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The Role of Plastic Flow in Processes of High-speed Sintering of Ceramic Materials under Pressure

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Abstract

A model to describe the kinetics of the compaction of conductive nitride ceramics using electropulse technologies is developed. The relationship between density and pressure is established on the basis of three components of the geometric, plastic and stressed state, which is affects the contact area between the particles. The model takes into account the change in the relative area of the interpartial contacts under the action of two mechanisms of mass transfer-diffusion and plastic flow.

It is shown that a decrease in the particle size of the powder leads to an in-crease in the diffusion contribution and a decrease in the plastic flow, at all other conditions being equal. And for the case of nano-sized particles, diffusion mass transfer is predominant. Increasing in the heating rate leads to a decrease in the contribution of dif-fusion mass transfer at equal temperatures, as well as to an increase in the temperature of the beginning of shrinkage.

The processes of plasma-plasma sintering, high-voltage electro-pulsed consolidation and hot pressing control the same mechanisms, plastic flow and diffusion mass transfer, which do not require, in the first approximation, the influence of the electric current on the properties of materials.

Keywords: spark-plasma sintering, high-voltage electrodischarge consolidation, sintering kinetics

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1. INTRODUCTION

At present, sintering technologies for powder materials, where electric current are using as a heating method, are becoming increasingly widespread [1]. This is hot press-ing with direct current transmission, spark-plasma sintering (SPS) and high-voltage electro discharge consolidification (HVEDC). They differ from each other by the param-eters of the acting current. Advantages of these technologies include high sintering rates and, more importantly, reduced macroscopic sintering temperatures and holding

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times in comparison with conventional sintering. However, until now systematic study and explanation of the processes and mechanisms of sintering of nitride ceramics in electropulse methods has not been carried out.

During hot pressing, the powder undergoes three stages of compaction: the rearrangement of the particles as a whole, the formation of contacts between individual powders and the actual compaction ($0.6 < D < 0.9$), and finally, the formation of individual closed pores and their slow "resorption" ($D > 0.9$). As shown by Fishmeister and colleagues [2, 3], the rearrangement of the particles as a whole by slipping at the initial stage leads to an insignificant compaction (the final density is not more than $0.63 < D$). The main effect of the rearrangement of the powder is that it leads to the formation of a dense structure with a high coordination number (CN) for individual powders. It is in this structure that further plastic deformation takes place, accompanied by the convergence of the centers of individual particles, which leads to compacting of the compact as a whole, and is also accompanied by a change in the area of interparticle contacts, which reduces the effective stress, and, as a consequence, deceleration the compaction process.

As follows from the above, at each individual moment of pressing time, the resistance of the powder to further compaction is determined by the number and size of the contacts between the particles. The relationship between density and pressure can be established by dividing the process into three components:

1. geometric - the density of the compact is determined by the deformation of the particles and can be characterized by the average CN and the average area of contacts per particle;

2. plastic - the size of the contacts depends on the local stress and temperature in the contact area and the deformation ability of the powder particles;

3. stress state - pressing pressure leads to the appearance of a spectrum of contact stresses, which can be replaced by the average value of the contact stresses, which is a function of the applied.

Because compacting occurs in the compact during the convergence of the center of the particles, in the process of shrinkage new pairs of particles will convergence to each other, increasing the CN and forming new interparticle contacts. For the model geometry of pressing of spherical powders, it is shown that an increase in CN is a continuous process. It increases from ~ 7 in the initial compact ($D \sim 0.63$) to ~ 14 in a dense body with separate closed pores along the grain boundaries ($D \sim 0.96$)

During compaction, each particle changes its shape and form contacts with neighbors until, at a close to theoretical density the structure of randomly packed spherical

particles does not go over into the structure of the polyhedra that, which fill the volume. Assuming that the process of compacting particles is homogeneous, these polyhedra will be similar to the Voronoi cells for the initial packing. The condensation can be represented as a proportional reduction of the Voronoi cells, and the deformation of the particles will be uniquely related to the faces of the decreasing particles, by distributing the material from the contact region along the mechanisms of plastic deformation and diffusion mass transfer.

