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Effect of temperature and heating rate on the sintering of leucite-based dental porcelains

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Abstract

The aim of this work was to determine the effect of temperature and heating rate on the densification of four leucite-based dental porcelains: two low-fusion (Dentsply–Ceramco and Ivoclar) and two high-fusion commercial porcelains (Dentsply–Ceramco). Porcelain powders were characterized by differential thermal analysis (DTA), X-ray diffraction (XRD), particle size distribution, helium picnometry, and by scanning electron microscopy. Test specimens were sintered from 600 to 1050 °C, with heating rates of 55 °C/min and 10 °C/min. The bulk density of the specimens was measured by the Archimedes method in water, and microstructures of fracture surfaces were analyzed by scanning electron microscopy (SEM). The results showed that densification of specimens increased with the increase in temperature. The increase in the heating rate had no effect on the densification of the porcelains studied. Both high-fusion materials and one of the low-fusing porcelains reached the maximum densification at a temperature that was 50 °C lower than that recommended by the manufactures.

Keywords: A. Sintering; D. Porcelain; Thermal analysis; Dentistry; Dental materials

1. Introduction

Feldspathic dental porcelain powders have been successfully used for many years in dentistry to construct crowns and fixed partial bridges. Porcelains may be used either alone or associated with a metal or ceramic framework to construct dental restorations and prostheses with high biocompatibility, high chemical stability and resistance to wear. The microstructure of a dental porcelain usually comprises a leucite ($K_2O{\cdot}Al_2O_3{\cdot}4SiO_2$) crystalline phase dispersed in a glass matrix. This crystalline phase was initially added only to adjust the thermal expansion coefficient of the porcelain, making it compatible with that of the metal substructure. However, it has been demonstrated that these second-phase particles are also responsible for the improvement of the material's fracture toughness [1–3].

In order to construct dental prostheses with leucite based porcelains, it is necessary to mix the porcelain powder with water to form a slurry that is applied to the refractory die or metal framework. After that, the porcelain must be heat treated at temperatures varying from 750 to 1100 °C in order to cause densification of the material. Densification occurs by means of a process that involves the viscous flow sintering of glass particles. It has already been demonstrated [4] that when a glass is heat treated for sufficient time and temperature within or above the glass transition temperature, crystallization immediately starts at the surface of the material. However, sometimes crystallization also occurs in the bulk material via heterogeneous nucleation.

Sintering and crystallization can occur consecutively or simultaneously. If crystallization occurs before sintering has been completed, the viscosity increases rapidly and the sintering process stops, resulting in a porous material [5,6]. In some situations, however, depending on the heating rate, the sintering process is faster than the crystallization process.

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Boccaccini et al. [7] reported that cylindrical compacts of glass powders for the system SiO_2–Al_2O_3–MgO–BaO, with a narrow particle size distribution (around 10 μm), could be almost fully densified when heat treated at 15 °C/min. However, this specific powder crystallized and therefore the compact only densified to 89% of the glass density when a heating rate of 1 °C/min was used. Porcelain manufactures usually recommend heating rates varying from 45 to 60 °C/min under vacuum and dwell times varying from 0 to 9 min. Such a fast heating rate is probably used to prevent crystallization and decrease the porosity in the material.

In clinical dentistry, it is very important to obtain dental restorations that are as dense as possible, since this will lead to better clinical performance on the long term. In addition, there is a lack of information in the literature regarding the effect of different heating rates and temperatures on the densification of dental porcelains. Therefore, the purpose of this work was to investigate the effect of temperature and heating rate on the densification of two low-fusion and two high-fusion commercial leucite dental porcelains. The hypothesis tested was that both the heating rate and the sintering temperature would significantly affect the final density of porcelain specimens.

2. Materials and methods

Four commercial leucite based porcelains were used, as shown in Table 1. Porcelain powders were characterized by: (a) chemical analysis using X-ray fluorescence (Shimadzu XRF-1500), (b) particle size distribution by X-ray sedimentation (SediGraph 5100-Micromeritics), (c) powder density by helium picnometry (Multi Pycnometer – Quanta Chrome®), which allows the accurate measurement of powder volume inside a chamber with known volume that is filled with a measurable helium gas volume [8]; density was then calculated as the ratio of powder mass measured in an analytical balance (Adventure – Ohaus) to measured powder volume, (d) X-ray diffraction analysis (Shimadzu-XRD 6000), using Cu Kα radiation, (e) differential thermal analysis (Netzsch, model 404) that was used to characterize the porcelain behavior during heating, with a heating rate of 10 °C/min in a platinum crucible, and (f) scanning electron microscopy (SEM, Jeol, JSM 6300) for powders etched in 2 wt% HF containing solution for 15 s.

