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Chemical Strengthening of Leucite-containing Dental Ceramics

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Abstract

In this investigation a procedure for increasing the flexural strength of leucite-containing dental ceramics by ion exchange with sodium at temperatures above the transformation range of the glass is presented. The method depends on a partial dissolution of the leucite phase and suppression of the phase transition of the persisting leucite in the surface layer of a work-piece, which causes a lower thermal expansion in the so-treated material. During cooling from high temperatures an internal pressure is built up in the surface layer due to the harder thermal contraction in the untreated inner part of the work-piece, which raises the flexural strength of the material. With the dental ceramic VMK 68 an increase of 75% could be measured after an ion exchange in NaCl at 830°C for 8 min.

In der Untersuchung wird ein Verfahren zur Steigerung der Biegefestigkeit leucithaltiger Dentalkeramik durch Ionentausch mit Natrium bei einer Temperatur oberhalb des Glaspunktes vorgestellt. Das Verfahren beruht auf der teilweisen Auflösung der Leucitphase und der Unterdrückung der Phasenumwandlung des persistierenden Leucits in der oberflächlichen Zone eines Werkstückes, woraus in diesem Bereich eine niedrigere thermische Dehnung resultiert. Beim Abkühlen aus dem plastischen Zustand wird durch die stärkere thermische Schrumpfung des unbeeinflußten Inneren des Werkstückes an der Oberfläche eine Druckzone aufgebaut, die die Biegefestigkeit der Keramik erhöht. Bei der untersuchten Keramik VMK68 konnte nach einem Ionentausch in NaCl bei 830°C über 8 min eine Zunahme der Biegefestigkeit um 75% gemessen werden.

Dans cette recherche une méthode pour augmenter la résistance à la flexion d'une céramique contenant de la leucite par un échange d'ions à une température plus élevée est décrite. La méthode repose sur la décomposition partielle de la phase de leucite et la suppression de la transformation de phase de la leucite persistante dans la couche superficielle, ce qui résulte, dans cette sphère, une expansion thermique réduite. Pendant le refroidissement de la céramique plastique, une pression s'établit, consécutive à la contraction plus forte de l'interieur non influencé de la pièce d'œuvre, ce qui augmente la résistance à la flexion de la céramique. Avec la céramique VMK 68, une augmentation de 75% de la résistance de la flexion a été mesurée après un échange d'ions dans NaCl à 830°C sur 8 min.

1 Introduction

A dental restoration for the functional recovery of the human masticatory system has to be carried out with the greatest possible preservation of dental hard tissue. Due to their excellent aesthetic properties and superior biocompatibility, ceramics are widely used for fixed dental prostheses. The low tensile strength of those materials, however, makes the application for delicate pieces difficult. As an example the restoration of an upper lateral incisor with a ceramic veneer might be described. This

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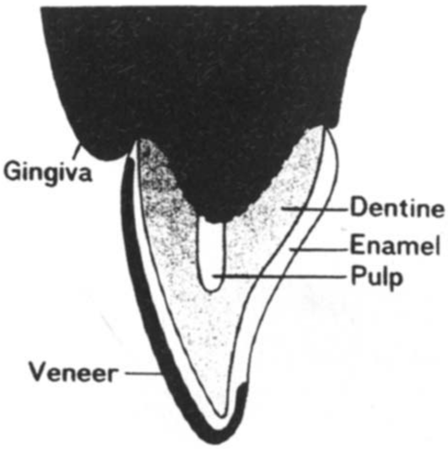