Artz and co-workers [3] obtained the dependences of CN - density for the mechanism of plastic flow and diffusion mass transfer, equations 1 and 2, respectively:

$$\begin{cases} Z^{\text{yield}}(D) = Z_0 + 9,5(D - D_0) & D < 0,85 \\ Z^{\text{yield}}(D) = Z_0 + 2 + 9,5(D - 0,85) + 881(D - 0,85)^3 & D > 0,85 \end{cases} \tag{1}$$

$$Z^{\text{diff}}(D) = Z_0 + C \left[\frac{D - D_0}{3D_0} - \left(\frac{D - D_0}{3D_0} \right)^2 \right] \tag{2}$$

And also the average values of the area of contacts, equations 3 and 4:

$$a^{yield} = 3(D - D_0) \tag{3}$$

$$a^{\text{diff}} = 5,5(D - D_0) \left[1 - (D - D_0) \right] \tag{4}$$

Dependences of the area of contacts and CN on the density for plastic flow and diffusion mass transfer are shown in Fig. 1.
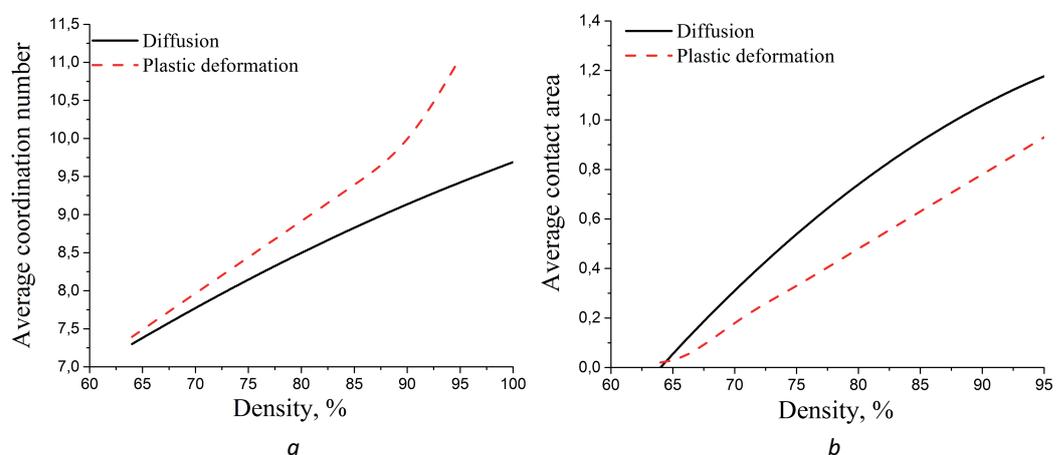

Figure 1: Dependence of the average coordination number (a) and the average area of contacts (b) on the relative density for cases of plastic deformation and diffusion mass transfer.

Expressions 1-4 completely describe the geometric component of the compaction process. Using them, we can proceed to determine the stresses at interparticle contacts and determine the rate of particle deformation during the sintering process.

The pressure applied to the compact leads to the appearance of forces acting on the particles from the side of interparticle contacts. Considering the random packing of particles, Molerus in [4] showed that the exact values of the forces can be replaced by their statistically averaged value - equation (5):

$$f = \frac{4\pi R^2}{ZD} \cdot p \qquad (5)$$

where p – pressure applied to the compact.