After characterization, the porcelain powder was shaped into beams (5 mm × 6 mm × 60 mm). Test specimens were fabricated by mixing the porcelain powder with water to form a slurry that was poured into a custom fabricated steel mold. The mold was filled with the porcelain slurry and placed on a vibrating table. The excess liquid brought to the surface was then removed using a tissue to absorb excess liquid. Specimens were then sintered in a Keramat-I (Knebel) furnace. The green density was determined by the geometric method. Test specimens were heat treated at different temperatures varying from 600 to 1050 °C, using a heating rate of 55 °C/min with dwell time at the sintering temperature of 0 min, 0 min, and 2 min 20 s in vacuum, for porcelain Ceramco I, Ceramco II and Finesse, respectively, and 60 °C/min with dwell time of 1 min for porcelain d.Sign. A double cooling schedule of 9 + 9 min was used for all compositions, as recommended by the manufacturers. The heat treatment at 10 °C/min was carried out only in the maximum temperature recommended by the manufacturer, i.e., 1000 °C for porcelains Ceramco I and Ceramco II, 800 °C for porcelain Finesse, and 870 °C for porcelain d.Sign.

The previously mentioned heating rates were selected in order to establish a comparison between the rates recommended by the manufacturers (55 °C/min or 60 °C/min) and an alternative rate (10 °C/min) that could hinder the full densification of a compact glass system. The objective of this comparison is to understand the reason why manufacturers recommend a significantly higher heating rate for these porcelains. This information is new and currently it is not available in the literature. After sintering, the density of the test specimens was measured by the Archimedes method in water. Fracture surfaces of the test specimens were etched with a solution of 2 wt% HF for 15 s in order to reveal the leucite particles when the materials were examined under scanning electron microscopy (SEM, Jeol, JSM 6300).

3. Results and discussion

The results of the chemical analysis are shown in Table 2. SiO_2, Al_2O_3, K_2O, Na_2O and CaO were the main constituents of the porcelains tested. Porcelain d.Sign showed lower amounts of SiO_2 than porcelain Ceramco I, Ceramco II and Finesse.

Table 1
Porcelains used in the study (shade A3-dentin).

Porcelain	Manufacturer/brand name	Batch number	Manufacturer's description
A	Dentsply Ceramco R&D, Burlington, USA/Ceramco I	D1738	High-fusing, leucite-based porcelain, used for metal–ceramic or all ceramic restorations, containing isometric leucite particles. Firing temperature: 1000 °C
B	Dentsply Ceramco R&D, Burlington, USA/Ceramco II	D1739	High-fusing, leucite-based porcelain, used for metal–ceramic or all ceramic restorations, containing leucite particles. Firing temperature: 1000 °C
C	Dentsply Ceramco R&D, Burlington, USA/Ceramco Finesse	D1740	Low-fusing, leucite-based porcelain, used for metal–ceramic or all ceramic restorations, containing fine-grained leucite particles. Firing temperature: 800 °C
D	Ivoclar, Schaan, Liechtenstein/d.Sign	54D2001-12	Low-fusing, leucite-based porcelain, used for metal–ceramic or all ceramic restorations, containing leucite particles and crystals of fluorapatite. Firing temperature: 875 °C

Table 2
Chemical composition of the porcelains Ceramco I, Ceramco II, Finesse (Dentsply–Ceramco), and d.Sign (Ivoclar–d.Sign).

	SiO_2	Al_2O_3	K_2O	Na_2O	CaO	BaO	ZnO	ZrO_2	TiO_2	P_2O_5	SnO_2	MgO	CeO_2	Tb_2O_3
Ceramco I	65.0	14.4	11.5	4.5	2.2	–	–	–	–	–	0.3	1.0	0.1	0.4
Ceramco II	62.9	14.1	12.6	3.4	3.1	1.5	–	–	–	–	–	–	1.4	0.9
Finesse	63.7	9.9	12.4	5.1	3.2	–	–	–	–	–	–	3.0	0.2	2.3
d.Sign	58.2	13.1	10.9	4.4	3.0	2.6	3.5	2.4	0.7	0.9	–	–	–	–

Also, d.Sing showed oxides such as ZnO, ZrO_2, TiO_2, and P_2O_5 that were not detected in the other three compositions. Terbium oxide is used to reproduce the fluorescent properties of natural teeth [9]. Trace quantities of other oxides such as NiO, Fe_2O_3, Rb_2O_3, and SrO were also detected by the X-ray fluorescence spectroscopy.

