Original paper

Effect of Cooling Condition on Leucite Crystals in Dental Porcelains

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X-ray diffractometry (XRD) was used to analyze the crystal phases of three commercial dentin and incisal porcelains prepared by normal cooling, quenching in water, and controlled slow annealing after normal firing. There were no remarkable differences in the contents of either tetragonal and cubic leucite in the fired porcelain discs prepared under the three cooling conditions. Furthermore, there were no significant differences in the parameters of the a-axis and c-axis of tetragonal leucite, and the a-axis of cubic leucite among them. These results suggest that the cooling condition has little effect on the microstructural changes of leucite crystals in the dental porcelains, since the leucite crystals were formed at a higher temperature range than the firing- and cooling-temperature range and were stabilized by incorporation of additives into the lattice.

INTRODUCTION

Our previous study[1] showed that six commercial feldspathic dental porcelain frits consisted of both tetragonal and cubic leucite crystals and a glass matrix. The average contents of tetragonal and cubic leucite for the four frits were 20.1-22.6 wt% and 0-2.6 wt%, respectively, whereas those for the other two were 11.5-11.6 wt% and 2.9-4.6 wt%, respectively. Mackert *et al.*[2] demonstrated that the low-temperature (tetragonal) and high-temperature (cubic) forms coexisted at 400℃, while only the cubic forms existed at 600℃ and 700℃. So, cubic leucite can not exist under general condition at room temperature. It was also reported that incorporation of some cations substituted for potassium resulted in the stabilization of cubic leucite at room temperature, as follows. Hermannsonn and Carlsson[3] reported that cubic leucite was formed in glass consisting of $K_2O-Al_2O_3-SiO_2$ containing small amounts of CaO, TiO_2, and ZnO. Prasad and Vaidyanathan[4] demonstrated that cubic leucite could be stabilized by addition of Cs_2CO_3 to the starting materials. Denry *et al.*[5] demonstrated that the stabilization of cubic leucite could also be obtained by the addition of pollucite ($Cs_2O \cdot Al_2O_3 \cdot 4SiO_2$) and the stabilization of cubic leucite reduced the flexure strength in leucite-reinforced porcelain. They[6] also reported that most of the leucite in feldspathic dental porcelains was different from the stoichiometric leucite composition.

On the other hand, there have been various controversial reports about the effects

of thermal treatment on leucite content.   Mackert et $al.$[7] reported that heat treatment during thermal expansion measurement was not sufficient to induce measurable leucite crystallization.   They also demonstrated that the isothermal anneal effect on the leucite content depended on the porcelains[8,9], whereas the cooling rate after firing significantly affected the leucite content[10].   Barreiro and Vicente[11] reported that no increase of leucite volume fraction was observed during isothermal heat treatments, from 800 to 1000℃, and for periods up to 1440 min, of a dental porcelain.   Therefore, there is no consistent conclusion as to whether the leucite contents of dental porcelains change with firing.   The aim of the present study was to investigate the effects of cooling conditions on the microstructure and amount of both tetragonal and cubic leucite crystals in feldspathic dental porcelains.

MATERIALS AND METHODS

Three commercial dentin and incisal porcelains and their firing conditions are given in Table 1.   The discs, 14 mm in diameter and 2 mm in thickness, were fired according to the manufacturers' directions using a vacuum furnace (Heraeus, Combilabor Heramat 2002, Hanau, Germany) and cooled by normal cooling in ambient air with natural convection, quenching in water at room temperature, and controlled slow annealing from final temperature to room temperature for 60 min using the furnace. After pulverization of the discs using a planetary micro mill (Fritch, Pulverisette 7, Idar-Oberstein, Germany), the crystal phases of these fired porcelains were analyzed by X-ray diffractometry (XRD) (Rigaku, Rotaflex RAD-rX, Tokyo, Japan).   To quantitatively determine the amount of each crystal phase, tetragonal leucite crystal $(K_2O \cdot Al_2O_3 \cdot 4SiO_2)$ powders were synthesized by firing of mixtures of $KHCO_3$, Al_2O_3, and SiO_2 at 1550℃ for 16 h.   To determine the amount of cubic leucite crystal in the porcelains, cubic leucite powders were synthesized by firing of the mixtures of Cs_2CO_3, $KHCO_3$, Al_2O_3, and SiO_2, containing Cs substituted for 25 at% of K, at 1550℃ for 8 h. Glass powders having a final composition (SiO_2 66.1, Al_2O_3 15.1, K_2O 8.9, Na_2O 9.9 wt%) were also prepared by firing of a mixture of $KHCO_3$, Al_2O_3, SiO_2, and Na_2CO_3 at 1500℃ for 16 h.   Standard mixtures of the glass and leucite (0, 10, 20, 30 and 40 wt%

