

Optical Transmissivity Changes of Thin Hydroxyapatite Sheets on Heating

^aJ. MAJLING, ^aŠ. SVETÍK, ^bJ. ANNUS, ^cJ. KRIŠTÍN, and ^dP. M. MARQUIS

^a*Department of Ceramics, Glass and Cement,
Faculty of Chemical Technology, Slovak University of Technology,
SK-812 37 Bratislava*

^b*Department of Physics,
Faculty of Chemical Technology, Slovak University of Technology,
SK-812 37 Bratislava*

^c*Central Laboratory of Electron-Optical Methods, Comenius University,
SK-842 12 Bratislava*

^d*School of Dentistry, The University of Birmingham,
Birmingham B4 6NN, United Kingdom*

Received 29 January 1977

Thin hydroxyapatite sheets, consisting either of superfine hydroxyapatite particles or particles increased in size by hydrothermal treatment, have been fabricated by a modified pressure casting procedure. The sheets were fairly well transparent after their fabrication and drying. On heating to 1000 °C the samples of superfine particles became opaque while the samples of hydrothermally treated gels remained essentially transparent.

By measuring the optical transmissivity of sheet preforms during their constant rate heating it is possible to determine the temperature interval in which the transition or partial transition between the transparent and the opaque state takes place.

Dilatometric measurements show an expansion of samples above 1000 °C, which is undoubtedly connected with creation of pores. Pore creation may be the reason also for the decrease of the transmissivity of specimens above *ca.* 750 °C.

Bulk transparent hydroxyapatite ceramics has been prepared by hot pressing [1, 2], microwave sintering [3], and also by the pressureless conventional sintering [4]. In last two instances the ceramics was prepared from powders which underwent the hydrothermal treatment. In our previous work [5] we have prepared well translucent hydroxyapatite at 1000 °C from superfine particles consolidated by ultrahigh pressure. However, hydroxyapatite preforms of this kind significantly bloated at 1200 °C, rendering the porous structure.

In this work we have developed and applied a new technique of the transmissivity measurements with the aim to monitor the creation of changes within the microstructure of the hydroxyapatite preforms during their thermal treatment and to show the preliminary results of its application. A prerequisite for such a measurement are transparent preforms which had been, in our case, prepared by pressing the wet hydroxyapatite gels into thin sheets (preforms). A change in transmissivity is compared to a change in the shrinkage of a sample with temperature.

In this contribution only the basic features of the applied method are illustrated. They indicate that the applied method will have some definite relevance to the control of the sintering process and the corresponding design of ceramic microstructures.

EXPERIMENTAL

Hydroxyapatite gel was prepared by precipitation from $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{HPO}_4$ solutions of pH adjusted to 11.5 and the $n(\text{Ca})/n(\text{P})$ ratio pre-set to 1.8. The precipitation was accomplished by pouring the 0.5 M solutions into the vessel of a mixer operated at a high revolving speed. The gel was filtered on a Büchner funnel and the thin filter cake was thoroughly permeated with distilled water.

The wet gel of paste consistency was pressed between steel plates which were covered by a densely woven fabric either with or without additional sorptive (drain) layers (filter paper, additional fabric layers) to remove the expressed water. The obtained thin sheets were separated from the fabric and slowly dried

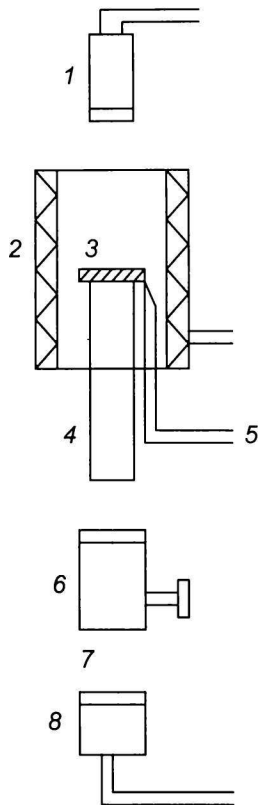


Fig. 1. Experimental set-up for optical transmissivity measurements. 1. White light source; 2. electric resistance furnace; 3. sample; 4. alumina tube support; 5. PtRh10/Pt thermocouple; 6. focusing camera; 7. optical cable; 8. photocell.

in closed Petri dishes at room temperature.