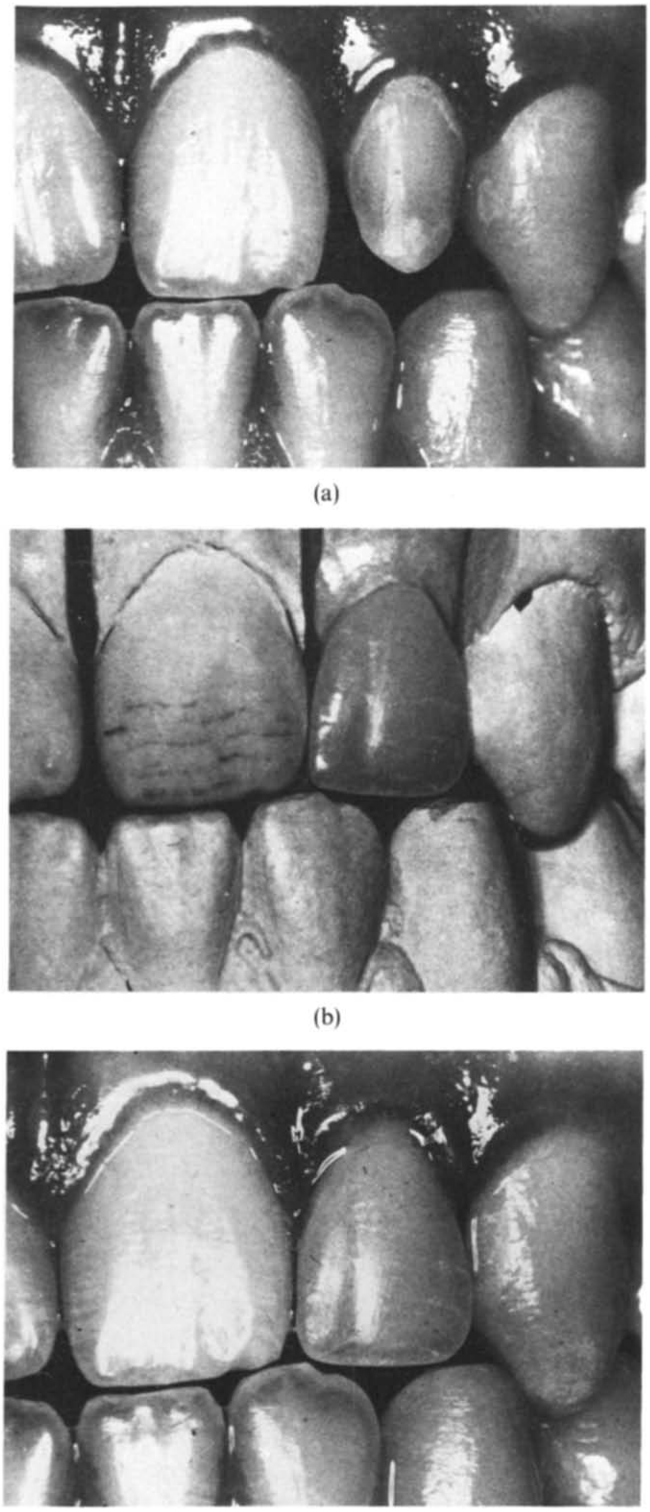
Fig. 1. Schematic sectional view of an upper incisor after reconstruction with a ceramic veneer.[1]

technique requires only a slight preparation of the dental enamel and then a thin ceramic veneer is bonded to the etched enamel (Fig. 1). In the actual clinical case shown (Fig. 2) an aesthetic correction of the hypoplastic left upper lateral incisor of a 17-year-old patient was necessary. The procedure is only slightly invasive and shows a good aesthetic result (Fig. 2(c)). But it implies the manufacturing of a ceramic veneer with a thickness of 0·5 mm up to 0·9 mm at most, which therefore is very sensitive to tensile stress. This illustrates the requirement for strengthening mechanisms for dental ceramics.

Leucite-containing dental ceramics are common and often used in dentistry. The development of the texture of leucite-containing dental ceramics can be explained in simple terms on the basis of the phase diagram potash feldspar–soda feldspar (Fig. 3). On cooling a potassium-rich melt at first leucite ($K[AlSi_2O_6]$) crystallizes in this melt. In the thermodynamical equilibrium the leucite reacts with the residual melt, forming feldspar ($K,Na[AlSi_3O_8]$). If, however, the melt is cooled rapidly, this reaction fails to appear, due to the high viscosity of the melt, and the residual melt solidifies in a vitreous state. Now the texture shows leucite crystals embedded in a glassy matrix.

