from commercially available blocks of IPS e.max CAD. Parallel cuts were made in the blocks using a low-speed rotatory saw (IsoMet 3000, Buehler, Lake Bluff, IL) with a diamond coated wafering blade (15HC, Buehler, Lake Bluff, IL) and alcohol as a lubricant. All samples were polished using Soflex discs (3M ESPE, Saint Paul, MN).

Sintering: Ceramic samples were divided into two groups for the experiments after sectioning. The set of experimental samples was sintered using a research microwave furnace (Microwave Research Application Inc), at 2000 W input power at a frequency of 2.45 GHz, as described previously (Pendola & Saha, 2015; Pendola *et al.*, 2015). The control samples were fired using Conventional Furnace Sintering (CFS), which was performed following the manufacturer's guidelines in two professional dental labs under the authors' supervision (Marotta's Lab in Farmingdale, LI, and Tech Square Lab, Manhattan, New York), using a regular dental furnace (Programat E5000, Ivoclar Vivadent, Amherst, NY).

SEM Imaging: Four (4) IPS e.max CAD samples sintered by MHS and Four (4) samples sintered by CFS were prepared by fracturing the ceramic beam to

expose the internal aspect of the material. Samples were encased in epoxy resin, cleaned in an ultrasonic bath for 20 minutes and then etched using 9.8 % HF acid for 5 seconds followed by an etch with 37 % phosphoric acid for 30 seconds, and rinsed with distilled water. After the etching and washing with water, the samples were dried and coated with 15 nm gold layer using a Cold Sputtering device (Leica EM SCD050, Buffalo Grove, IL) to prepare the samples for the imaging process. Samples were imaged using SEM (Hitachi S-3400N, SE2 detector, 3kV, 150pA probe), images analyzed with the software MountainsMap Premium, (Digital Surf, France), using the next analysis sequence: Single image reconstruction: to produce a 3D rendering of the SEM image using an oblique low-angle lighting (shape from shading), assuming a homogeneous lighting through the whole image.

Motifs analysis: To evaluate the crystal size and number of crystals observed in the SEM images, based on a shape detection algorithm, with a 10 % tolerance.

X-Ray Diffraction Analysis: Eleven (11) samples of IPS e.max CAD (four (4) control, five (5) experimental) were reduced to powder, using a high speed dental drill (Kavo 636, Biberach, Germany) with a diamond bur, with alcohol as the irrigation liquid, which was collected during the process to save the ceramic particles suspended. For every sample, collected liquid was evaporated, leaving the pulverized ceramic. The powder obtained from each sample (1 ml) was stored separately in sample vials, to prevent contamination and/or misplacing. For analysis, the samples were placed on a glass microscope slide coated with a thin layer of Vaseline and analyzed by XRD system (Miniflex II, Rigaku, TX), at 30 kV / 15 mA, over an angle range from 15° to 80°. The angle was stepped at a rate of 4 degrees per minute, with a sampling width of 0.02 degrees in rotation. The results were collected using the software designed for the system (SmartLab, Rigaku, TX). Peak detection was performed using IgorPro 6.3 (Wavemetrics, Lake Oswego, OR), using a multi-peak detection algorithm, assuming a Gaussian function shape for every peak.

RESULTS

X-RAY DIFFRACTION ANALYSIS: X-Ray diffraction was used to evaluate the material phases present in the glass ceramics samples after sintering and to some

extent, the relative degree of crystallinity in the ceramic. Four (4) samples of IPS e.max fired using CFS and five (5) samples sintered using MHS were analyzed. The curves obtained were averaged and then compared. MHS samples exhibited peaks with larger amplitude in the lithium disilicate range when compared with CFS samples, for both averaged and individual samples. The peaks reached for each ceramic sample fired with CFS were 1400 cps, 1476 cps, 1440 cps and 1756 cps. The samples processed with MHS showed peaks of 1853 cps, 1576 cps, 1680 cps, 1633 cps and 1512 cps. Averaged curves showed peaks of 1400 cps in CFS samples and 1564 cps in the MHS samples, in the angle range corresponding to lithium disilicate. One-Way ANOVA showed the difference between the XRD averaged curves of MHS samples and CFS samples to be statistically significant ($P < 0.05$).