A portion of the wet gel (filter cake) was ultrasonically dispersed in distilled water to a suspension which was subsequently heated in an autoclave at 200°C for 2 h. The sonication was accomplished using the Ultragen device of Technosonics, Nové Mesto n. Váhom, Slovakia. The suspension was filtered and additional thin sheets were prepared in a manner already described.

The dry sheets were heated in an electric furnace and the change in their optical transmissivity with temperature was measured using the experimental set-up presented in Fig. 1. A white light from the source passes through the sample positioned on an alumina tube support inserted into an electric resistance furnace. The transmitted light enters the focusing camera connected to a photocell by an optical cable. The sample temperature is measured by the PtRh10/Pt thermocouple. The furnace temperature control and data acquisition was accomplished using PC.

Fracture surfaces of specimens were investigated by the Jeol JSM 840 scanning electron microscope.

RESULTS AND DISCUSSION

At fabrication of hydroxyapatite thin sheets the

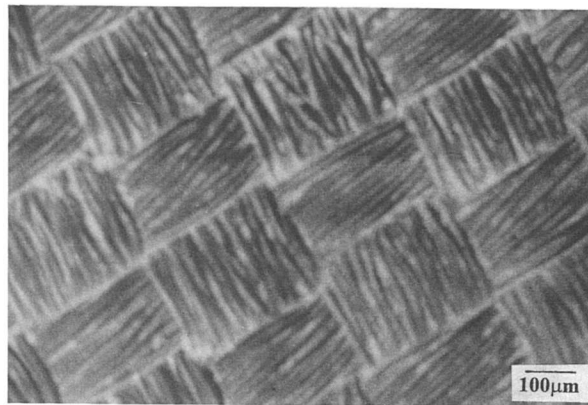


Fig. 2. SEM of the hydroxyapatite sheet surface.

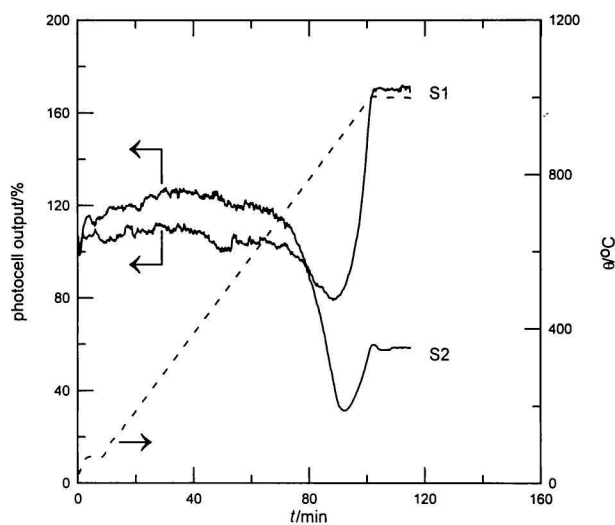


Fig. 3. Changes in the relative photocell outputs with temperature. S1 – sample from the hydrothermally treated gel; S2 – sample from the precipitated gel. (---) temperature/time dependence.

gel moves laterally between plates. Its resulting thickness (*ca.* 0.3–0.8 mm) depends mostly on the gel consistency, rate of pressure increase, maximum pressure applied, and conditions of water drain. Pieces of *ca.* 2 cm² sheets can be obtained by this procedure. The surface of sheets is a replica of the fabric morphology (Fig. 2). The sheets are transparent in a wet state with only slightly decreased transparency after drying at ambient temperature.