The second-order phase transition of leucite from the tetragonal low-temperature phase to the cubic high-temperature phase causes a high-thermal expansion, which increases the thermal expansion of the whole ceramic system. The cubic high-temperature phase shows only little thermal expansion.

The purpose of the following investigation is to increase the tensile stress of leucite-containing dental ceramics by ion exchange, based on the idea of treating the surface layer of a finished work-piece at temperatures above the transformation range of the glass by ion exchange in a sodium-containing salt bath, thus shifting the chemical composition in this area in the direction of soda feldspar, which would mean a destabilization and dissolution of the leucite. This would produce a surface layer with a lower thermal expansion, which is put under pressure during cooling due to the higher thermal


(a)

(b)

(c)

Fig. 2. (a) 17-Year-old patient, hypoplastic upper lateral incisor. (b) Ceramic veneer on the plaster model. (c) Hypoplastic incisor, reconstructed with a ceramic veneer.

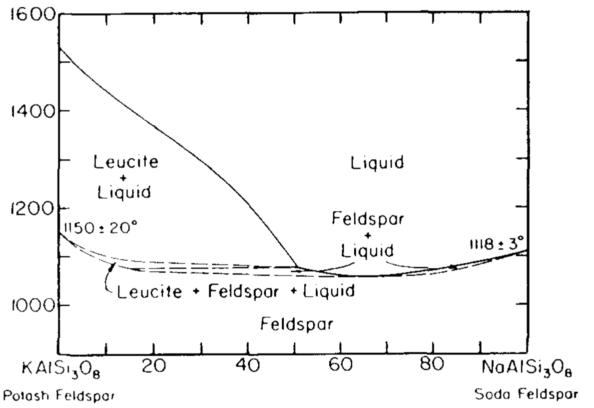


Fig. 3. Phase diagram of the system potash feldspar–soda feldspar.[2]

expansion of the inner part of the work-piece. This surface pressure has to be additionally overcome, before micro-flaws due to tensile stress can force their way deeper into the material, thus reaching a higher value of strength.

2 Material and Method

In this investigation the leucite-containing dental ceramic VMK 68-551 (Vita Zahnfabrik, Bad Säckingen, FRG) was used.

To analyse the effect of the sodium ions on the leucite phase, the ion exchange was first done with ceramic power, which provides a large surface for this process and therefore maximizes the effect. NaI (Merck, Darmstadt, FRG, Art.-No. 6523, p.a. quality) and NaCl (Merck, Art.-No. 6404 E, p.a. quality) were chosen for the ion exchange, because the melting points were measured at 656°C and 804°C respectively (differential thermal analysis, Netzsch DTA 404) and were therefore above the transformation range of the ceramic material. Two volume units of the salt and one volume unit of the ceramic powder were mixed and heated in a quartz glass test-tube to 700°C with NaI and to 830°C with NaCl. The temperature was measured with a Pt/PtRh10-thermocouple next to the test-tube giving an accuracy of ± 5 K. The effects on the leucite phase were determined by means of X-ray diffraction analysis (Stoe Powder Diffraction System, Cu$K\alpha_1$-radiation, 30 mA, 45 kV).

The measurement of the thermal expansion of the ceramic before and after ion exchange was done with a dilatometer (Netzsch TMA 402).

Measurement of the flexural strength was performed according to the German industrial standard DIN 13 927.[3] Each test specimen was indented at one end beyond the support of the test device for attaching a wire and suspending it in the salt melt. Thus a wetting of the whole surface of the specimens with the molten salt was guaranteed and the specimens kept their shape despite the high temperature. Before suspending the samples in the melt, they were preheated for 2 min at the temperature of exchange to avoid thermal stress and the formation of stress-induced cracking.

The changes in the chemical composition of the ceramic after ion exchange were determined by microprobe analysis (Zeiss DSM 960, Link Analytical System).