Further, to determine the dependence of the shrinkage rates on the density, it is necessary to break the entire density interval into two regions with a principally different geometry-the initial stage and the final stage of sintering. Figure 2 shows the dependence of the proportion of open and closed porosity on the density.
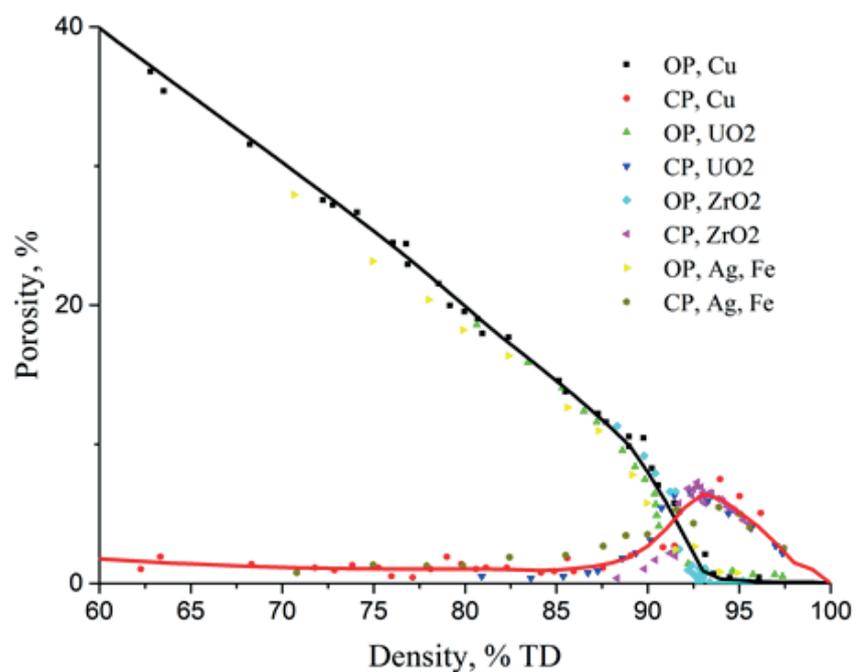

Figure 2: Change in open and closed porosity during sintering and pressing powders.

From Fig. 2 it clearly follows that up to density values of about 87%, all porosity is open. In the range of 87-93% density, a rapid increase in the fraction of closed porosity begins, and at a density of 93%, almost all of the porosity becomes closed.

Therefore, the initial sintering stage (up to a density of 93%) can be suitably described using a two-particle sintering model for two spherical particles, whereas the final stage (density > 93%) can be considered as closing an isolated pore [5].

In the case of a competing effect of two mechanisms of mass transfer-plastic flow and diffusion, the effective value of the stresses in interparticle contacts will be composed of stresses caused by the force and capillary forces p_s arising on the curved surface of the neck:

$$\sigma = \frac{4\pi R^2}{ZD} \cdot \frac{p}{a} + p_S;$$

$$\to \sigma = \frac{4\pi R^2}{ZD} \cdot \frac{p}{a} + \frac{2R - 3x}{x^2}\xi \qquad (6)$$

$$p_S = \gamma\left(\frac{1}{\rho} - \frac{1}{x}\right), \quad \rho = \frac{x^2}{2(R-x)};$$

ξ- surface energy, x- cervical radius equal to $x = (D - D_0)^{1/2}R$.

For the case of plastic deformation, take the dependence of the strain rate on the stress in the form of a power law, as in equation 7:

$$\bar{\dot{e}} = \epsilon_0\left(\frac{\bar{\sigma}}{\sigma_0}\right)^n \qquad (7)$$

where $\bar{\dot{e}}$ и $\bar{\sigma}$ - equivalent strain rate and stress, respectively, and ϵ_0, σ_0, n – constant, characteristic for the material.

The rate of deformation from dimensional considerations must be equal to $\dot{\gamma} = C\bar{\dot{e}}x$. Using Hertz's solutions to deform two elastic spheres when squeezing, we obtain (8):

$$\bar{\sigma} = \frac{1}{3}\sigma; \quad \dot{\gamma} = \frac{9\pi}{16}\bar{\dot{e}}x \qquad (8)$$

Substituting these values into equation (7), we obtain:

$$\dot{\gamma} = \frac{9\pi^2}{16}x\epsilon_0\left(\frac{\bar{\sigma}}{3\sigma_0}\right)^n \qquad (9)$$

Differentiating equation (3), we obtain the dependence of the compaction rate on the strain rate:

$$\dot{D} = 3(D^2 D_0)^{1/3}\frac{\dot{\gamma}}{R} \qquad (10)$$

Combining equations (9) and (10), we obtain:

$$\dot{D}_{yeld} = 16,64 \cdot (D^2 D_0)^{1/3}\frac{x}{R}\epsilon_0\left(\frac{\bar{\sigma}}{3\sigma_0}\right)^n \qquad (11)$$

where $\dot{D}_{yeld}$- compaction rate, by the mechanism of plastic flow.