Fig. 3 shows the measured changes in the relative photocell output with temperature for two samples, *i.e.* S1, the sheet preform prepared from hydrothermally treated gel, and S2, the sheet preform prepared directly from the precipitated gel. Both samples were heated at a rate of 10°C min⁻¹ with a ramp at 1000°C. The transmissivity of samples with similar thickness increases slightly at low temperatures, which is as-

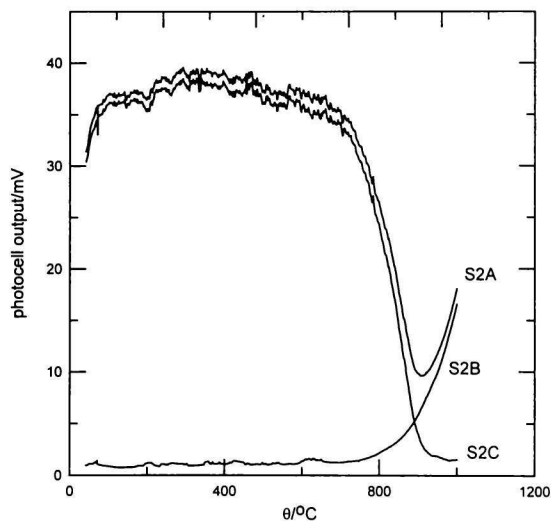


Fig. 4. Elimination of the thermal radiation effect. S2A – first run, sample fully opaque after the experiment; S2B – repeated run with opaque sample; S2C – “deconvoluted” photocell output.

sociated with the loss of capillary-bound water. The rapid decrease of transmissivity starts at temperature *ca.* 750 °C, reaching the minimum value at 900 °C in both cases. Then it increases up to 1000 °C. When the temperature is not changed on this level, the transmissivity of sheets does not change either.

The decrease in the transmissivity of the sample S1 is lower and the increase at temperatures above 900 °C is higher than in the case of S2. The sample S2 was fully opaque after the experiment while S1 was fairly well transparent. The increase in the photocell output can be only partially contributed to the increase in the transmissivity of samples. The major part of this increase is associated with an increase of the intrinsic thermal radiation of samples with temperature.

Elimination of the Effect of Thermal Radiation

Fig. 4 shows the characteristic curve (S2A) depicting the change in the photocell output of the sample heated at the same conditions as in the former case.

The sample cooled in the furnace to room temperature was of white colour (fully opaque). The “cool furnace” photocell output for this opaque specimen was *ca.* 1.5 mV.

The change in the photocell output during repeated heating of this opaque sample is given by the curve S2B. This curve represents the “clean” thermal radiation of the sample. It is becoming significant at approximately 700 °C, with an exponential increase at higher temperatures. Curve S2C is obtained by subtraction of the output data of the curve S2B (thermal radiation) from those of the curve S2A (thermal + transmitted radiation) and shows the photocell output corresponding only to changes in the transmissivity

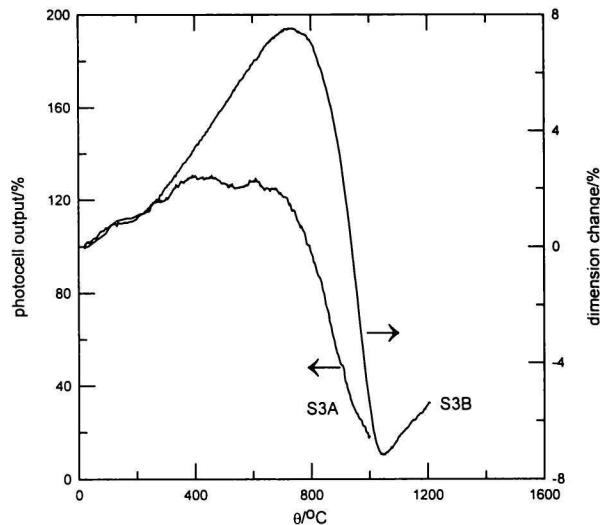


Fig. 5. Dependence of the transmissivity (S3A) and dimension (S3B) on temperature. S3A – deconvoluted photocell output; S3B – dilatometric measurement.

of the sample. Thus the temperature interval wherein the decrease in the transmissivity of the sample takes place can be identified with a greater precision.