3 Results

Figure 4 gives an impression of grain size and shape of the ceramic powder used in this investigation. In Fig. 5 the results of the ion exchange with the ceramic powder, obtained by means of powder diffraction analysis, are put together. For comparison the upper curve (Fig. 5(a)) shows the powder diffraction patterns of the untreated ceramic material. The peaks belong to the tetragonal low-temperature modification of the leucite,[4] the raised baseline is caused by the glassy phase. After an ion exchange in NaI at 700°C for 1 h the diffraction pattern changed (Fig. 5(b)), the crystalline phase now consists of cubic high leucite,[4] i.e. the phase transition of leucite is suppressed by sodium. The quantity of the crystalline phase is not reduced, but the maximum of the baseline is shifted to lower 2-theta values, which indicates structural changes in the glassy phase. After an ion exchange of 4 min at 830°C in NaCl, in addition to the stabilization of the cubic leucite modification, a reduction of the leucite phase is obvious, proved by the reduction of the peak heights (Fig. 5(c)). After 1 h of ion exchange in

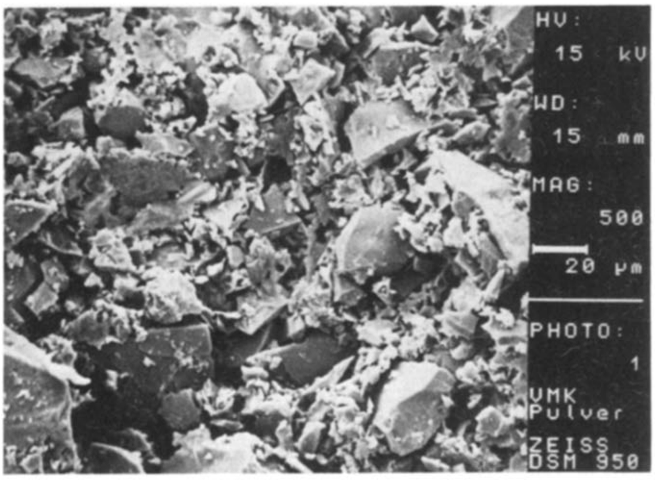


Fig. 4. Electron micrograph of the ceramic powder used.

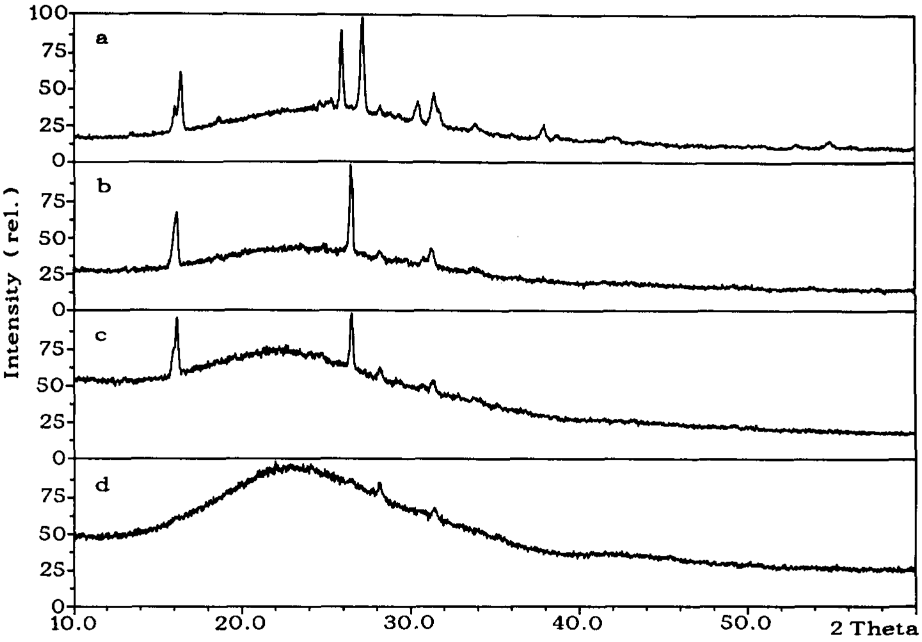


Fig. 5. Powder diffraction patterns: (a) Untreated material; (b) ceramic after ion exchange in NaI for 1 h at 700°C; (c) ceramic after ion exchange in NaCl for 4 min at 830°C; (d) ceramic after ion exchange in NaCl for 1 h at 830°C.