Particle size analysis of the porcelain powders showed large particle size distributions with sizes varying from 0.2 to 65 μm, with 90% of the porcelain powder particles smaller than 60 μm for Ceramco I, Ceramco II, and d.Sign and 40 μm for porcelain Finesse (Fig. 1). The mean particle diameters were around 16 μm, 18 μm, 15 μm and 21 μm for porcelains Ceramco I, Ceramco II, Finesse, and d.Sign, respectively.

X-ray diffraction patterns of porcelains Ceramco II, Finesse and d.Sign (Fig. 2) showed the typical pattern of a glassy phase (broad band at around 25° of 2θ) and only tetragonal leucite as crystalline phase. Porcelain Ceramco I showed leucite as the predominant crystalline phase and quartz as a minor phase, besides the amorphous phase. As shown in Fig. 3, the etched powders have particles with a high amount of leucite in their surface, especially those of porcelain Ceramco I and Ceramco II, and these results are in agreement with the X-ray diffraction, since the peak intensities in the diffraction patterns were higher for these materials.

The differential thermal analysis results are shown in Fig. 4. The DTA trace for porcelain Ceramco I showed two small endothermic peaks at 715 ° and 914 °C, corresponding to two glass transition temperatures (T_g), indicating a possible mixture of glass phases. The peaks at 715 °C, 465 °C and 670 °C correspond to the T_g for porcelains Ceramco II, Finesse and d.Sign, respectively. The peak at about 110 °C is characteristic of water desorption. No exothermic peaks, corresponding to crystallization temperature (T_c), were observed in the DTA curves. This result indicated that the glass phase had reduced tendency of crystallization, even when a relatively low heating rate of 10 °C/min was used. Composition C (Finesse) showed lower T_g values compared to the other compositions probably due to the lower amount of Al_2O_3 [10] and higher amount of Na_2O and K_2O, which are glass modifiers and tend to decrease glass viscosity at lower temperatures (around 740 °C) [11]. In addition, porcelain Finesse contains CaO and MgO in a ratio of almost 1:1, what usually decreases the viscosity of glasses as a result of the phenomenon known as effect of combined ions [11]. Although an endothermic effect has been demonstrated between 605 and 625 °C due to the low-high leucite transformation [12,13], this effect was not observed in this investigation probably because of the low amount of leucite observed for these porcelains. Cesar et al. [14] reported values of 0.22, 0.22, 0.06 and 0.15 volume fraction of leucite for compositions Ceramco I, Ceramco II, Finesse and d.Sign, respectively.

Table 3 shows the results of bulk density of the porcelains sintered at the heating rates recommended by the manufacturers (55 °C/min for Ceramcos I and II, and Finesse or 60 °C/min for d.Sign) and at the relatively slow rate (10 °C/min) at the final temperature recommended. It was observed for all investigated porcelains that there was no effect of the heating rate on the density of the specimens and therefore the first part of the hypothesis of the work had to be rejected.

Fig. 5 shows the experimental densification curves for the porcelains at the heating rate of 55 °C/min. The data regarding porcelain densification using 10 °C/min, at 1000 °C, 1000 °C, 800 °C and 875 °C for porcelains Ceramco I, Ceramco II,

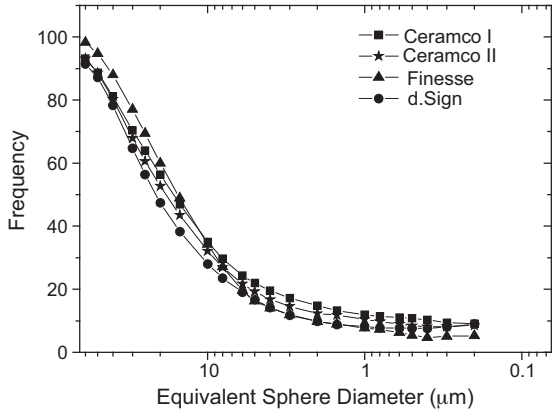

Fig. 1. Particle size distribution of porcelains Ceramco I (A), Ceramco II (B), Finesse (C) (Dentsply–Ceramco), and (D) d.Sign (Ivoclar–d.Sign).

