A preliminary study of the graded dental porcelain ceramic structures fabricated via binder jetting 3D printing

Hadi Miyanaji[a], Li Yang[a], Shanshan Zhang[a], Amirali Zandinejad[b]

[a]Department of Industrial Engineering, J.B. Speed School of Engineering

[b]Department of Oral Health & Rehabilitation, School of Dentistry

University of Louisville, KY, 40292

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Abstract

Dental porcelain is a common material used for various dental restoration structures including crowns, bridges and veneers. However, the current designs of all-ceramic porcelain restorations lack sufficient mechanical property controls, which results in increased failure rates. In this study, dental porcelain ceramics with graded compositions were fabricated by binder jetting 3D printing system in the attempt to actively control their mechanical performance. The graded structures were produced by two different fabrication routes, which are lamination stacking and continuous fabrication. In the lamination stacking route, porcelain laminates with different compositions were fabricated individually and stacked up for the sintering to form integrated structures with graded properties. In the continuous fabrication, samples with graded structure were printed continuously in the 3D printing machine. Microstructural evaluations with the samples demonstrated the feasibility of achieving good structural integrity for the dental porcelain parts fabricated by the continuous method.

Keywords: Dental porcelain, aluminous porcelain, graded structure, 3D printing

1. INTRODUCTION

Dental porcelain has been used for denture teeth since 1790 and currently are widely used in dentistry these days as natural-looking tooth restorations thanks to their numerous advantages such as color, strength, aesthetic, opacity, translucency, durability etc. [1, 2]. The major applications of dental porcelain include artificial tooth constructions such as single unit full porcelain crowns, porcelain crowns and bridgework, inlays, onlays, labial facing veneers, and denture teeth [3]. There exist two basic types of ceramic restorations – all-ceramic and metal-ceramic. The newer all-ceramic systems generally comprise a body made from ceramics instead of the traditionally used metals, with at least one additional porcelain layer. All-ceramic systems are made from a ceramic with substantial crystal content (> 50 vol. %) from which their higher strength and toughness are obtained. These material systems can provide more natural translucency with no loss of mechanical strength, therefore have drawn increasing interest in the past two decades. Currently the all-ceramic restorations are fabricated by either slip casting based method or more accurate CAD-CAM method [4, 5]. In the CAD-CAM method, the ceramic feedstock are pre-sintered and then milled with a CNC milling machine using special diamond tool. Then the machined parts are further sintered to acquire the final density and appearance. On the other hand, metal-ceramic systems are still commonly used. In these material systems, several layers of porcelain powder in aqueous slurry are sequentially fused to a metal framework to simulate natural teeth [4]. These layers have three different levels of translucency. The first and opaque layer is used to mask the dark metal substrate. The intermediate layer, the so-called dentine, is the principal bulk construction of the artificial tooth structure and is also used to provide translucency of the porcelain. The upper and most translucent layer is called the enamel or incisal porcelain. Each layer must subsequently be fused in an electric or vacuum furnace at about 1000°C to obtain the optimal properties [4, 5, 6].

Currently one of the biggest disadvantages of ceramic materials including dental porcelains is its low toughness. This drawback causes most of the failures in both types of aforementioned porcelain restorations. In general, failures in porcelain restorations could be categorized into three groups, chipping, bulk fracture and interface delamination. Chipping failure could occur in both types of restorations, and bulk fracture mainly occurs in the all ceramic restorations, both due to the brittleness of dental porcelain. Interface delamination occurs in the interface of metal-porcelain restorations because of weak bonding between metal and porcelain. Fig 1 and 2 show the chipping and bulk fracture in porcelain restorations created under biting forces [10, 11, 12, 13].

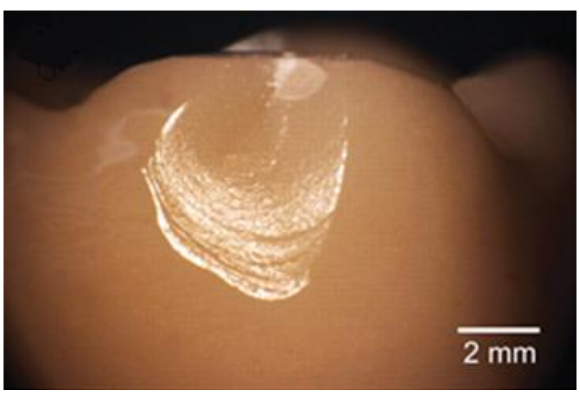


Fig 1. Chipping failure

Fig 2. Bulk fracture

Recently it was found that natural teeth have graded structure, meaning that their properties are not the same in different regions. The natural teeth have a relatively soft core and harder surface (graded structure), which is speculated as one of the main reasons of the good fracture resistance of the natural teeth [14, 15]. With the capability of producing graded structures directly from a CAD model with adequate accuracy and minimal waste, additive manufacturing (AM) holds great potential for the fabrication of dental restorations with both colors and properties mimicking the natural teeth.