NaCl at 830°C the leucite is completely dissolved (Fig. 5(d)).

The thermal expansion of the leucite was measured by means of high-temperature powder diffraction (Fig. 6). The low leucite of the untreated material shows the expected high volume increase up to 550°C (Fig. 6(a)), measured in steps of 100 K and repeated in the temperature range of 300°C up to 600°C with steps of 50 K. The sodium-stabilized high leucite shows in contrast to this an obviously lower expansion of volume (Fig. 6(b)).

This influences the thermal expansion of the whole ceramic material: after an ion exchange in NaCl the thermal expansion is distinctly reduced, the coefficient of thermal expansion of the untreated material was determined in this measurement at $13{\cdot}1 \times 10^{-6}$/K (Fig. 7(b)) but reaches only $9{\cdot}3 \times 10^{-6}$/K after the ion exchange (Fig. 7(a)), a decrease of 30%. The characteristic temperatures are not fundamentally changed, the transformation range is increased by 25 K from 572°C to 597°C, the softening point lies about 5 K higher.

The texture of the sintered ceramic can be emphasized by etching with 5% aqueous solution of

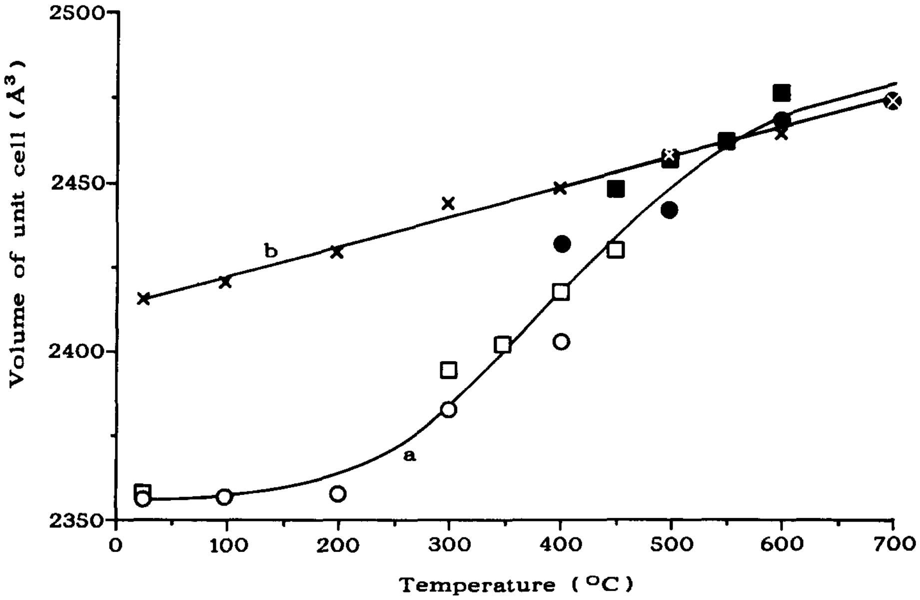


Fig. 6. Volume of leucite unit cell in dependence on temperature. (a) Low leucite in untreated material ○, ●, first measurement; □, ■, second measurement; ○, □, tetragonal; ●, ■, cubic; (b) high leucite, stabilized by ion exchange with NaCl.