The X-Ray diffraction curves for CFS samples also exhibited more accessory peaks in the angle range between 60° to 80° which were not present in the MHS samples (Fig. 1).

The statistical analysis of the XRD averaged profiles of samples sintered using MHS and samples sintered using CFS (Tukey Simultaneous CIs) showed there is a significant difference between both materials.

Comparing the profiles of within the sets of samples (MHS vs. MHS and CFS vs. CFS), One-Way ANOVA test showed the material composition of the samples sintered with MHS did not exhibit a significant difference to each another. Conversely, the set of samples sintered with CFS showed significant differences within its group (Fig. 2).

Fig. 1 X-Ray diffraction curves for CFS (Top) and MHS (Bottom). Note the difference in intensity of the peaks and the detection of small peaks in the range of 60° to 80° for samples sintered with CFS.

SEM ANALYSIS: The SEM analysis was performed to analyze sintered samples. The images showed that samples sintered with MHS had a larger size crystals as compared with samples sintered with CFS. Also, MHS samples showed less porosity, and more a homogeneous surface than samples sintered with CFS (Fig. 3).

The analysis of SEM images was performed with a microscopy software (Mountains Map, Digital Surf, France). The 3D images were obtained using a non-luminance algorithm, to determine the local contours and amplifying the elements by 15 % and 20 %. The 3D reconstruction helped to notice the difference between the images shown in Figure 3. Figure 4 shows the 3D reconstruction of the SEM image of IPS e.max CAD, 10,000x magnification.

Figure 4 shows the 3D reconstruction of IPS e.max CAD sintered using CFS. It is possible to notice the crystals are proportionally lesser than the voids. Figure 5 shows the 3D reconstruction of a IPS e.max sample sintered using MHS, and the ratio of crystals over voids is higher compared with CFS samples.

Fig. 2. ANOVA (One Way) Sidak Test was used to compare the profiles within the groups of samples (MHS and CFS).

Fig. 3. SEM analysis shows the different crystal formation on IPS e.max when sintered with Conventional Sintering (TOP) and MHS (BOTTOM).

Fig. 5. 3D rendering of a SEM image of IPS e.max CAD sintered using MHS (x10,000).

A specific function, denominated Motifs detection, was used to detect the repetitive elements (lithium disilicate crystals) in the sample, based on a shape detection filter.

The analysis of the crystals detected in the SEM images using the Motifs algorithm showed a mean perimeter of 8.765 μm for the crystals present in the ceramics produced using MHS, and 7.285 μm for the crystals observed in the samples obtained using CFS. Also, the mean number of crystals detected in the images was 4464 (+1146) for MHS samples and 5238 (+279.5) for CFS samples. This suggests a small number of larger crystal are present in the same SEM image field when MHS is used. Crystal size differences are statistically significant (Multiple T-test, $P < 0.001$ and 2-Way ANOVA).

Fig. 4. 3D rendering of SEM image of IPS e.max CAD sintered using CFS (x10,000).

Fig. 6. Crystal number and perimeter differences for samples sintered with microwaves (blue) and conventional (red) furnaces.

DISCUSSION AND CONCLUSIONS

The improvements in the mechanical properties are likely to be related to microstructure changes, as occurs in other materials, as shown by Gonzaga *et al.* (2011) and Xie *et al.* (1999).

