Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Apparent viscosity reduction during microwave sintering of amorphous silica

A.G. Eremeev[a], S.V. Egorov[a], A.A. Sorokin[a], Yu.V. Bykov[a], K.I. Rybakov[a,b,*]

[a] Institute of Applied Physics, Russian Academy of Sciences, Nizhny Novgorod, Russia
[b] Lobachevsky State University of Nizhny Novgorod, Nizhny Novgorod, Russia

ARTICLE INFO

Keywords:
A: Microwave processing
B: Electron microscopy
B: Microstructure-final
D: SiO_2

ABSTRACT

The sintering of arrays of spherical particles of amorphous SiO_2 was investigated experimentally under microwave (24 GHz) and conventional heating. The materials under study were compacts formed by gravitational sedimentation of monodisperse silica microspheres (1 μm in diameter). The kinetics of neck growth between individual particles was investigated by analyzing SEM images. It was found that the rates of viscous mass transport under microwave heating were significantly higher than those under conventional heating. The values of the viscosity obtained under microwave heating were significantly (by more than an order of magnitude) lower compared to conventional heating. Possible reasons for the viscosity decrease observed under microwave heating may be associated with the influence of water vapor and the action of the electromagnetic field on impurity ions. The interrelation of the observed effect with flash sintering and microwave-enhanced mass transport is discussed.

1. Introduction

Microwave heating has been known for about three decades to cause enhancement of diffusion-based mass transport phenomena in the solid state, including such processes as sintering, joining, annealing etc. [1] The physical reasons for the observed enhancement of processing rates in solid materials under microwave heating (often referred to as the "microwave effect") remain unclear. For the most part, the "microwave effect" was observed in the experimental studies of high-temperature treatment of polycrystalline materials. However, the high-temperature behavior of such materials is complicated due to many different fundamental mass transport mechanisms with almost equal activation energies taking place concurrently.

In recent years a considerable research interest has been attracted to the so called flash sintering processes [2]. Very high densification rates and very short sintering times (sometimes as short as few seconds) were demonstrated when the samples were heated volumetrically – either by dc electric currents (as a supplement to conventional heating) [3,4] or by microwaves [5]. By now it has become generally accepted that the main factor leading to flash sintering is the development of an overheating instability (thermal runaway) in the material. However, as was first pointed out in [4], the increased temperature per se is insufficient to explain the observed ultra-high sintering rates unless additional mass transport mechanisms are activated. A review of the proposed mechanisms can be found, e.g., in [2].

It has been demonstrated experimentally that ultra-rapid (flash) densification of ceramics, at least in the case of microwave heating, is based on transient liquid phase sintering [5,6]. Chaim [7,8] demonstrated that a similar mechanism is responsible for densification during spark plasma sintering (SPS). In essence, the possibility of such a mechanism was suggested by Narayan [9–11] who emphasized the dominant role of selective melting of grain boundaries in field–assisted sintering. While Narayan argued that selective melting of grain boundaries comes as a result of electric field-induced generation of defects, in [5,6] it has been suggested that the grain boundary melting originates primarily from the difference in the melting temperature between the bulk of grains and the near-boundary area, where the crystalline structure is disordered due to the abundance of defects and impurities. The melted or amorphized phases can act as sites of preferential absorption of electromagnetic energy and paths for enhanced mass transport [6,7].

Amorphous and glass-like materials represent the limiting case of media exhibiting no long-range order in the structure. A specific response of such materials to microwave heating was reported in many studies. For example, it has been observed that microwaves accelerate the crystallization kinetics of glass of Li_2O-SiO_2 composition [12] and enhance the process of devitrification in the CaO-ZrO_2-SiO_2 system [13]. In [14] the amorphous lead zirconate titanate (PZT) thin films

* Corresponding author at: Institute of Applied Physics, 46 Ulyanov St., Nizhny Novgorod 603950, Russia.
E-mail address: rybakov@appl.sci-nnov.ru (K.I. Rybakov).

http://dx.doi.org/10.1016/j.ceramint.2017.10.113
Received 11 September 2017; Received in revised form 16 October 2017; Accepted 17 October 2017

were crystallized into the perovskite phase at a temperature of 450 °C at microwave heating, whereas a temperature above 650 °C was needed for crystallization by conventional thermal processing. In a comparative study of the evolution of a silica aerogel under microwave and conventional heating a decrease in the material's viscosity was observed at microwave heating [15].

This paper describes an experimental study of neck growth during microwave and conventional sintering of monodisperse spherical particles of amorphous SiO_2. The possibility of microwave (susceptor-assisted) sintering of a similar material to full density was demonstrated earlier [16]. The objective of this study was to find out whether there is a microwave enhancement of mass transport in an amorphous material during sintering in a simplistic, "model" configuration. The kinetics of neck growth during sintering of amorphous spheres was first described by Kuczynski [17]. Later, the method was further elaborated for revealing the diffusion mechanisms dominating at different stages of sintering [18].

2. Experiment

The samples for the study were prepared by gravitational sedimentation of 99.9% pure SiO_2 microspheres with a diameter of 1.0 ± 0.1 μm (Geltech, Inc.) in distilled water and subsequent drying of the sediment. The obtained compacts, 6 mm in diameter and about 0.5 mm in thickness, were annealed either in the applicator of a 24 GHz 3.5 kW gyrotron-based system [19] or in a conventional resistive oven. In both cases identical heating regimes were used, consisting of a ramp-up at a rate of 60 °C/min up to a preset annealing temperature and a hold at this temperature for 0–30 h. The annealing temperatures varied from 850 °C to 1300 °C. The computer control circuit of the gyrotron system implemented the preset temperature-time schedule of heating with an accuracy better than ± 3 °C. For microwave heating the compacts were placed in a two-layer thermal insulation arrangement made of Al_2O_3-based ceramics (Fig. 1, a). In the case of conventional heating, the samples were put into a preheated oven. An XRD study performed using a *Rigaku Ultima IV* diffractometer confirmed that there was no crystallization in the annealed samples.