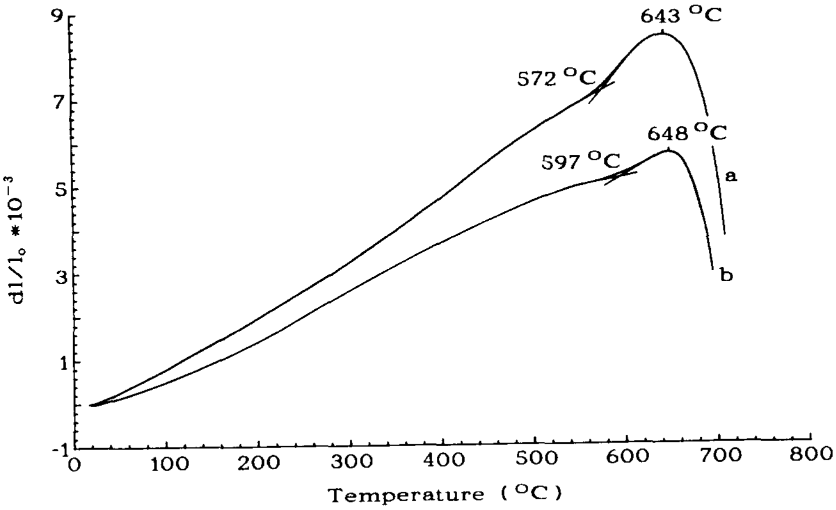


Fig. 7. Thermal expansion (heating rate 5 K/min): (a) untreated material; (b) ceramic after ion exchange in NaCl for 4 min at 830°C.

hydrofluoric acid. The leucite is attacked more easily than the glassy phase and therefore appears as a negative form (Fig. 8). Circular areas of dendritic crystallized leucite are visible. After the ion exchange in NaCl the texture has obviously changed (Fig. 9). A distinct leucite phase is no longer identifiable, only some regions are slightly similar to the texture of the initial state.

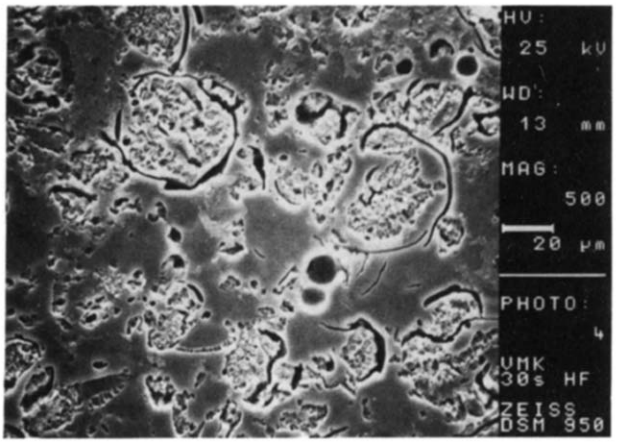


Fig. 8. Texture of a baked ceramic specimen, etched for 30 s with 5% hydrofluoric acid.

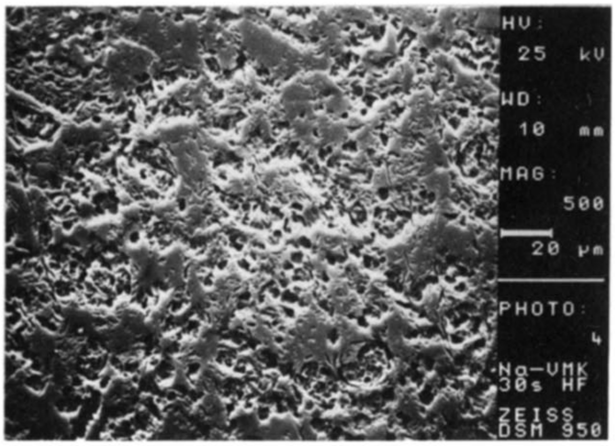


Fig. 9. Texture of a ceramic specimen after ion exchange in NaCl for 9 min at 830°C, etched for 30 s with 5% hydrofluoric acid.

The increase of flexural strength obtained with this method is shown in Fig. 10, measured according to the German industrial standard DIN 13 927.[3] The maximum is reached after an ion exchange of 8 min $(2{\cdot}8\sqrt{\mathrm{min}})$. The strength rises from 72 N/mm^2 to 125 N/mm^2, which means an increase of 75%. The ion exchange has no effect on the aesthetic appearance of the material.