While binder jetting 3D printing (3DP) process is relatively less commonly used for direct manufacturing of functional parts, there have been studies that utilize it to make ceramic parts. This process offers some potential advantages in ceramic printing, such as the flexibility with different ceramic materials, the relatively high feature resolution, and easy process control; therefore binder jetting was adopted for this study with future developments in mind. In the present study, the ExOne M-Lab was utilized in an attempt to fabricate graded structure samples from off-the-shelf commercial porcelain and alumina powders used commonly for dental applications. Then the microstructure of the samples and integrity of bonding created between different compositions were characterized in details.

2. *Materials and Methodology*

For this research, off-the-shell dental porcelain was used as the base material, and alumina powder was used as the additive to the base material for graded composition control. Alumina was selected as the additive since it is one of the main ingredients of the current dental porcelain materials, and therefore does not pose additional material compatibility issue. Table 1 shows the compositions of the pure porcelain used in this research. In order to evaluate microstructural and mechanical properties, Laminate structures with dimensions of 25x2x1.5 mm were designed according to ASTM C1161-13. Due to the limitation of the powder bed based AM systems with multi-material printing, two different procedures were taken for the fabrication of these samples in graded compositions, which are namely lamination stacking and continuous fabrication. For the lamination stacking method, samples with two different compositions were printed separately and stacked together in a way that their total thickness was 1.5. A thin layer of the binder was applied manually between two compositions in the attempt to help form a good bonding between layers in the sintering stage. On the other hand, for the continuous fabrication method, the first laminate was printed out with powders with the first composition, then the process was paused to change the powder supply into the powders with the second composition. After the powder change, the process was resumed, therefore the graded structure was directly formed by the printing process. In the study, the two composition used were pure porcelain and porcelain containing 10% wt. alumina (10% alumina porcelain). Therefore, for the continuous fabrication, the feed chamber of the machine was filled with pure porcelain first, and a sample with thickness of 0.75 mm was printed in the build chamber. After the first part of the sample was printed, the feed chamber was completely cleaned and refilled with the 10% alumina porcelain. Thereafter, 10% alumina porcelain was printed over the pure porcelain in the build chamber with the thickness of 0.75 mm.

Also, it is worth mentioning that 10% vt. flow agent was added to pure porcelain for improving the overall powder flowability by serving as a lubrication interface [19]. Surface-modified R972 SiO2 powder (COSMOS Plastic & Chemicals) was used as the flow agent. The powder is composed of >99.8% fumed silica treated with dimethyldichlorosilane (DDS), with an average particle size of 16nm. Due to the small particle size and low packing density of this flow agent, it was expected that the addition of the flow agent does not have significant effect on the microstructure and mechanical performance of the dental porcelain. The system used for the fabrication is the ExOne M-Lab, and the binder used for the process was the ExOne PM-B-SR1-04, an ether solvent based binder, which was originally developed for stainless steel but was found to be usable for the dental porcelain.

Table 1. Chemical composition of used dental porcelain

SiO_2 %	Al_2O_3 %	K_2O %	Na_2O %
55-61	13-16	11-15	4-6

After printing, the specimens were dried in the oven at 150°C for 1 hour. Dried samples were sintered in the ExOne furnace. For this purpose, samples were held at 500°C for 30 minutes to burn out the binders and then at 850°C for another 30 minutes for sintering. The sintering route selected for this study was based on the results from the preliminary process development of the same material [20]. The sintered samples were then used for microstructural characterizations. In order to analyze the microstructure of each compositions as well as bonding integrity between two compositions, the specimens were polished, etched with 5% hydrofluoric acid (HF) for 30 s, and finally sputter-coated with palladium. SEM and EDAX systems were then utilized to take microstructure images and to determine the compositions of the specified areas, respectively.

