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Review article

A review of two-step sintering for ceramics

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ABSTRACT

The development of high-density ceramic materials with fine-grained microstructures has been studied to considerably improve their properties for high-performance applications. Many alternatives have been searched to refine their microstructure by changing their composition and/or processing. Among such alternatives, the densification of ceramic materials by sintering curve control is an effective, simple and economical microstructure refinement method. Thus, different thermal treatment techniques such as spark plasma sintering and microstructural forms of control such as the control of sintering conditions have been used to obtain nanostructured materials. One of the techniques widely used in recent years is two-step sintering. Two-step sintering (TSS) is a promising method used to obtain high-density bodies and smaller grain sizes. Two TSS methodologies are known: sintering with thermal pretreatment at a low sintering temperature, followed by a second stage at elevated temperature, and the more recent approach presented by Chen and Wang, which has been the most widely used. In addition to the sintering conditions (temperature, heating rate and sintering holding times) that must be suitable for each composition type, the starting materials, particle size and processing method may influence the obtained microstructure, especially the reduced grain size and increased densification. The current review of two-step sintering presents the effect of this technique on the grain density and sizes of different ceramic materials. The influence of the addition of doping agents and its effect on the mechanical properties in different systems is also presented in the current study.

Contents

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1. Introduction

The properties of polycrystalline ceramics are controlled by the microstructure. The density, grain size and presence of heterogeneities in the microstructure are carefully controlled to improve the properties and reliability of ceramics [1]. Highly dense ceramics with nanometric or submicrometric grain size are difficult to obtain through conventional sintering.

However, there are some manufacturing routes available for the production of these ceramics, including colloidal powder processing with controlled distribution of particle sizes [2,3], the use of sintering additives [4], pressure-assisted sintering [5,6], spark plasma sintering (SPS) [7] and pulsed electric current sintering (PECS) [8]. These sintering methods may not be cost-effective for any materials because the devices are more complex, expensive and difficult to implement.

Solid-phase sintering requires relatively high temperatures to facilitate diffusion and, through different mechanisms, promote material densification. However, diffusion is the matter transport mechanism, which promotes not only densification but also grain growth. Therefore, sintering conditions that allow densification to occur without simultaneously stimulating grain growth are suitable for microstructural refinement. This dissociation between densification and grain growth is what allows highly dense ceramics and nanometric grains to be produced [9].

An outstanding technique used to manipulate the microstructure during the sintering stage is known as rate-controlled sintering (RCS), which was first reported in 1965 [18]. There are several studies about this issue; however, the equipment advance and the improvement in the theoretical and empirical models related to the microstructure development and densification allowed the advancement in the RCS technique.

In the 1990s, Chu et al. [10] introduced the two-step sintering (TSS) technique, which is described in the current study as TSS-C. According to this technique, the first stage (pretreatment) was performed at a relatively low temperature and was followed by a higher-temperature stage and subsequent cooling. The process allows refinement of the microstructure and, thus, improvement of the material properties.

Later, Chen and Wang [11] suggested a modification in the two-step sintering technique. This modification, which is identified in the current study as TSS-CW, has become widely used. This technique consists of suppressing the accelerated grain growth, which usually occurs in the final sintering stage. High-temperature heating is performed and is followed by structural freezing. Fast cooling at a constant rate suppresses grain growth but allows densification to occur [11,12]. The technique may be successfully applied to many ceramic materials, thus enabling high-density microstructure refinement and improving several properties of the materials.

The aim of the current review is to present the state of the art of two-step sintering applied to ceramic materials. Thus, the study is divided into three main topics. First, a brief history of the two-step sintering technique (TSS) evolution will be presented, followed by a presentation of papers that used the methodology suggested by Chu (TSS-C) and, finally, studies that addressed the two-step sintering technique suggested by Chen and Wang (TSS-CW). This section shows the effect of the addition of doping agents and that of the processing characteristics on the grain density and size in each ceramic material type identified in the literature and compares it to conventional sintering (CS). It also presents a CS contribution to the improvement of mechanical properties.

2. Historical context

Studies about controlled sintering methodology date back to the mid-1960s, which was when the first studies on the RCS method emerged [13–24]. This term was first introduced by Palmour and Johnson in 1965 [18]; the methodology consists of microstructure refinement by sintering curve manipulation, and it features advantages such as simplicity and economy. The procedure consists of determining the relationship between the densification rate and the grain growth rate, thus suggesting temperature and sintering time values for material densification [20,21]. Therefore, ultrafine nickel powders were sintered at controlled rates, and high-density materials (~99% relative density) with a grain size smaller than 100 nm were obtained.

Thus, controlled-rate sintering is an effective methodology in the obtainment of dense bodies with a nanocrystalline structure [21].

In 1991, Chu et al. [10] conducted a study about the sintering process of conventional alumina (Al_2O_3) and magnesium oxide (MgO) powders. Conventional isothermal sintering and pre-coarsening at a low temperature were comparatively evaluated before the use of conventional isothermal sintering. The two-step sintering technique suggested by Chu (TSS-C) was favorable for systems with wide-particle-size-distribution conventional powders, and it produced uniform ceramic bodies in a simple way [10].

However, in 2000, Chen and Wang [11] suggested a new methodology for the two-step sintering (TSS-CW) technique, according to which the ceramic body is rapidly subjected to a high temperature and is subsequently cooled and kept at a lower temperature (sintering holding time). The authors report that densification occurs with no grain growth in a certain temperature range called the "kinetic window". Residual porosity is eliminated at this temperature level during sintering with no grain growth, which occurs at the final stage [11,12]. The grain growth suppression, but not its densification, is determined by a network of grain boundaries anchored by joints in the triple points, which have higher activation energy for migration than the grain boundaries. However, the critical density must be achieved in the first stage so that there are sufficient triple joints throughout the body [12].

A sufficiently high relative density (70% or higher) is recommended in this first stage [11,25]. The sintering temperature decreases to a critical level, leading the triple joints to interrupt the grain growth, whereas densification is not affected. The samples must then be exposed to prolonged heating at a low temperature in the second isothermal stage [11]. Fig. 1 schematically depicts the comparison between the TSS-C and TSS-CW sintering curves.

3. Two-step sintering method by Chu

The two-step sintering suggested by Chu (TSS-C) was applied to different ceramic materials. Huang et al. [26] evaluated the obtainment of silicon nitride (Si_3N_4) through this method and found increased material densification, although the grain size growth