Elemental analysis on the surface of a specimen after an ion exchange of 9 min shows a distinct reduction of the potassium content, an increase of the sodium content and a slight uptake of chloride (Table 1). The distribution of sodium is shown in Fig. 11. For 9 min at 830°C the sodium ions diffuse about 500 µm into the ceramic. The diffusion constant of sodium, calculated from the obtained curve, is drawn in Fig. 12. It shows a hyperbolic dependence on the sodium concentration.

Table 1. Microprobe analysis of a ceramic specimen after an ion exchange in NaCl at 830°C for 9 min in comparison to the untreated material

Oxide	*Untreated* (*wt%*)	*After ion exchange* (*wt%*)
SiO_2	63·96	63·65
Al_2O_3	15·73	15·86
Na_2O	5·81	18·02
K_2O	8·92	0·25
CaO	1·58	1·24
BaO	3·99	0·37
Cl	—	0·62
Σ	99·99	100·01

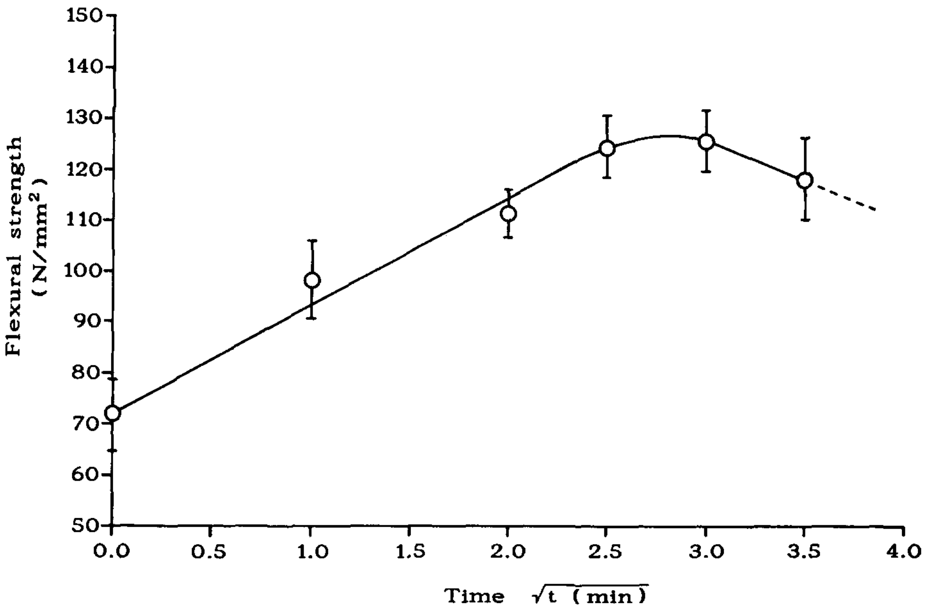


Fig. 10. Flexural strength of the ceramic according to DIN 13 927 after ion exchange in NaCl at 830°C.

4 Discussion

The investigation proves the theoretical considerations discussed by way of introduction, not only in regard to the dissolution of the leucite phase after an ion exchange with sodium, but also the resulting increase in flexural strength. A high sodium content favourably stabilizes the cubic phase of the persisting leucite down to room temperature, which also reduces the thermal expansion of the so-treated ceramic.

The slight uptake of chloride ions is negligible with regard to the corrosion resistance in the biological environment, particularly because, due to the compression stress at the surface, a lower solubility of the ceramic can be expected.[5] The clinical indication for this procedure is especially given in cases where, owing to little space, no reinforced ceramic core material can be used, for instance with the veneer technique or in conservative dentistry.