Table 1   Materials and firing conditions used in this study

Code	Brand name	Shade	Start temp.	Final temp.	Heating rate	Holding time
VB	Vintage body[1]	A3B	680℃	940℃	50℃/min	—
VI	Vintage incisal[1]	59	680℃	940℃	50℃/min	—
CD	Carrara dentin[2]	A3	450℃	845℃	80℃/min	2 min
CI	Carrara incisal[2]	59	450℃	845℃	80℃/min	2 min
DD	Deguceram gold dentin[3]	A3	450℃	780℃	55℃/min	1 min
DI	Deguceram gold incisal[3]	3	450℃	780℃	55℃/min	1 min

[1] Shofu, Kyoto, Japan
[2] Elephant Industries, Hoorn, Holland
[3] Degussa AG, Frankfurt, Germany

of tetragonal, and 0, 5, and 10 wt% of cubic leucite) were prepared for quantitative XRD.

An internal standard, pure silicon powder, was used to correct for potential absorption differences between leucite and the glass matrix. Diffraction patterns were recorded in the 2θ range 24 to 30° at the rate of 0.5° 2θ/min using copper $K\alpha$ radiation (40 kV and 120 mA) and a curved graphite monochromator. In this 2θ range, the peak intensities of (004) at 25.9° and (400) at 27.3° due to tetragonal leucite (JCPDS No.38-1423) and the intensity of Si (111) peak at 28.44° (JCPDS No.27-1403) were taken for quantitative analysis. The peak angle and intensity were obtained from the digitized measurement profiles by a peak search software package with smoothing and background treatment (Rigaku, RINT 2000, Tokyo, Japan). The total corrected peak intensities of (004) and (400) of tetragonal leucite for each standard were plotted against the weight fraction of tetragonal leucite and an excellent, nearly linear plot was obtained ($r=0.996$). Furthermore, the calibration line for (400) of the cubic leucite against the weight fraction was also obtained from the peak intensity around 26.6° in the XRD patterns of the mixtures ($r=0.981$). Using these regression lines, the weight fractions of tetragonal and cubic leucite in the specimens were calculated from their peak intensities in the XRD patterns. Furthermore, the lattice parameters of the a- and c-axes of tetragonal leucite and the a-axis of cubic leucite were derived from the diffraction peak angles of (400) and (004) of tetragonal leucite and (400) of cubic leucite, respectively. The measurements were repeated three times for each condition. Details of the XRD measurements were described previously[12].

The chemical compositions of the fired discs prepared by normal cooling were analyzed by fluorescent X-ray spectroscopy (RIX3001, Rigaku, Tokyo, Japan) at 30 kV-100 mA. After qualitative analysis, the weight percentages of the detected elements as oxides were quantitatively analyzed on the polished disc surface, 10 mm in diameter.

RESULTS

Figure 1 shows XRD patterns of the fired dental porcelains prepared by normal cooling. All the porcelains consisted of leucite crystals and a glass phase. Most of the diffraction peaks were identified as tetragonal leucite, and several small peaks due to cubic leucite were also observed. From the peak intensity of both (004) and (400) of tetragonal leucite and (400) of cubic leucite in these diffraction patterns, the contents of both tetragonal and cubic leucite crystals were determined.

Table 2 shows the contents of tetragonal and cubic leucite crystals in the fired porcelain discs prepared by normal cooling, quenching in water, and controlled slow annealing. The average contents of tetragonal leucite of VB, VI, CD, and DD prepared by the controlled slow annealing were slightly higher than those after normal cooling and quenching ($p<0.05$). However, the differences in the average values were not remarkable. There were no significant differences in the contents of tetragonal leucite for CI and DI prepared by the three kinds of cooling conditions. Furthermore,
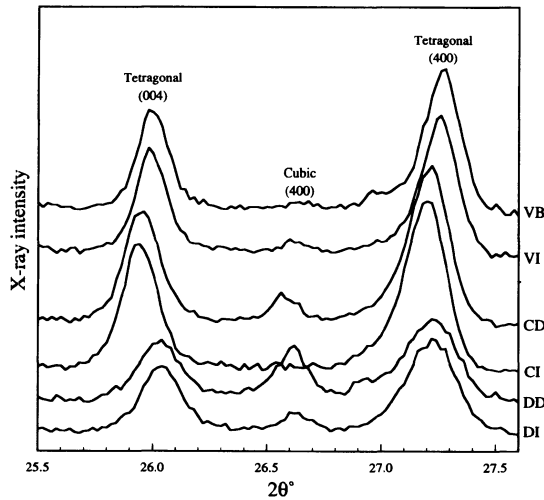
Fig. 1 2XRD patterns of the fired porcelains
after normal cooling.

