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SINTERING OF HYDROXYAPATITE CERAMICS, WITH THE AID OF OPTICAL TRANSMITTANCE – TEMPERATURE SPECTRA

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Abstract

The optical transmittance – temperature spectra of well-translucent thin pellets of hydroxyapatite prepared by the high isostatic pressure consolidation of xerogel particles were measured by a newly-developed thermal analysis technique. From these spectra, it was possible to identify temperature intervals with increased or decreased levels of light transmittance, clearly associated with microstructural changes. The thermal processing of treated pellets was stopped at temperatures deliberately chosen with respect to the specific transmittance states. Samples with increased transparency were prepared when the heating of pellets was stopped at the temperatures of the locally highest light transmittance measured.

Keywords: hydroxyapatite, thermal technique, transmittance

Introduction

In a previous report [1], we briefly described a novel thermal technique, for the measurement of the changes in optical transmittance of suitable polycrystalline preforms with temperature up to 1200°C.

Transparent, squeeze-cast gels of hydroxyapatite in the form of thin sheets were used as green preforms.

The present technique was also used to study the crystallization of glasses in the system $LiCl–Li_2O–B_2O_3$ [2].

Recently, after improvements in the measuring method, transmittance curves were measured for high-pressure densified (CIP) hydroxyapatite pellets, and the advantage of the adjustment of the thermal treatment of samples with respect to the specific features of the spectra recorded was pointed out. As a result, ceramics were prepared with enhanced physical properties.

Comparable conventional hot-stage techniques (FP84HT of Mettler Toledo, or KSPS 1000 of A. Krüss Optronic) rely predominantly on the visual inspection of samples and are mostly operative on organic samples in a decreased temperature range.

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Experimental

The present measurements were performed with an LTS 130 instrument designed by the Data System Laboratory, Bratislava. It is an advanced version of the system described in [1] and is based on a computer-controlled conventional furnace operating at up to 1300°C with a built-in optical transmittance instrument. The pellets of materials are radiated on their upper side by focused light, form a high-efficiency LED (light-emitting diode). The transmitted light is collected by an objective and is fed to a sensitive Si photodiode. The temperature control, data acquisition and storage of the measured transmittance is performed with icon-based software which runs under Windows on a PC.

The hydroxyapatite gel was prepared by the usual precipitation from $(NH_4)_2HPO_4$ and $Ca(NO_3)_2$ solutions [3, 4]. Before drying, it was filtered on a Buchner funnel, and twice ultrasonically redispersed and washed in ethanol. Its phase purity was tested by XRD. Thin pellets (1 mm) with a square cross-section of 12 mm^2 were pressed at 50 MPa in a steel die, and were subsequently isostatically pressed at 1000 MPa in a special pressure chamber.

Results and discussion

The prepared hydroxyapatite gel, after calcination at 1200°C, was an X-ray pure product, with no tricalcium phosphate detected.

The pellets used in the experiments were slightly yellow after isostatic pressing and were fairly well-translucent in correspondence to the light transmittance at the start of the measurement (Fig. 1).

Three samples were measured in the present series of experiments. Only two recorded curves (spectra) are shown in Fig. 1 (samples 1 and 3). No smoothing of the curves was applied in the processing of the data.

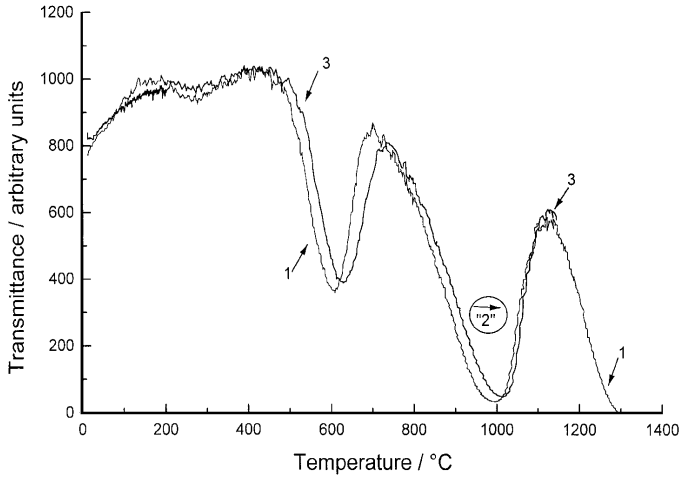

Fig. 1 Light transmittance – temperature records (spectra) of hydroxyapatite polycrystalline preforms; 1 – heating rate 20°C min^{-1}, 3 – heating rate 30°C min^{-1}

Sample 1 was heated at a rate of 20°C min^{-1}, sample 2 at a rate of 25°C min^{-1} and sample 3 at a rate of 30°C min^{-1}. The experiment with sample 1 was finished at 1300°C, at which temperature the furnace was switched off. This sample was nearly opaque after cooling to room temperature (Fig. 2a). The record for sample 2 is not included in Fig. 1 in the interest of the better clarity of the picture. The furnace was switched off at 1050°C in this experiment, at a point midway between the local corresponding transmittance minima and maxima, at approximately 1000 and 1120°C, respectively. The translucency of this sample, after cooling, was higher than that of sample 1 (Fig. 2b).

