Mechanical Treatment of ZrB_2 -SiC Powders and Sintered Ceramic Composites Properties

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Abstract The effect of mechanical treatment by planetary ball milling on the properties of hot pressed ZrB_2 -SiC ceramics was studied. It has been shown that material densification after mechanical treatment is finished on initial stages of sintering process. Addition of SiC leads to essentially increasing of sample density up to 99% of a theoretical one for powder with 20% SiC, as compared with ZrB_2 not higher when 76%. It has been shown that all defects which were accumulated during mechanical treatment are annealed during hot pressure process and there are no any changes of coherently diffracting domain (CDD) values in sintered ceramics. The model was suggested to describe of three-layered porous composite synthesis at the conditions of hot isostatic pressing and investigate the porosity evolution during synthesis. Model takes into account the conjugate heat exchange between sintered materials and walls of the reactor.

Keywords High temperature · Hot pressured process · Milling
Modeling

Introduction

The refractory compounds are the basic components of materials used in high-temperature engineering, as thermal protection of space vehicles, in electronics, etc. Among materials with high melting temperature, the special attention is attracted

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with ceramic composites based on ZrB_2 , however strong covalent bonds are the reason of low atom diffusion mobility that essentially stipulate sintered samples.

It is known [1] that addition of SiC leads to decreasing melting temperature of ZrB_2 -SiC system and therefore one can obtain a higher density of sintered material. Besides this, ZrB_2 -SiC ceramics are characterized a high thermochemical stability, including high stability to oxidation in conditions of extra-high temperatures.

The composites ZrB_2 -SiC are usually obtained by sintering of powders under pressure at temperatures higher when 2000 °C [2] and for lowering of a sintering temperature, the powders undergo a mechanical treatment using high-energy (planetary) mills. In this case, subsequent sintering will be activated due to increasing of numbers defects, acceleration of diffusion processes and simplification of plastic flows during sintering [3], and process of sintering one can carry out under pressure, i.e., to realize a mode of hot pressing or SPS process [4]. Unfortunately, data on influence of mechanical treatment on properties of powders and the process of subsequent hot pressure are investigated not enough.

Today, new composite material synthesis attracts numerous investigators, and it is characterized by complex ideas and combined technologies. It connects with the necessity to obtain the materials with specific properties, for example, materials resistant to high thermal and mechanical loading simultaneous. Porous composites can be considered as a suitable example [5, 6]. Because the technologies are very complex and multiple-factor, mathematical modeling is used for the investigation. Theory and technologies of sintering are described for example in [7–10]. Numerous authors describe the temperature change in complex areas, residual stresses, density, porosity viscosity and mechanical properties evolution, the junction formation between individual particles, etc. The series of publications is devoted to the modeling of new material synthesis for the conditions of the heating combined with mechanical loading or to the study of possible stationary conversion regimes [11–14]. However, the coupling models taking into account the interrelation between the heat and mechanical processes and the conditions of conjugate heat exchange occurred not very often. Even so, when commercial software's are available, there are a lot of problems in the modeling [15]. Applications of coupling models [16, 17] to particular technology situations were described in [18, 19]. Generalized model of viscous elastic body of Maxwell type was used in [18] to describe the synthesis process combined with the extrusion. In [19], the material consolidation for the conditions of stress-assisted spark plasma sintering was studied taking into account conjugate heat exchange.

So, the aim of this paper is the study of influence of mechanical treatment of ZrB_2 -SiC powders on their properties and properties of sintered by hot pressured ceramic composites and to develop simple model for the formation of porous ceramic composite consisting of three layers.

Materials and Experimental Procedure

The researches were carried out on powder mixtures ZrB_2 ($d_{50} = 2.5$ microns) SiC ($d_{50} = 4.2$ microns) with the SiC contents 10, 15 and 20 vol.%. The mechanical treatments of powders were made in a planetary mill at centrifugal acceleration approximately 30 g; the duration of processing was up to 20 min. The hot pressure of ceramic composites was carried out at temperature 1800 °C and pressure 50 MPa with isothermal sintering 30 min. A raw density of mixtures, phases and its structure and coherently diffracting domains (CDD) using x-ray with $\text{CuK}\alpha$ irradiation have been measured accordingly [5]. Scanning electron microscope observations operated at 20–30 kV were used to determine the structure and average grain size using Tescan VEGA-3SBH.