A disadvantage of this process is the high working temperature, because the shape of the work-piece might change. For the practical application of this method an investment compound has to be developed, which on the one hand guarantees the

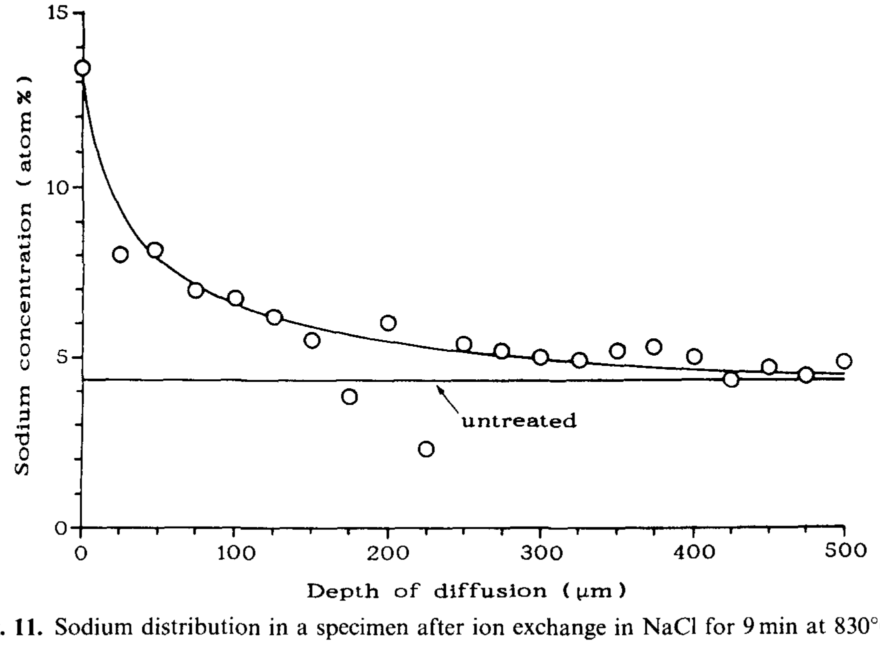


Fig. 11. Sodium distribution in a specimen after ion exchange in NaCl for 9 min at 830°C.

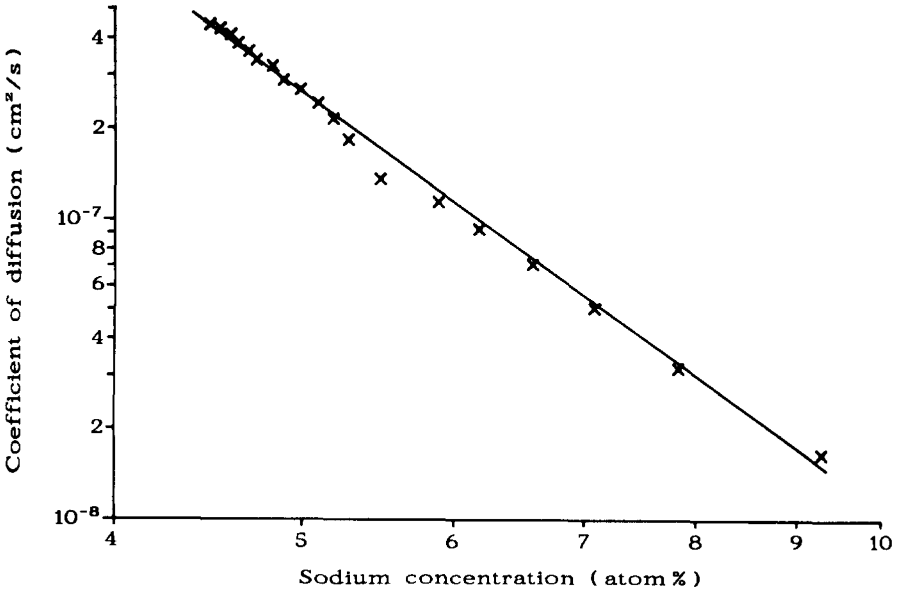


Fig. 12. Variation of the diffusion coefficient of sodium with the sodium concentration.

dimensions of the work-piece and on the other hand should not obstruct the ion exchange.

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