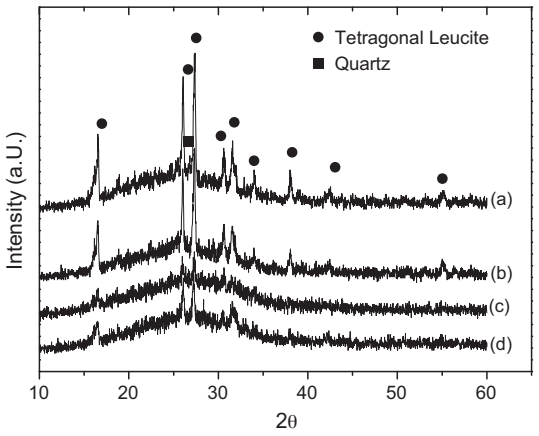

Fig. 2. X-ray diffraction patterns of porcelains: (a) Ceramco I, (b) Ceramco II, (c) Finesse (Dentsply–Ceramco), and (d) d.Sign (Ivoclar–d.Sign), before sintering.

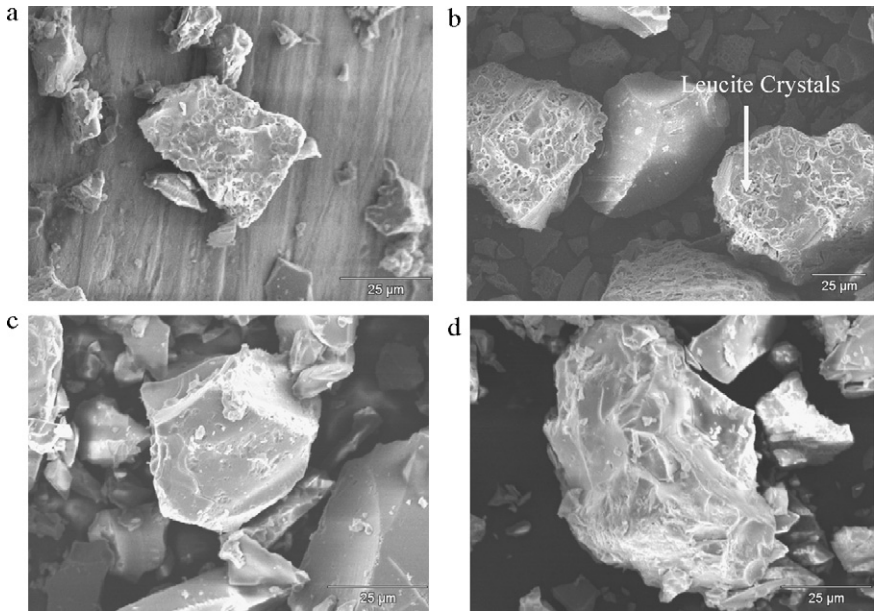

Fig. 3. SEM micrographs of the etched powders of porcelain: (a) Ceramco I, (b) Ceramco II, (c) Finesse (Dentsply–Ceramco), and (d) d.Sign (Ivoclar–d.Sign).

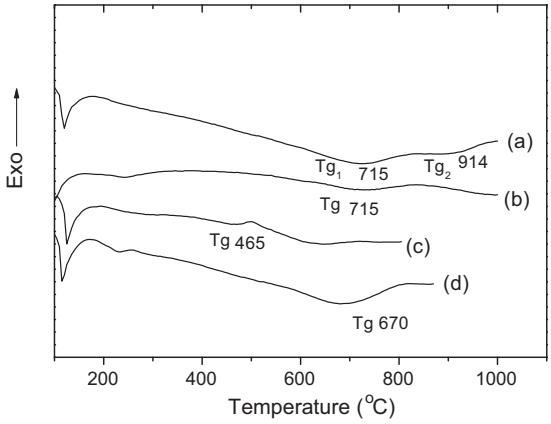

Fig. 4. DTA curves, at 10 °C/min, of porcelains Ceramco I (a), Ceramco II (b), Finesse (c), (Dentsply–Ceramco) and d.Sign (Ivoclar–d.Sign) (d).