3. Results and discussion

Dental porcelains are normally composed of silica, glass modifiers, feldspar, and coloring agents. Silica is contained in dental porcelain in two different forms [18]. The first type is in the form of amorphous feldspathic glass that consists of silica, alumina and a flux. In this type of porcelain silica is the major glass former in the porcelain. The second type of silica is in the form of refractory crystalline quartz particles which are dispersed through the glassy phase to act as pinning points for crack propagations. One example of the second type is the Feldspar, which is a naturally occurring glass that contains silica, fluxes and alumina, all bound together [19, 20]. The evolution of the phases for dental porcelains is rather complicated. The phase diagram of a typical dental porcelains is shown in Fig 3. As can be observed, depending on the sintering temperature and the composition, porcelain may have different phases. Since the samples were sintered at 850° C, according to the diagram it is expected to have Potash Feldspar and Tridymite (Silica crystals) in the microstructure.

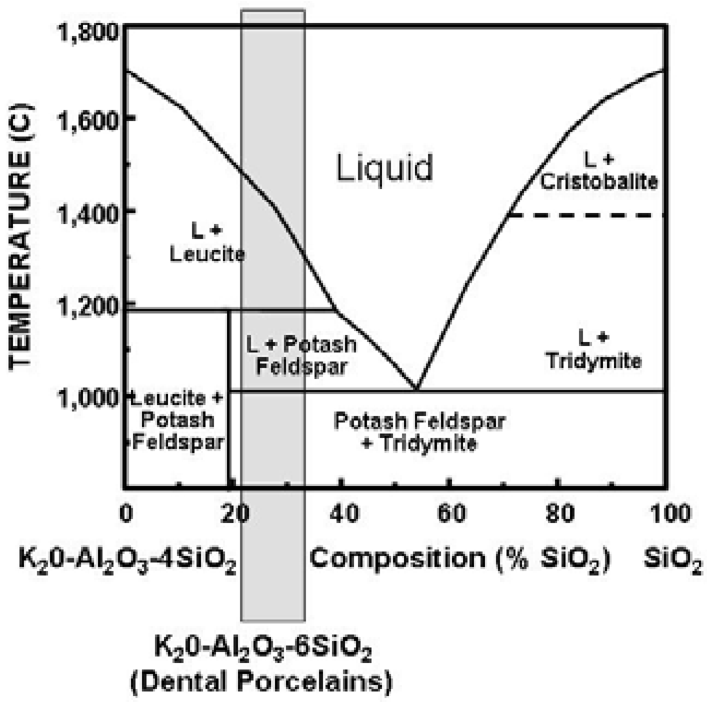


Fig 3. Phase diagram of porcelains

Fig 4 shows the SEM microscopy of the pure porcelain and 10% alumina porcelain samples. From Fig. 4(a) the tiny alumina and silica crystals completely surrounded by glassy matrix in pure porcelain microstructure. Silica crystals can barely be observed in the glassy matrix due to its similar refractive indexes compared to the glassy matrix. Fig 4 (b) shows the microstructure of 10% alumina porcelain. This micrograph is taken by back-scatter detector. The obvious difference between the microstructures of pure porcelain and the 10% alumina porcelain is a result of alumina crystal formation. The addition of alumina crystals to the feldspathic glass matrix would result in an increase in the flexural strength of the material, since crack propagation through the alumina particles requires higher stress-levels. Depending on the strength of the bond between the reinforcing particles and the glassy matrix, cracks may be diverted around the alumina crystals rather instead of propagating along the original directions. As a result, more tortuous crack paths are produced, which enhances the strength of the porcelain. Moreover, the alumina crystals also impart rigidity to the structure at elevated temperatures, reducing the chances of distortion and shrinkage when the lower softening point materials are added. The reduced shrinkage may have several beneficial effects. With less shrinkage, the stresses generated in the porcelain during firing could potentially be reduced. Consequently, the likelihood of microcrack formation will be less, and the resulting restorations will be stronger and tougher [5].

EDAX analysis of the pure porcelain matrix is presented in Fig 5. In addition to Si and Al which are dominant elements as explained (table 1), K and Na elements can be observed in the microstructure. These elements are represented as Potassium oxide (K_2O), Sodium oxide (Na_2O) in the microstructure and act as a modifier or flux. A modifier or flux is a mineral that melts at a low temperature. The main function is to lower the function temperature of dental porcelain by interrupting the integrity of the silica network [7, 8, 9, 10]. With the addition of K_2O and Na_2O, some of the silica tetrahedral covalent bonds will be broken, therefore the atoms are able to move more easily at lower temperatures. This improved mobility is responsible for the decreased viscosity and lower softening temperature [7, 8].

