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ScienceDirect

Journal of the European Ceramic Society 35 (2015) 1599–1603

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Direct indication of a higher central temperature achieved during spark plasma sintering process of a zeolite

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Received 30 June 2014; received in revised form 12 November 2014; accepted 17 November 2014
Available online 4 December 2014

Abstract

The transition between transparent and opaque of as-sintered zeolite samples is employed to study the temperature distribution of non-conducting samples during spark plasma sintering (SPS) process in this paper. The results show that temperature gradients exist in both radial and axial directions, which provide direct evidence of temperature distribution in the SPS process. The sample prepared at 1325 °C is transparent in the center and opaque in the edge, which suggests that the temperature of the center is higher than the edge and the temperature differential is about 26 °C by the thermal analysis model based on the experimental data in ANSYS code. The axial temperature gradient is also present in the as-sintered sample obtained at 1315 °C. The transparent part of the upper surface is larger than the lower surface, which illustrates that the temperature of the upper surface was higher than the lower surface and the difference is about 5 °C.

Keywords: Spark plasma sintering; Temperature distribution; Glass; Disorder; Zeolites

1. Introduction

Spark plasma sintering (SPS, also known as plasma-activated sintering or field activated sintering) is a newly developed sintering technique for consolidation of powders.[1–4] This technique has some general benefits over traditional hot pressing or hot isostatic pressing,[5] such as fast heating rates, short sintering time and low sintering temperatures.[6–8] Owing to these benefits the SPS technique has been widely used to produce metals, ceramics, polymers and also composites in recent years.[9-13]

Although SPS is used to prepare various kinds of materials, the sintering mechanism is not very clear. Lately, many researchers have been focused on the temperature distribution of the SPS process. For example, Wang et al.[14] reported a microstructure inhomogeneity phenomenon in Al_2O_3 sintered bodies. The results showed that the edge of the sintered bodies was denser than the inside and Vickers hardness decreased gradually in the polished cross-section parallel to the direction of pressure from the edge to center. The reasons of these phenomena were that there was a gradient field of temperature in this plasma-activated sintering (PAS) process. Vanmeensel et al.[15] performed the finite element calculations to investigate temperature distribution during field activated sintering by ANSYS code. They observed the radial temperature gradient distribution inside the TiN specimen was much larger than in the 3Y-ZrO_2 specimen during the final holding period at 1500 °C. In addition, they implied that the temperature of center part was lower than the edge in the same surface in the 3Y-ZrO_2 specimen. Mondalek et al.[16] carried out numerical simulations to study the distribution of electric current and temperature in two types of materials. Their results showed that the center temperature of the alumina specimen was lower than the edge temperature before 80 s and it would be reverse after 80 s. Voisin et al.[17] used a structural transformation activated in a TiAl alloy as a marker of the sample temperature and performed finite element modeling to evaluate the temperature distribution. They found the center

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http://dx.doi.org/10.1016/j.jeurceramsoc.2014.11.012
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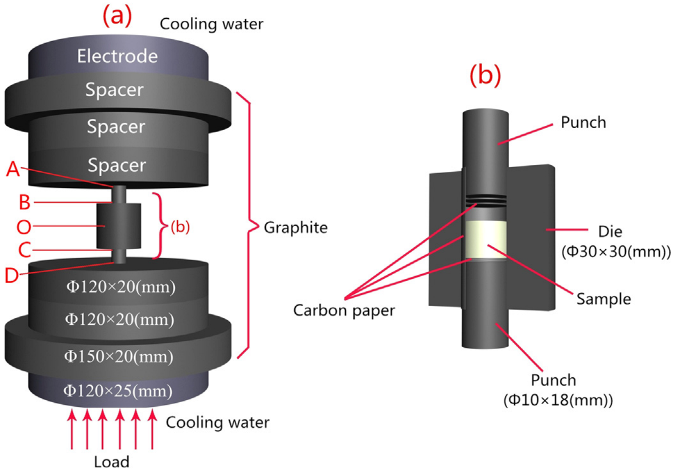

Fig. 1. A schematic of (a) the spark plasma sintering apparatus, (b) die, punches and sample (A, B, C, D and O were different temperature measurement points).