Now we consider the case when diffusion is the determining contribution to the compaction. The condensation in this case is due to the diffusion mass transfer of the material from the contact area to the region of the formed neck, which leads to the convergence of the centers of the two particles. Then the compaction rate will be equal to the rate of material transfer by the diffusion mechanism along grain boundaries and

through the volume of particles. This problem was solved by Wilkinson [5], equation 12:

$$\dot{D}_{\text{diff}} = \frac{(\delta D_{gb} + \rho D_v)\Omega}{kTR^3} Z \cdot F(D) \cdot p_{\text{eff}}, \tag{12}$$

$$F(D) = 12 D^{1/3} D_0^{2/3} \left[\left(\left(\frac{D}{D_0} \right)^{1/3} - 1 \right) \cdot \left(Z_0 + C \left(\left(\frac{D}{D_0} \right)^{1/3} - 1 \right) \right) \right]^{-1} \tag{13}$$

where $\dot{D}_{\text{diff}}$-compaction rate due to diffusion mass transfer, Ω- atomic volume, δD_{gb} - composition of the width of the boundary by the coefficient of boundary diffusion, D_v- bulk diffusion coefficient.

Then, jointly solving the obtained equations, it is possible to determine the kinetics of shrinkage of the powder compact during sintering, depending on external parameters - temperature, applied pressure and size of powder particles.

2. RESULTS AND DISCUSSIONS

For numerical solution of differential equations (11-12), describing the change in density from time, temperature and pressure, we use the mathematical package Mathcad-Prime - 4.0.

The main regularities of compaction from sintering regimes for uranium, titanium and zirconium nitrides are close in view of the closeness of their properties. In the future, we will use the material parameters calculated for the stoichiometric nitride of titanium, which, because of the non-stoichiometry of the powders studied, will differ with the real parameters, but allow us to qualitatively evaluate and compare with the experimental results the results of modeling.

The main parameter that distinguishes hot pressing, SPS and HVEDC is the heating rate of the sintered material, while the physical mechanisms leading to sintering of the powder are the same.

The relative contribution of these mechanisms - plastic flow and diffusion mass transfer - depends mainly on the size of the sintered particles.

The dependence of the compaction on time at average heating rates, characteristic for both hot pressing and for SPS (100 K / min) for different diameters of sintered powders is shown in Fig. 3.

From the results obtained from the model, it can be seen that the rate of compaction by plastic deformation is almost independent of the change in the diameter of the particles within the limits typical for commonly used powder (1-10 µm). Only the transition to nanopowders leads to an insignificant acceleration of the process. However, as can
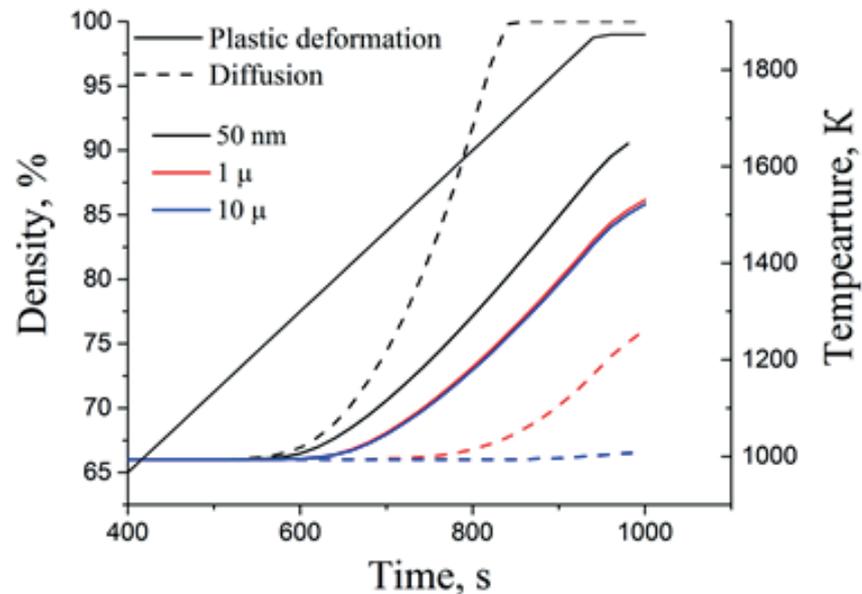
Figure 3: Dependence of the sintering kinetics on the particle size (100 K / min, 100 MPa).

be seen from Fig. 3, the decrease in the size of the powders leads to a sharp increase in the relative rate of diffusion mass transfer, which is associated with an increase in the degree of curvature of the neck, and, accordingly, an increase in the driving force of diffusion mass transfer. It follows from the calculated data that only sintering of nanopowders is controlled, mainly, by diffusion mass transfer.