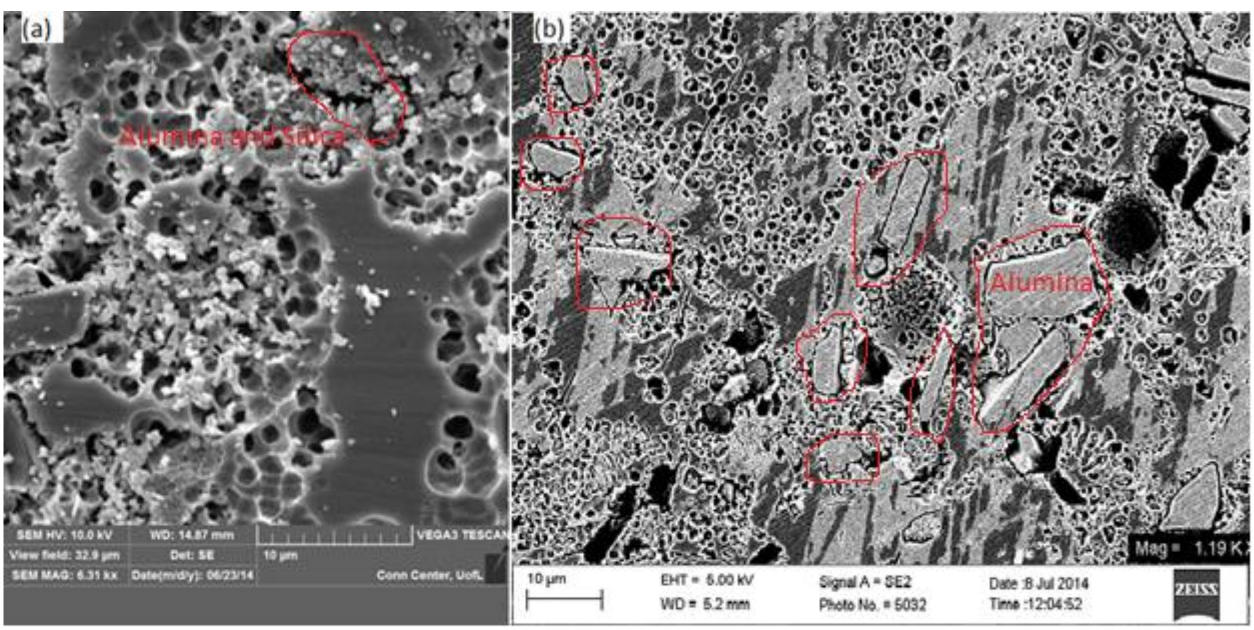


Fig 4. Microstructure of (a) pure porcelain sintered (b) 10% alumina porcelain at 850’ C for 30 minutes

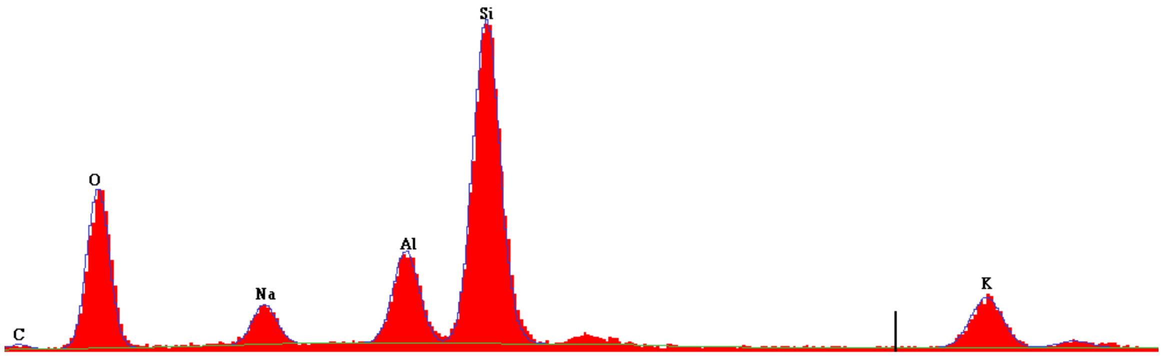


Fig 5. EDAX analysis of the pure porcelain microstructure

Fig. 6 shows a sample before sintering produced by the lamination stacking method. After sintering, it was observed that a weak bonding was created between two compositions, and delamination was obvious despite the manual application of binder between the two laminates before the sintering. It was believed that the lack of initial bonding which would be formed during the printing and in-process drying, as well as the differences between thermal expansions and tendency of ceramics to slump during sintering, are two likely causes for the delamination.