Due to the composite nature of the material (lithium disilicate crystals inside a glass matrix), the images do not show a packed grain configuration such as those obtained from polycrystalline ceramics, such as dental zirconia. SEM images of MHS processed lithium disilicate glass ceramics showed larger crystals than those found in CFS samples. The increased crystal size in MHS samples is determined by the larger size of the perimeter of the crystals (Fig. 9), and by the larger mean area occupied by the crystals in the sample (3.155 mm² for MHS samples, compared with 2.245 mm² for CFS samples). This increase in crystal size, using MHS has been previously reported in a thermal model described by Chatterjee *et al.* (1998). Mahmoud *et al.* (2012, 2015), where sintered ceramics using a variable frequency microwave furnace exhibited similar grain structure to that reported here. Thompson *et al.* (1995) have argued that smaller crystals in the lithium disilicate system will reduce the strength of the material, as the flaws will have a higher probability of propagating within the larger glass matrix areas.

X-Ray Diffraction (XRD) showed higher peak intensity in the lithium disilicate band (24°-26°) in the MHS samples as compared to the CFS samples. XRD profiles from work reported here, are consistent with the findings of other authors such as Kang (2005), Goharian *et al.* (2010), Yuan *et al.* (2013) and Lien *et al.* (2015). Interestingly, the larger peak on the lithium disilicate band detected in MHS samples suggest to a higher degree of crystallinity, as shown by Vasudevan

et al. (2013), who found these higher peaks in XRD were correlated with higher crystallinity in ZTA ceramics. It is possible that MHS produced a higher degree of crystallinity in lithium disilicate glass ceramics samples. In an early paper, Cozzi *et al.* (1993), showed that microwave heating (2.45 GHz, 500° to 600°C) produced a higher crystallinity levels on lithium disilicate glass ceramics obtained from lithium aluminosilicate rods. Therefore, it could be possible a similar effect when heating the material to higher temperatures, under similar conditions.

The findings of Mahmoud *et al.* (2012, 2015), reports similar XRD patterns, for lithium disilicate glass ceramics using multiple frequency microwaves and with conventional sintering. The curves are similar to the XRD curves of glass ceramics sintered using MHS, suggesting that the composition of the material is not altered when sintered using microwaves. Since the XRD curves are similar not only between MHS and conventional sintering and are also similar to the curves obtained using high frequency microwave sintering without susceptors, that suggest the role of the susceptors in the final sintering results is marginal.

The improvements in the mechanical properties in samples sintered using MHS (Pendola & Saha; Pendola *et al.*) appear to be due to the modification in the microstructure of the material. Increased interlocking of the crystals within the glass matrix and the larger size of those crystals probably impair or arrest the propagations of cracks in the material, along with a larger number of crystals produced by MHS.

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PENDOLA, M. & CARTER, J. Modificación de cristales de cerámicas de vidrio de disilicato de litio sinterizadas con microondas. *Int. J. Odontostomat.*, 11(4):461-466, 2017.

RESUMEN: Las microondas son una interesante alternativa para procesar cerámicas dentales. Está bien documentado que el Sinterizado Híbrido por Microondas (MHS) permite ahorros importantes de tiempo y energía. Sin embargo, poco se ha publicado respecto a sus efectos en cerámicas de disilicato de litio, un material bastante popular en odontología en estos días. En este artículo analizamos la microestructura de cerámicas de disilicato de litio sinterizada con MHS comparada con el sinterizado convencional. Sinterizamos muestras de cerámicas de disilicato de litio usando MHS y hornos convencionales, y analizamos las muestras usando difracción de rayos X y SEM. Las muestras sintetizadas usando MHS tienen una mayor fase cristalina, con mayor número de cristales. Estos cristales tienen además perímetros mayores, comparados con las muestras sinterizadas en hornos convencionales. MHS produce patrones de cristalización y proporción de cristal/matrix diferentes a las producidos por sinterizado convencional. Esto puede asociarse a las mejoras en propiedades mecánicas reportadas previamente.

PALABRAS CLAVE: sinterizado por microondas, cerámicas de vidrio, fase cristalina, cerámicas dentales.

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