Results and Discussion

Mechanical Treatment of ZrB_2 -SiC Powders in Planetary Milling

In Fig. 1, the dependence of relative density ρ_r/ρ_t (ρ_r raw density, ρ_t theoretical density) versus treatment time is presented. As one can see, for all powders, the increasing of treatment time was accompanied by increasing its raw density, and particles morphology are essentially changed from separate particles in the beginning state up to agglomerate formation at the end of treatment, Fig. 2. Before treatment, the smallest raw density had ZrB_2 powder, however after processing its density had increased essentially more, than raw densities of powder mixtures with SiC, these mixtures in an initial state had a very close values ρ_r/ρ_t , but after

Fig. 1 The dependencies of raw density of ZrB_2 -SiC powders after mechanical treatment in planetary milling

Fig. 2 The changing of powder morphology during milling time

Fig. 3 CDD versus milling times of powder and sintered ceramics

treatment, the higher raw density had powder with the maximal contents of SiC. The x-ray phase analysis of mixtures had shown that during treatment, there are no any changes, addition of SiC to mixtures leads to appearing of peaks belongs to it. With increasing of time treatment, we have found a broadening of peaks due to an increasing number of lattice defects and decreasing of CDD, or grain sizes from 46 up to 37 nm, Fig. 3.

Mathematical Model of Three-Layer Composite Synthesis During Hot Isostatic Pressing

The mathematical model corresponds to Fig. 4, where the reactor is presented. It is assumed that powder mixture behavior can be described similarly to viscous liquid. At the initial time moment, we have in the chamber three layers of powders with different chemical compositions and properties. Mechanical and thermal-physical

Fig. 4 Illustration to the problem formulation

properties of green powders are known. The contact between layers is assumed as an ideal, in a first approximation. Macroscopic thermal stresses are small. Friction with walls is negligibly small too. The dependencies of the properties on porosity are taken into account. In turn, the porosity changes during the heating and loading. Heat exchange of powder mixture with the walls leads to the appearance of not uniform temperature field and can be the cause for not uniform composition change in the layers during synthesis. As a result, mathematical problem formulation will include two parts: mechanical and thermal-kinetical. Correctness of this approximation is confirmed by the results [18].

Mechanical part of the problem consists of one-dimensional motion equation and rheology relation

$$\rho \rho_s \left(\frac{\partial V}{\partial t} + V \frac{\partial V}{\partial z} \right) = \frac{\partial \sigma}{\partial z} \quad (1)$$

$$\sigma = \left(\zeta + \frac{4}{3} \mu_v \right) \frac{dV}{dz}, \quad (2)$$

where V is the component of velocity vector and σ is the component of stress tensor in the loading direction, ζ and μ_v are the volume and shear viscosity; ρ is relative density connecting with the porosity η by the relation $\rho = 1 - \eta$. Porosity changes correspondingly to some law depending on many physical parameters. Physical properties are different for each layer. Load is given. In the contact plane between plunger and flayer A, the loading condition takes a place

$$z = \xi(t) : -p(t) = \sigma = \left(\zeta + \frac{4}{3} \mu_V \right) \frac{dV}{dz}$$

This model is similar to [20], however, the thermal-kinetical part of the model takes into consideration the heat exchange between different materials including the losses to the plunger, the heating from the wall, etc. That is, we have two-dimensional problem containing the thermal conductivity equations for the plunger, bottom, and walls.

$$c_k \rho_k \frac{\partial T_k}{\partial t} = \frac{\partial}{\partial z} \left(\lambda_k \frac{\partial T_k}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left(\lambda_k r \frac{\partial T_k}{\partial r} \right), \quad k = 1, 2, 3 \quad (3)$$

and for powder layers

$$c_k \rho \rho_{ks} \left(\frac{\partial T_k}{\partial t} + V \frac{\partial T_k}{\partial z} \right) = \frac{\partial}{\partial z} \left(\lambda_k \frac{\partial T_k}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left(\lambda_k r \frac{\partial T_k}{\partial r} \right) + \sigma \frac{\partial V}{\partial z}, \quad k = A, B, C \quad (4)$$

Here, c_k, ρ_k, λ_k —are the heat capacities, densities, and effective thermal conductivities of materials.