Fig 6. Graded structure sample before sintering

The samples produced by continuous method are shown in Fig. 7. With this method, good bonding was visually observed between two laminations after sintering. Fig. 8 (a) shows the microstructure of the specimens with pure porcelain and 10% alumina porcelain (separated by the black line) fabricated by continuous fabrication method. In addition, the microstructure of 10% alumina porcelain at higher magnification is shown in Fig 8 (b). As it can be observed, feldspar glass is dominant in the microstructure. Also, only one side of the sample appears to contain alumina crystals dispersed uniformly in a glassy matrix. These crystals range in size from approximately 2 to 20 µm. From Fig. 8, it is also clear that there is no distinguishable interface between these two compositions, which indicates that good bonding has been created between pure porcelain and the 10% alumina porcelain composition. The only distinct difference between two microstructures is the amount of the alumina crystals which is higher in one side than other.

Fig 7. Samples after printing

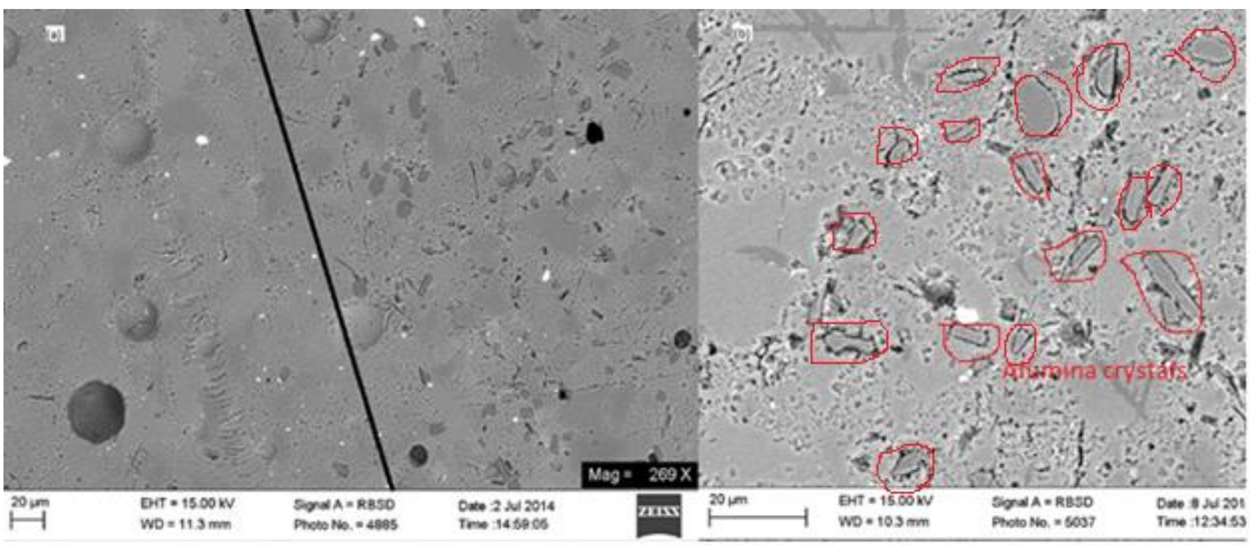


Fig 8. Micrographs of (a) graded structure (b) 10% alumina porcelain

Presence of alumina crystals in one side of the sample was confirmed by two methods, morphology and EDAX. Fig. 9 shows the SEM microscopy of the alumina powder. As it can be observed, the dispersed crystalline phase in the microstructure of porcelain (Fig. 8b) has the same morphology and size range as the crystals in Fig. 9. EDAX result also clearly suggested that the crystals observed in the microstructure are alumina particles, as is shown in Fig. 10. Therefore, it was concluded that the graded structures were successfully fabricated by the 3DP process and retained after the sintering.

It is also worth noting that since the crystalline alumina concentration in one side is greater than that of the other side. In fact, some porosity is evident in both sides from Fig. 8. The pure porcelain side contains less pores, which appeared as black areas on the back-scattered electron micrographs. Porosity in the side with 10% alumina addition is largely associated with the un-melted alumina crystals during the sintering.