It was previously shown that for powders with a particle diameter of 1 μm, the main mechanism of compaction is plastic flow, then the parameter applied most strongly to shrinkage should be the pressure applied to the compact. The results of compaction calculations for various applied pressures are shown in Fig. 4.

Initially, the design model was constructed for random dense packing of spherical powders, which leads to an initial density of 0.63. In reality, an increase in pressure leads to the fact that the process of self-sintering begins with different initial press densities, which should influence to the kinetics of further compaction.

Calculation of the compaction process according to the parameters relevant HVEDC presented in Fig. 5. The analysis of the results shows that the speed of the compaction process is maximal during the passage of the current pulse, then at a practically constant temperature the shrinkage goes linearly at approximately constant temperature, which correlates with the conclusions of the authors of the papers in which the shrinkage kinetics of the material were experimentally studied.

The increase in pressure leads to an increase in the final density of compacts and the shrinkage rate both at the heating stage and at the holding stage (Figure 6). These
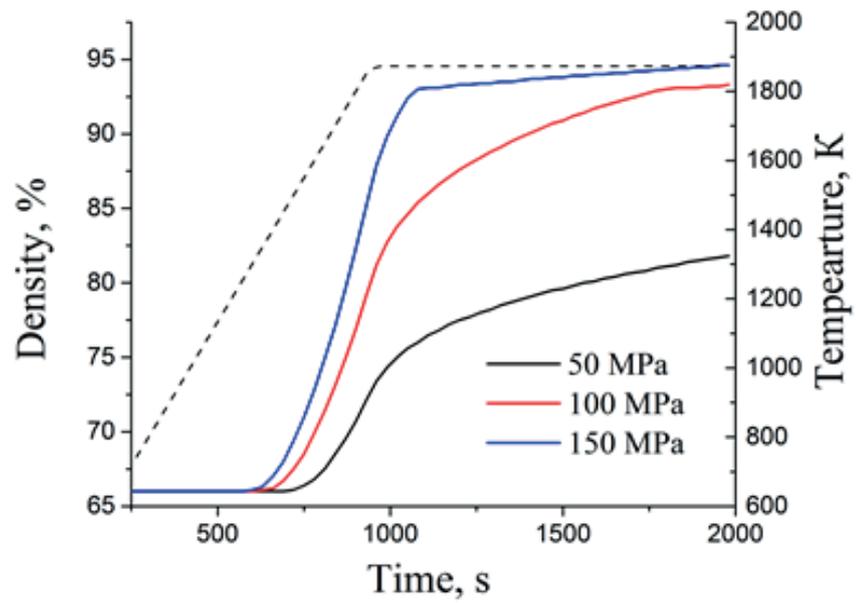
Figure 4: Dependence of the sintering kinetics on the applied pressure (100 K / min, 2 μm) in the tight packing model of spheres.
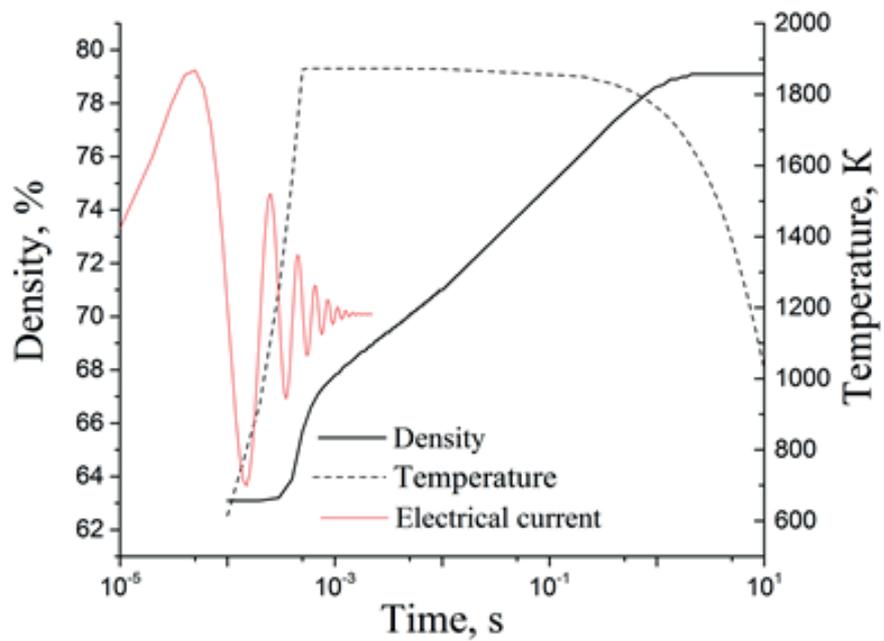