Table 2 Content [wt%: mean (s.d.)] of tetragonal and cubic leucite in the fired
porcelains after normal cooling, quenching in water, and controlled slow
annealing

	Porcelain	Normal cooling	Quenching	Annealing
	VB	21.5 (0.7)	21.4 (0.9)	22.7 (0.7)
	VI	20.1 (0.4)	20.5 (0.6)	21.5 (0.6)
Tetragonal	CD	21.1 (0.5)	22.2 (0.5)	23.1 (0.6)
leucite	CI	22.1 (0.3)	22.2 (0.4)	22.3 (0.1)
	DD	14.9 (0.7)	15.1 (1.1)	16.8 (0.5)
	DI	16.6 (0.3)	16.5 (0.6)	16.2 (0.4)
	VB	0.9 (0.3)	0.6 (0.2)	0.8 (0.1)
	VI	0.8 (0.3)	0.7 (0.1)	0.8 (0.1)
Cubic	CD	3.4 (0.2)	3.5 (0.2)	3.4 (0.0)
leucite	CI	—	—	—
	DD	4.1 (0.2)	4.0 (0.5)	4.3 (0.1)
	DI	2.6 (0.3)	2.7 (0.4)	2.4 (0.3)

there were no significant differences in the contents of cubic leucite of any of the por-
celains prepared under the three cooling conditions. These results suggest that the
cooling conditions have little effect on the contents of tetragonal and cubic leucite
crystals.

Table 3 shows the lattice parameters of both the a- and c-axes of tetragonal
leucite and the a-axis of cubic leucite in the fired porcelains prepared by normal cool-
ing, quenching in water, and controlled slow annealing. The parameters of the a-axis
of tetragonal leucite of these dental porcelains were larger than those of the
stoichiometric tetragonal leucite ($a=1.30654$ nm, JCPDS No.38-1423), whereas those of
the c-axis were smaller ($c=1.37554$ nm, JCPDS No.38-1423). Furthermore, there were
no significant differences in these lattice parameters of the leucite in the fired

Table 3 Lattice parameter [nm: mean (s.d.)] of a- and c-axes of tetragonal leucite and a-axis of cubic leucite in the fired porcelains after normal cooling, quenching in water, and controlled slow annealing

	Porcelain	Normal cooling	Quenching	Annealing
a-axis of tetragonal leucite	VB	1.3072 (0.0004)	1.3076 (0.0004)	1.3077 (0.0002)
	VI	1.3071 (0.0006)	1.3077 (0.0002)	1.3072 (0.0004)
	CD	1.3099 (0.0002)	1.3103 (0.0002)	1.3100 (0.0002)
	CI	1.3096 (0.0002)	1.3103 (0.0002)	1.3098 (0.0003)
	DD	1.3093 (0.0008)	1.3096 (0.0014)	1.3099 (0.0002)
	DI	1.3099 (0.0002)	1.3095 (0.0016)	1.3103 (0.0002)
c-axis of tetragonal leucite	VB	1.3695 (0.0008)	1.3687 (0.0008)	1.3692 (0.0004)
	VI	1.3692 (0.0006)	1.3688 (0.0006)	1.3692 (0.0002)
	CD	1.3713 (0.0002)	1.3712 (0.0002)	1.3715 (0.0008)
	CI	1.3712 (0.0002)	1.3708 (0.0002)	1.3712 (0.0006)
	DD	1.3680 (0.0011)	1.3675 (0.0011)	1.3668 (0.0007)
	DI	1.3672 (0.0004)	1.3672 (0.0004)	1.3672 (0.0002)
a-axis of cubic leucite	VB	1.3383 (0.0010)	1.3388 (0.0018)	1.3379 (0.0018)
	VI	1.3380 (0.0004)	1.3373 (0.0006)	1.3375 (0.0006)
	CD	1.3387 (0.0005)	1.3385 (0.0002)	1.3391 (0.0002)
	CI	—	—	—
	DD	1.3380 (0.0008)	1.3380 (0.0009)	1.3380 (0.0009)
	DI	1.3369 (0.0007)	1.3378 (0.0009)	1.3372 (0.0009)