Comparison of Changes in Transmissivity and Shrinkage

Fig. 5 shows the change in the transmissivity of a sample (S3A) with a delayed decrease in the transmissivity in comparison to the sample S2C (Fig. 4). From the dry gel corresponding to this sample a pellet was fabricated by a steel die pressing at 100 MPa, for which the dilatometric measurement is given also in Fig. 5 (curve S3B).

The two samples of the same gel are equal in size of primary particles but differ significantly in green density. It is seen from the figure, however, that the decrease in the transmissivity of the first sample with temperature is strongly linked to the shrinkage of the second sample and both curves imply strong change of the original sample microstructure in this temperature interval.

The sample S3B according to the dilatometric curve shows a slight bloating in the temperature interval up to 800 °C because its expansion in this interval exceeds the value corresponding to the thermal expansion coefficient of pure hydroxyapatite ($\alpha_{\text{hap}} = 13.7 \times 10^{-6} \text{ °C}^{-1}$) [6]. The second bloating starts at the temperature above 1050 °C and there is a continuous and sudden transition from a shrinkage of the sample to its expansion. Similar expansion of hydroxyapatite pellets was observed in our previous work [5]. In this, however, the shrinkage ended at 900 °C and bloating did not follow the shrinkage immediately, but started at 1200 °C.