Sample 3 was heated to a temperature at which, according to the pattern recorded, the transmittance was just behind the local transmittance maximum (1125°C). As in the previous case, the furnace was switched off at this end-point temperature. Sample 3 was best transparent in comparison to samples 1 and 2, after its cooling to room temperature (Fig. 2c).

For a provisional interpretation of the spectra, we may conclude that the systematic shifts in peaks and minima positions are caused by the difference in heating rates applied. Generally speaking, the decrease in transmittance at a particular temperature means that light-absorbing or dissipating species are created in the structure of a material or, if already present, their size changes with temperature to disfavour light transmittance relative to light scattering.

All changes in light transmittance observed in the present experiments were irreversible and not reproduced on repeated heating of samples. The local minimum at nearly 600°C is believed to reflect the cracking of the remnant ethanol molecules, precipitating elementary carbon, which subsequently vanishes on oxidation at higher temperatures. The only evidence of this assertion is the completely black colour of the sample when its heating is stopped at 600°C.

The decrease in light transmittance from approximately 700°C coincides with a shrinkage of the sample, as evidenced by independent dilatometric measurements. This shrinkage is essentially finished at temperatures below 950°C [4]. The creation of larger pores may be hypothesized at temperatures above 700°C, responsible for a decrease in the light transmittance. It is not probable, however, that these will be swiftly healed on further heating (in the temperature interval between 1000 and 1150°C). The increase in the transmittance above 1000°C may account for the partial recovery of the structure, mostly by crystal growth.

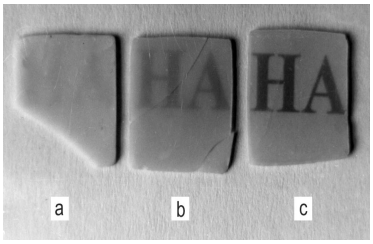

Fig. 2 Comparison of transparency of samples; a – heating rate 20°C min^{-1}, end-temperature 1300°C, b – heating rate 25°C min^{-1}, end-temperature 1050°C, c – heating rate 30°C min^{-1}, end-temperature 1120°C

A detailed interpretation of the records in Fig. 1 remains a matter of continued interest. It necessitates a direct evaluation of microstructural changes by means of SEM and TEM methods. Measurements at constant temperature will permit a study of the kinetics of microstructure evolution, but the nature of the prevailing process must be identified independently.

From a practical aspect, the measured patterns are quite sensitive indicators of the temperatures at which the attainment of microstructures is presumed, with an increased or decreased population of light-dissipating faults. Exploration of other heating profiles and the atmosphere maintenance in heating runs may bring further information concerning the positive control of the microstructure development.

With respect to the very good reproducibility of the results, it may be concluded that measurement of the optical transmittance of polycrystalline (translucent or transparent) specimens in the course of their heating is a hopeful approach for a proper selection and tuning of the processing parameters in order to develop desired ceramic microstructures.

Conclusions

Results are presented concerning a novel type of thermo-optical measurement, consisting in the recording of the light transmittance of suitable polycrystalline samples as a function of temperature. It is shown that the transmittance states are preserved during the sudden cooling of sample to room temperature. The deliberately tuned interruption of the thermal process at temperatures with favourable transmittance states affords samples with improved optical and consequently mechanical properties.

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References

1 J. Majling, Š. Svetík, J. Annus, J. Krištín and P. M. Marquis, Chemical Papers, 51 (1977) 268.
2 P. Znášik, Š. Svetík, J. Kozánková, J. Majling and M. Jamnicky, Termanal'97, Proceedings of the 14th International Conference on Thermal Analysis, CHTF STU Bratislava 1997, p. 86.
3 M. Jarcho, C. Bolen, M. Thomas, J. Bobick, J. Kay and R. Doremus, J. Mater. Sci., 11 (1976) 2027.
4 J. Majling, P. Znášik, A. Palová, Š. Svetík, Š. Kovalík, D. K. Agrawal and R. Roy, J. Mater. Res., 12 (1977) 198.