Finesse and d.Sign, respectively, are not shown in the figure since the values were similar to those obtained at 55 °C/min (for Ceramco I, Ceramco II, and Finesse) and 60 °C/min (for d.Sign) (Table 3). Densities of porcelain powders are also shown in Table 3, and these values were used to calculate the relative density (ρ_r) of sintered specimens. Porcelains Ceramco I, Ceramco II, and Finesse reached the maximum densification at temperatures that were 50 °C lower than those specified by the manufacturer, i.e., 950 °, 950 °, 750 °C, respectively, as observed in Fig. 5. A similar result was observed for porcelain d.Sign, but the maximum densification occurred at 850 °C, which is 25 °C lower than the temperature recommended by the manufacturer. An interesting aspect that can be observed in Fig. 5 is that porcelain A (Ceramco I) had the lowest relative density ($\rho_r \sim 0.96$) probably due to the second vitreous phase, with T_g around 914 °C, which is more viscous than the vitreous phases of porcelains B (Ceramco II), C (Finesse) and D (d.Sign), which have T_g below 715 °C, and/or because the presence of crystalline quartz (SiO_2). This finding is important for the development of new dental porcelains since it indicates that adding a second vitreous or crystalline phase with higher viscosity to the porcelain may jeopardize the full densification of the restoration.

DTA results (Fig. 4) showed that all porcelains studied had reduced tendency for crystal growth, indicating that crystallization and sintering were not concurrent, and the densification, in this case, was not dependent on the heating rate. Fig. 6a, d, g and j shows the microstructures observed on the fracture surfaces of materials Ceramco I, Ceramco II, Finesse and d.Sign sintered at temperatures that were, respectively, 150 °C, 150 °C, 100 °C, and 75 °C below the temperature recommended by the manufacturers. It is possible to note in these micrographs that the large particles are at the initial Frenkel stage, which is characterized by the formation of a neck

Table 3
Sintering temperature and arithmetic means and standard deviations of powder density and bulk density values of the sintered specimens of the dental porcelains of this investigation.

Porcelain	Powder density (ρ_p) (g/cm^3)	Sintering temperature (°C)	Bulk density (ρ_b) (g/cm^3)		
			60 °C/min	55 °C/min	10 °C/min
Ceramco I	2.525 ± 0.002			2.429 ± 0.013	2.407 ± 0.019
Ceramco II	2.456 ± 0.009	1000		2.437 ± 0.007	2.439 ± 0.025
Finesse	2.556 ± 0.140	800		2.502 ± 0.025	2.486 ± 0.013
d.Sign	2.600 ± 0.005	875	2.545 ± 0.013		2.522 ± 0.023

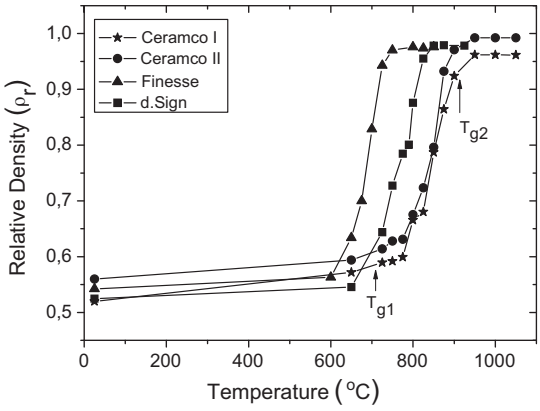

Fig. 5. Densification curves of the non-isothermal sintering, at heating rate of 55 °C/min, for porcelains Ceramco I (A), Ceramco II (B), Finesse (C) (Dentsply–Ceramco) and 60 °C/min for porcelain d.Sign (Ivoclar–d.Sign) (D). The symbols T_{g1} and T_{g2} indicate, respectively, the first and second glass transition temperatures for porcelain Ceramco I.

between neighboring particles and large porosity [5]. With the increase in sintering temperature, the pores shrank and porosity was reduced (central column of SEM images). At higher temperatures (800 °C for porcelain Finesse, 875 °C for porcelain d.Sign, and 1000 °C for porcelains Ceramco I and Ceramco II), specimens are at the final stage of sintering and the density value was saturated at $\rho_r \sim 0.96$ for porcelain Ceramco I, ∼0.99 for Ceramco II, ∼0.98 for Finesse, and ∼0.98 for porcelain d.Sign, since the values of relative density (Fig. 5) reached a steady state after the heat treatment temperature surpassed that recommended by the manufacturer.

Prado et al. [5] reported that residual porosity is a recurrent problem regarding viscous flow sintering and showed that it is very difficult to achieve full densification even in the absence of glass phase crystallization. Since the DTA results (Fig. 4) showed that the four porcelains had reduced tendency of crystal growth, the saturation of densification cannot be attributed to crystallization. The residual porosity, which hindered the full densification, was probably caused by bubble formation due to the release of dissolved gas and/or entrapped insoluble gases in the initial pores (Fig. 6). Gases dissolved in the interior of glasses (water vapor, N_2, CO_2, for example) are released with difficulty by larger particles during the sintering process, since this phenomenon is related to a diffusion process that depends on sintering time, temperature and viscosity [15,16].