Table 4 Chemical composition (wt%) of the fired porcelain discs after normal cooling

Oxide	VB	VI	CD	CI	DD	DI
Na_2O	5.19	4.90	5.35	5.84	9.19	9.05
Al_2O_3	20.16	20.27	14.62	14.41	16.03	16.15
SiO_2	59.31	59.41	62.11	62.64	60.29	60.02
K_2O	12.74	13.08	14.27	14.00	13.06	13.36
CaO	1.73	1.73	0.97	0.92	0.17	0.18
ZrO_2	0.30	0.15	0.36	0.09	0.12	0.03
Fe_2O_3	0.06	0.10	0.07	0.11	0.03	0.05
MgO	0.30	0.24	—	—	—	—
Sb_2O_3	—	—	0.85	0.77	—	—
BaO	—	—	0.77	0.99	—	—
Y_2O_3	—	—	0.20	0.12	0.26	0.23
SnO_2	—	—	0.35	—	0.24	—
CeO_2	—	—	—	—	0.45	0.81
Others	0.21	0.12	0.07	0.11	0.17	0.12

porcelain discs prepared under the three different cooling conditions.

Table 4 shows the chemical composition, using fluorescent X-ray spectroscopy, of the fired porcelain disc prepared by the normal cooling. Our previous papers[1,12] reported the chemical composition of these porcelains analyzed by energy dispersive X-ray spectroscopy. The fluorescent X-ray spectrum data were obtained from a much wider area, 10 mm in diameter, of the fired specimen than for EDX, and the data for the trace elements were more reliable than those by EDX. Sb was clearly detected in

CI and CD and the amounts of elements such as Zr, Fe, Mg, Ba, Y, Sn, and Ce containing less than 1 wt% could be determined. It was found that CD, CI, DD, and DI contained various elements with small contents.

DISCUSSIONS

Lattice parameter data demonstrated that the composition of leucite crystal in the dental porcelains was different from that of stoichiometric leucite crystal, $K_2O \cdot Al_2O_3 \cdot 4SiO_2$, and varied in each one. It seems that the composition of the leucite of VB and VI was closest to the stoichiometry because the parameters of both the a-axis and c-axis of tetragonal leucite were closest to those of the stoichiometric leucite among the six dental porcelains. On the other hand, the leucite of DD and DI contained the highest amounts of impurity because they showed the largest difference between the parameters of both axes of tetragonal leucite to the stoichiometric parameters.

It is known that leucite crystal exists in a relatively small formation region in the phase diagram for the K_2O-Al_2O_3-SiO_2 system[13]. Therefore, the atomic ratios of K:Al:Si of leucite crystals can slightly vary from the stoichiometric ratio 1:1:2. The structure of tetragonal leucite relies on the framework of (Si, Al) O_4 tetrahedrons sharing corners to form rings of six and rings of four tetrahedra[14,15]. The potassium ions are situated in the center of large channels. The location of the potassium ions in the open channels of the leucite structure results in easy ion exchange with other interframework cations. As shown in Table 4, various cations were detected in these commercial porcelains. It is possible that potassium ions of leucite are exchanged by some of these cations. Although boron was not detected in the present study, it is known that boron makes a network similar to that of aluminum[16]. Our previous study[13] demonstrated that the dental porcelain frits consist of various ions and are mixtures of three or four powders. Denry et al.[6] also demonstrated that most of the leucite crystals in feldspathic dental porcelains were different from stoichiometric leucite. From these previous reports, it was concluded that there is no consistent composition of leucite in commercial dental porcelains. Also, in case of the segregation of some cations at high concentrations into leucite crystals, tetragonal leucite were partially stabilized to the cubic phase.

There were no significant differences in the lattice parameters of the a-axis of cubic leucite between the porcelains and between cooling conditions. These values were slightly smaller than those of stoichiometric cubic leucite ($a = 1.343$ nm, JCPDS No.31-967). It implies that the framework of the cubic form in the dental porcelains is a stable lattice structure with the incorporation of inter-framework ions.

When feldspar is heated at temperatures between 1150℃ and 1530℃, it undergoes incongruent melting to form crystals of leucite in a liquid glass[17]. This temperature range is higher than the fired temperature during the production of a dental prosthesis. It is also a reason why these were no remarkable effects of the cooling conditions on the contents and the microstructure of leucite crystal.

Acknowledgment

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