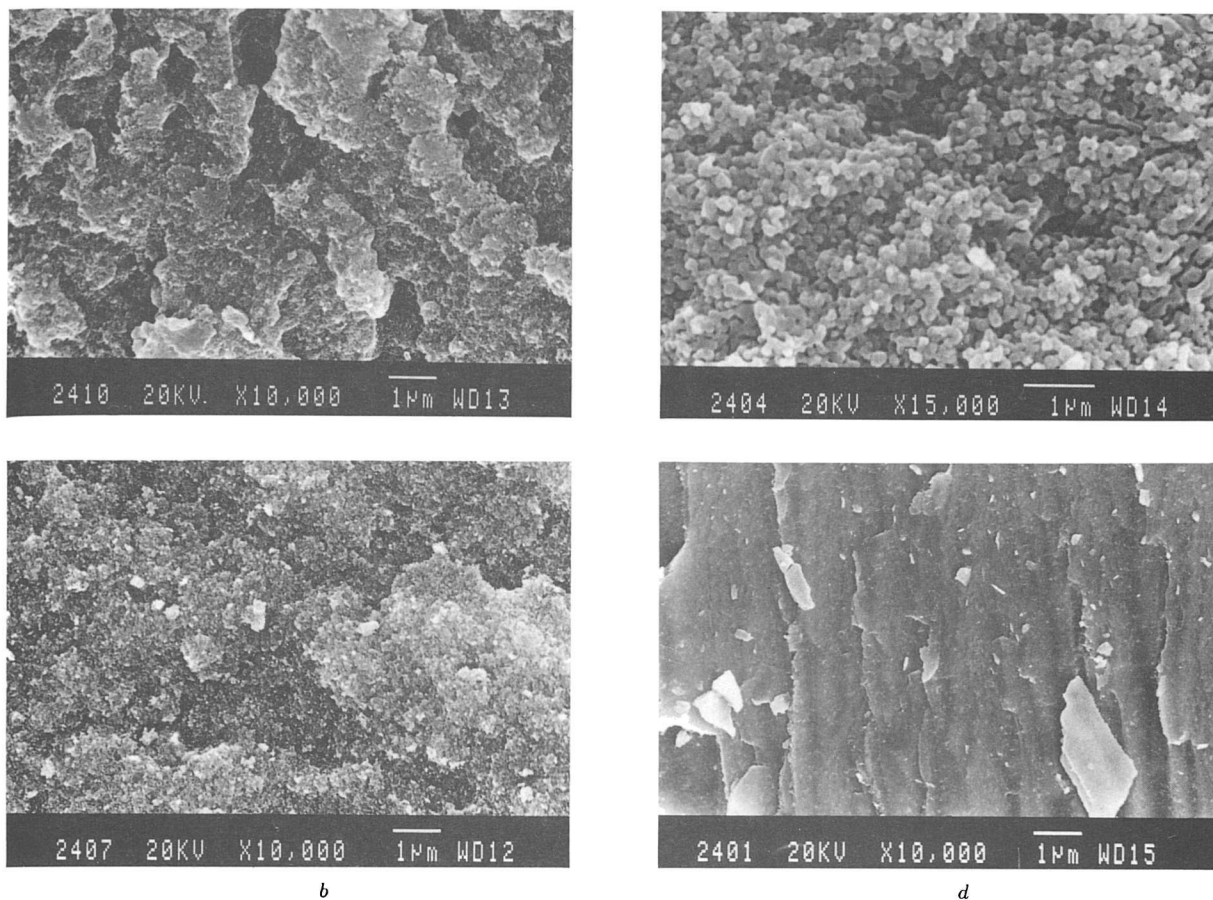


Fig. 6. SEM fracture surfaces of samples S1 and S2. *a, b* – samples (S1, S2) heated to 700 °C; *d* – samples (S1, S2) heated to 1000 °C.

SEM Measurements

The fracture surfaces of samples S1 and S2 were investigated by SEM and are depicted in Fig. 6. Figs. 6*a* and 6*b* show the fracture surfaces of specimens S1 and S2, respectively, heated to 700 °C threshold temperature the start of the sudden decrease in transmissivity (Fig. 3). No significant difference is seen in size of the primary crystals. The microstructure from finer particles (Fig. 6*a*) is, however, more irregular with more pronounced domains of particle clusters.

Figs. 6*c* and 6*d* show the fracture surfaces of the above-mentioned respective specimens heated to 1000 °C. The sample S1 (Fig. 6*c*), which became opaque (expanded), contains evenly distributed large pores with crystals appreciably increased in size. The sample S2 (Fig. 6*d*) is a dense sample wherein the crystal growth did not proceed significantly. More detailed microstructure evaluation is necessary in this case to see properly the grain boundaries geometry.

CONCLUSION

The results presented briefly describe the procedure for fabrication of thin transparent sheets from

wet hydroxyapatite gels and a method for measurement of the changes in the optical transmissivity of the fabricated specimens on their heating. It is believed that creation of relatively large pores is responsible for decrease in the optical transparency of samples. The introduced method enables an “on line” monitoring of microstructure changes in samples during their thermal treatment.

This contribution shows only preliminary results. More systematic measurements are necessary, especially those which would relate the decrease in transmissivity of specimens to nature and size of defects created in their matrices.

REFERENCES

1. Takagi, M., Mochida, M., Uchida, N., Saito, K., and Uematsu, K., *J. Mater. Sci., Materials in Medicine* 3, 199 (1992).
2. Ioku, K., Somiya, S., and Yoshimura, M., *J. Mater. Sci. Letters* 8, 1203 (1989).
3. Agrawal, D. K., Fang, Y., Roy, D. M., and Roy, R., *Mat. Res. Soc. Symp. Proc.* 269, 231 (1992).
4. Fang, Y., Agrawal, D. K., Roy, D. M., and Roy, R., *J. Mater. Res.* 9, 180 (1994).

5. Majling, J., Znášik, P., Palova, A., Svetík, Š, Kovalík, Š, Agrawal, D. K., and Roy, R., *J. Mater. Res.* 12, 198 (1977).

6. Nakamura, S., Otsuka, R., Ouki, H., Akao, M., Miura, N., and Yamamoto, T. *Thermochim. Acta* 165, 57 (1990).

Translated by J. Majling