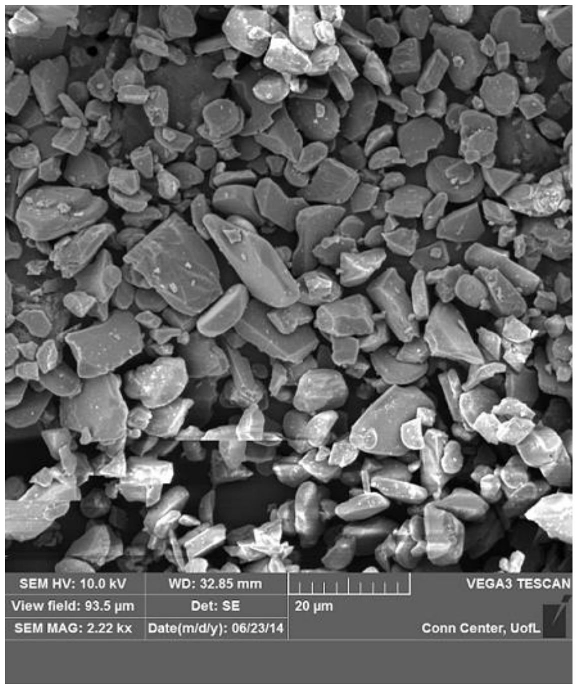
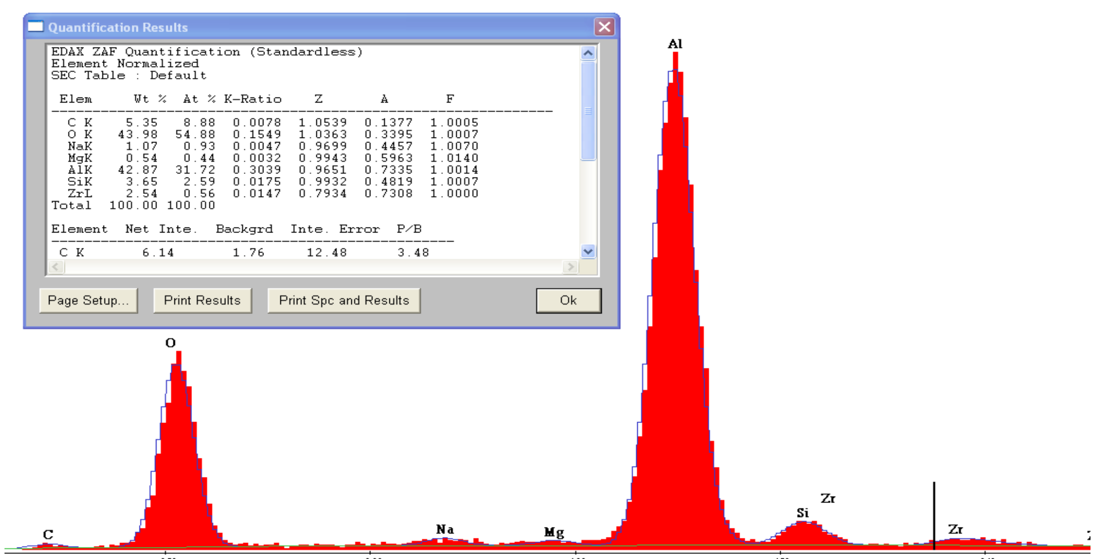


Fig 9. Morphology of Alumina powder



Elem	Wt %	At %	K-Ratio	Z	A	F
C K	5.35	8.88	0.0078	1.0539	0.1377	1.0005
O K	43.98	54.88	0.1549	1.0363	0.3395	1.0007
NaK	1.07	0.93	0.0047	0.9699	0.4457	1.0070
MgK	0.54	0.44	0.0032	0.9943	0.5963	1.0140
AlK	42.87	31.72	0.3039	0.9651	0.7335	1.0014
SiK	3.65	2.59	0.0175	0.9932	0.4819	1.0007
ZrL	2.54	0.56	0.0147	0.7934	0.7308	1.0000
Total	100.00	100.00				

Element	Net Inte.	Backgrd	Inte. Error	P/B
C K	6.14	1.76	12.48	3.48

Fig 10. EDAX results of crystals observed in the microstructure

4. Conclusion

In the present study, the binder jetting 3DP process was adopted to produce porcelain parts with graded structure. For this purpose, the ExOne M-Lab machine was utilized to print out the samples. A process route that enables direct fabrication of graded dental ceramic structures was successfully demonstrated. Microstructural tests were conducted to evaluate the integrity of bonding between layers of two different compositions of the fabricated graded structures. Presence of alumina crystals in only one side of the microstructure was confirmed by EDAX analysis and SEM microscopy. In addition, it was found that good bonding without any interface delamination was created between the two compositions using the 3DP process. In conclusion, this work showed very encouraging preliminary results for the direct fabrication of high quality graded ceramic structures for multiple future applications.

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