Based on the results of this work, the null hypothesis proposed was partially accepted because though the heating rate had no effect on the density of the porcelain specimens, the sintering temperature affected significantly the density values obtained.

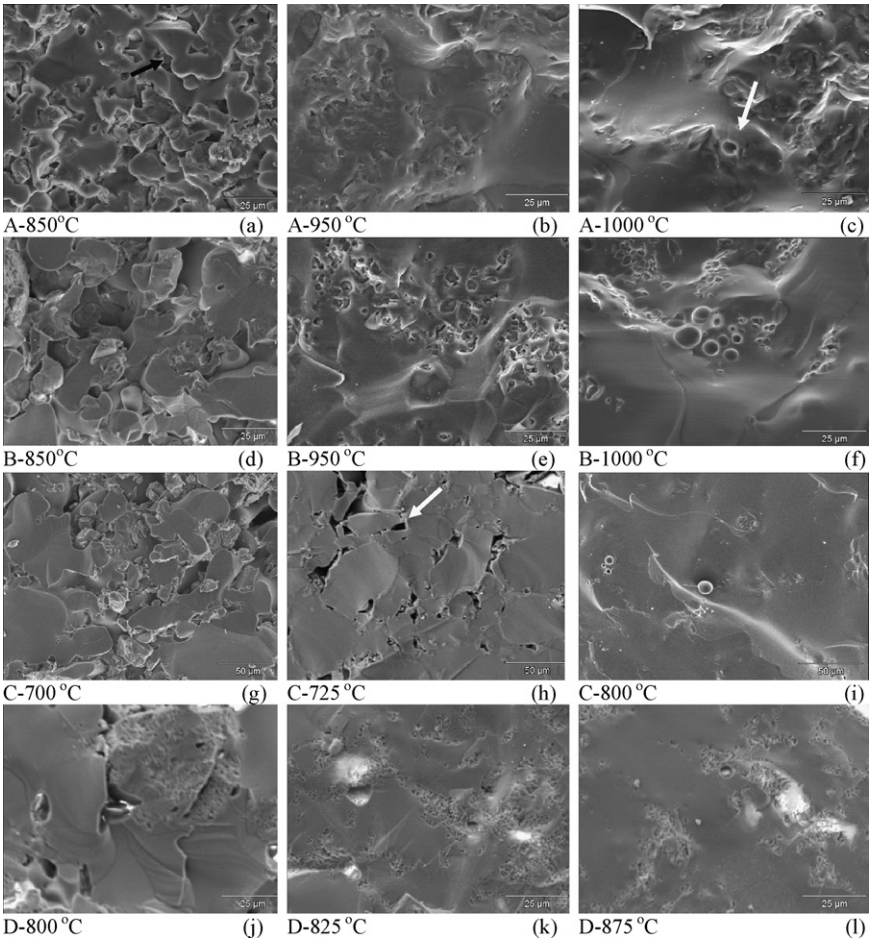

Fig. 6. SEM micrographs of the fractured surface of porcelains: Ceramco I (A), Ceramco II (B), Finesse (C) (Dentsply–Ceramco), and d.Sign (D) (Ivoclar–d.Sign). The letters indicate the porcelain type and the heat treatment temperature of each one is specified in the figure. Black arrow shows necks between particles and white arrows shows pores or bubbles.

4. Conclusion

No significant difference in densification was observed by increasing the heating rate from 10 °C/min to 55 °C/min, for low-fusing (800 °C and 875 °C) and high-fusing (1000 °C) porcelains. This result was explained by the reduced tendency of crystallization of the glassy phase for the four porcelains, as determined by DTA. In this case, crystallization and sintering were not concurrent. The full densification ($\rho_r = 1$) could not be achieved and this was attributed to entrapped insoluble gases in the initial pores of the compact and/or bubble formation that were a consequence of the release of gas dissolved in the glass matrix. Porcelains Ceramco I, Ceramco II, and Finesse (Dentsply–Ceramco) reached the maximum densification at a temperature 50 °C lower than that specified by the manufactures. For porcelain d.Sign (Ivoclar–d.Sign), this temperature was 25 °C lower than that of the manufacturer. From the clinical point of view, it is possible to conclude that dental technicians can save time and energy by reducing the sintering temperature of these commercial porcelains with no negative effect on the final density of the restoration.

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