A key point in the comparative studies is the accordance between the temperature measurements at microwave and conventional heating. The temperature of the samples during microwave heating was measured by a one-color optical fiber thermometer *Luxtron*. The sapphire light guide was introduced into the thermal insulation arrangement so that thermal radiation was collected from the surface of the sample (Fig. 1, a).

For calibration of the optical temperature measurements separate tests were undertaken. At first, the optical fiber thermometer readings were calibrated by microwave heating of small-size aluminum and copper pieces positioned instead of the SiO_2 samples in the thermal insulation. Their melting temperatures, T_m(Al) = 658.7 °C and T_m(Cu) = 1083 °C, were used as the reference points. The fitting parameters of the optical fiber thermometer were chosen so that the difference between the measured melting temperature values and the reference data did not exceed 5 °C. Then the emissivity of the SiO_2 samples was determined using the readings of an unshielded B-type *Pt-Rh* thermocouple which touched the upper surface of the sample (Fig. 1, b). It should be noted that due to small thickness of the SiO_2 samples there was no appreciable temperature non-uniformities inside the samples.

The microstructure of samples was studied using the scanning electron microscope (SEM) *Jeol JSM-6390LA*. For SEM studies the samples were coated with platinum with the coating layer thickness of approximately 15 nm. The SEM images were taken in the central part of the surface of the samples. An example of an SEM image of the microstructure of a microwave annealed sample is shown in Fig. 2. The neck diameter was determined via direct manual measurement of the narrowest width of the contact zone between a pair of adjoining spheres on printed copies of SEM images. The results of measurements were

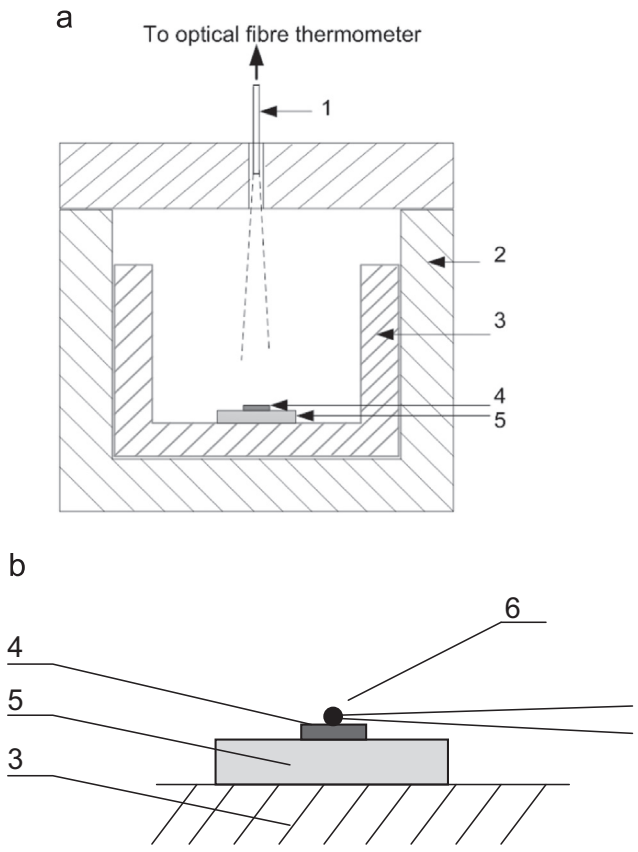

Fig. 1. (a) Schematic view of a sample undergoing microwave heating; (b) temperature calibration test configuration: 1 – light guide, 2 – porous alumina thermal insulation, 3 – alumina ceramic crucible, 4 – sample, 5 – fused quartz support, 6 – thermocouple.

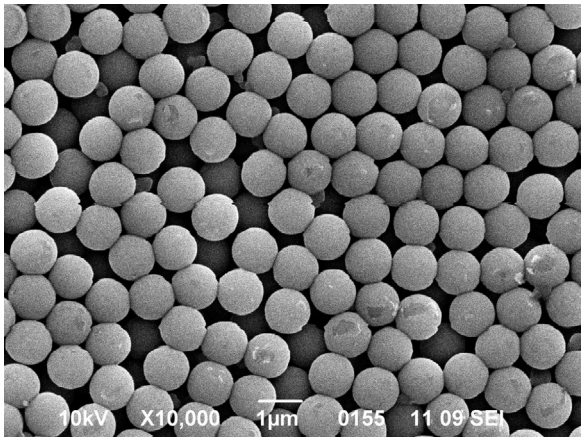

Fig. 2. Example of an SEM image of a sample after microwave annealing (temperature 1050 °C, hold time 30 min).

averaged over an ensemble of particles located within a frame of $14 \times 11.1\ \mu m^2$ (10,000× magnification) which contained 60 – 100 necks. The resulting neck diameter error was determined taking into account the accuracy of direct length measuring, the dispersion of the measured data and the uncertainty in the determination of neck bounds:

$$\delta d = \frac{\Delta l}{l_b} + \frac{\sqrt{(\sigma_d t_{\alpha,n-1})^2 + \left(\frac{\Delta l}{3} t_{\alpha,\infty}\right)^2}}{\langle d \rangle} \quad (1)$$

where δd is relative error of neck diameter, Δl is the instrument error, l_b is the length of an etalon bar being measured on the magnified image,