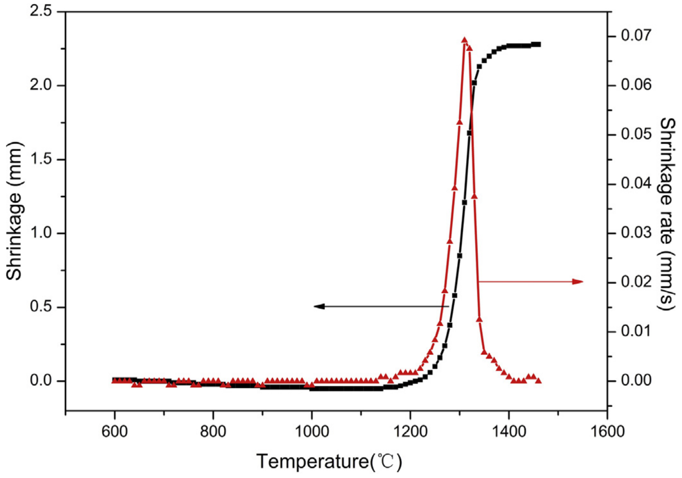

Fig. 2. The shrinkage and shrinkage rate depending on the temperature under a pressure of 50 MPa.

temperature was slightly higher than the edge in TiAl sample, and the data of experiment and simulation exhibited a good agreement. There have been many literatures that used simulation methods to investigate the temperature distribution of samples produced by SPS. However, the temperature distribution in the non-conducting samples is still disputable due to the effects of die, punches and samples. The experimental works are rarely covered on the temperature distribution of non-conducting materials because it's very difficult to find a temperature-sensitive non-conducting material for investigating the temperature distribution directly at high temperature region. In addition, the densification process isn't considered in many simulation works.

Recently, we have been developing the facile and environmentally friendly approach for the preparation of transparent high silica bulk glass and Er^{3+}/Yb^{3+} codoped high silica glass by SPS of microporous zeolite (ZSM-5) precursor powders.[18,19] It was found that aluminosilicate zeolite would suffer from an order-disorder transition (ODT) and transform to transparent glass during SPS process within very short time when the temperature reached above 1250 °C, which indicated that zeolite would be a suitable candidate material for investigating the temperature distribution of the SPS process.[20]

In this paper, the transition between transparent and opaque of as-sintered zeolite samples was used to study the temperature distribution of non-conducting samples during SPS cycle. The thermal analysis based on the experimental data in the finite element code ANSYS was employed for estimating the temperature gradient.

2. Experimental procedure

ZSM-5 powders synthesized by the hydrothermal method were used in this study. The powders were loaded in a Φ10-mm graphite (ISO-68, Toyo Tanso) die, and then put the die into an SPS apparatus (Dr. Sinter 725; Sumitomo Coal Mining Co., Tokyo, Japan). The sizes of the SPS's components are shown schematically in Fig. 1. The temperature was measured using optical pyrometers. An optical pyrometer was focused on the external surface (position O) of graphite die to measure the temperature from 575 °C to the final sintering temperature. Another one was used to measure the temperature of position A, B, C and D of the punches. All the optical pyrometers were corrected. The heating rate was 100 °C min^{-1} when the temperature rose from 600 °C to the final temperature. And the pulse on/off ratio was 12:2. A 50 MPa uniaxial pressure was applied during the SPS process. The powders were sintered under vacuum at different temperatures (position O) from 1300 °C to 1400 °C with no holding time. The temperature distribution was intuitively indicated by the schematic diagrams of samples.

3. Results and discussion

Fig. 2 shows the dependence of shrinkage and shrinkage rate to the temperature. It could be found that the shrinkage started at 1200 °C and ended at 1400 °C. The shrinkage rate increased dramatically when the temperature exceeded 1250 °C and then reduced sharply until the temperature rose to 1350 °C. The recorded maximum shrinkage rate was 0.069 mm s^{-1} at 1310 °C. It was indicated that the order-disorder transition process of ZSM-5 started about 1250 °C and ended near 1350 °C. Thus this material is very sensitive to the temperature at the range of 1250–1350 °C. This temperature window appears useful for studying the temperature distribution in SPS experiment.

Five temperatures were selected as the final sintering temperature, which were 1300, 1325, 1350, 1375 and 1400 °C, respectively. The photographs of the samples prepared at the above temperature points are shown in Fig. 3. It was observed that the sample sintered at 1300 °C was not transparent, which indicated that the sintering did not complete. With the temperature increased, the samples were become transparent. One interesting result was that the sample sintered at 1325 °C was transparent in the center and the samples obtained above 1350 °C were completely transparent. It was shown clearly that the temperature gradient existed between the center and edge of sample during SPS process. The samples switched from a white bulk to a completely transparent glass in a narrow temperature range,