The conditions of ideal heat contact are assumed in the interfaces between different materials («1–2»; «1–3» and «2–3», and «A–B», «B–C» also etc.) The symmetry condition is correct for the axis $r = 0$. The radiation heat exchange with environment takes a place on the surface of plunger. Lateral surfaces of press-tool are heated by radiation. The heater temperature T_w changes by given law that determines the powders mixtures rate. The moving boundary $\xi(t)$ is calculated during problem solution.

At the initial time moment, all properties and initial porosity are given, the velocity and stresses are zero. Then, the porosity θ evolution leads to the properties change and in a first approximation, these relations are

$$c_k = c_{k0}(1 - \theta); \quad \rho_k = \rho_{k0}(1 - \theta); \quad \lambda_k = \lambda_{k0} \exp\left(-\frac{1, 5\theta}{1 - \theta}\right);$$

$$\mu_V = \mu_{V0} \frac{3(1 - \theta)^2}{3 - \theta(1 - \theta)}; \quad \zeta_V = \mu_V \frac{4}{3} \frac{1 - \theta}{\theta}$$

and we can study numerically the problem of three-layered composite sintering under pressure.

To realize numerically the proposed model, we develop a special algorithm based on implicit difference schemes and taking into account the difference mesh deformation in the calculation area with moving boundaries. The calculations showed that the result (porosity, properties, layer size, etc.) depends on the applied pressure, composition of green substances (powders), and heating regime. For example, different layer thickness evolutions are presented in Fig. 5 for identical

Fig. 5 Layer thickness versus time for **a** identical properties of layers ($P = 40$ MPa) and **b** for layers with different properties ($P = 20$ MPa). Layer A (1), B (2), C (3)

Fig. 6 Temperature along the axis Oz . Time $t = 12$ (a), 25 (b) and 45 s (c). The regime corresponds to Fig. 2b

(a) and different materials (b). It was found that the temperature field is inhomogeneous. It happens because materials have different properties, porosity evolution for various materials (layers) occurs with different kinetical parameters, there are viscous dissipation in the volume and heat losses from the sintered materials to the walls and bottom of the reactor. This corresponds to known experimental data [5, 6]. The temperature field is presented in Fig. 6 for three time moments (12, 25 and 45 s). One can see that the specimen size diminishes. It occupies the area between vertical dotted lines. The figures are presented in the coordinate system associated with interface 1-A.

Hot Pressured $\text{ZrB}_2\text{-SiC}$ Ceramics After Mechanical Treatment of Powders

After hot pressure of ceramics, the phase content does not change, and increasing of treatment time in a planetary mill before sintering does not change a CDD on sintered materials, Fig. 3. This means that all defects are annealed during hot pressure process. In Fig. 7, the densities of hot pressured samples are shown.

Fig. 7 Relative density ρ/ρ_t of hot pressured ceramics versus milling time of powder

Fig. 8 The dependence of parabolic index n of sintering process versus SiC content in powder

As one can see, addition of SiC leads to essentially increasing of sample density—its values up to 99% of a theoretical one for powder with 20% SiC, as compared with ZrB_2 not higher when 76%. This is agreeing well with data [21]. So, these raw densities of powders seem very well for sintering process of ceramics.

The experimental data of relative density changes of sintered materials are well described by simple function like $Y = aX^n$ where parameter n characterizes a speed of density change. Its may be easy to determine by re-plotting these dependencies in log–log coordinates, then the inclination of a straight line will be equal to this parameter. Thus, defined parameter “ n ” is shown in Fig. 8, and as one can see the

addition of SiC to mixture leads to decreasing up to four time its value. This means besides the sample density after hot pressure, that material densification is finished on initial stages of sintering process.

Conclusions

- Mathematical problem of three-layered composite sintering under pressure was proposed in this work. Numerical realization of the problem was carried out. It was detected that the temperature field is nonhomogeneous due to difference in the properties of sintered materials and walls of the reactor. It was found that the porosity changes in a different way in the layers, and its changing are nonhomogeneous along the loading direction.
- It was shown that material densification after mechanical treatment is finished on initial stages of sintering process.
- Addition of SiC leads to essentially increasing of sample density up to 99% of a theoretical one for powder with 20% SiC, as compared with ZrB₂ not higher when 76%.
- It was shown that all defects which were accumulated during mechanical treatment are annealed during hot pressure process and there are no any changes of CDD values in sintered ceramics.

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