Figure 5: Kinetics of temperature and relative density variation during HVEDC, particle diameter 2 μm, pressure - 200 MPa.

phenomena are directly related to the effective stresses acting on the particle, as discussed above.
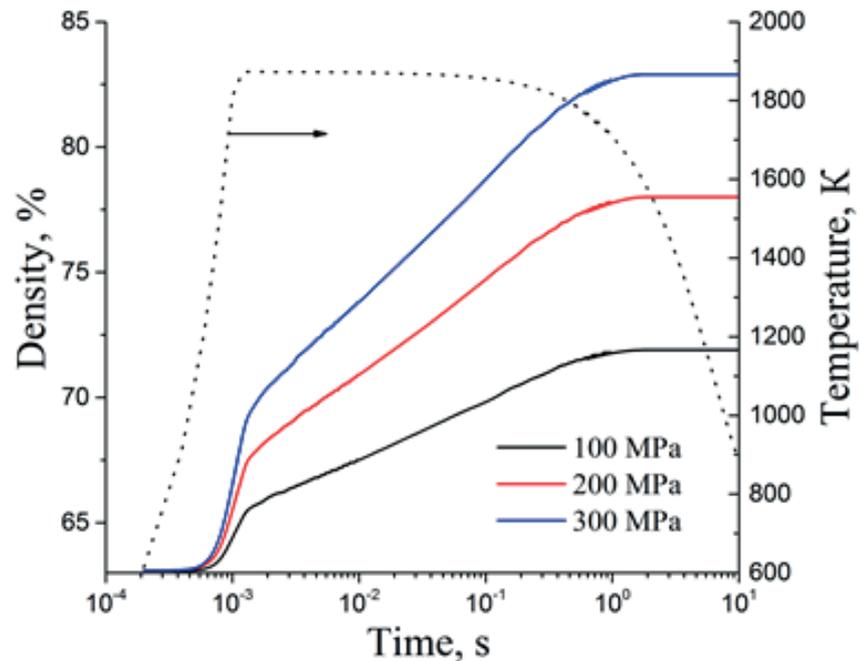
Figure 6: Influence of the pressure value on the shrinkage kinetics of powders with HVEDC, particle diameter 1 μm.

3. CONCLUSIONS

1. A model that allows describing the kinetics of densification of conducting nitride ceramics using electropulse technologies is proposed. The model takes into account the change in the relative area of interparticle contacts under the action of two mechanisms of mass transfer-diffusion and plastic flow.

2. It is shown that a decrease in the particle size of the powder leads to an increase in the diffusion contribution and a decrease in the plastic flow, in equal all other conditions. And for the case of nano-sized particles, diffusion mass transfer is predominant.

3. An increase in the rate of heating leads to a decrease in the contribution of diffusion mass transfer at equal temperatures, as well as an increase in the temperature of the beginning of shrinkage.

4. The processes of spark-plasma sintering, high-voltage electro discharge consolidation and hot pressing are controlled by the same mechanisms, plastic flow and diffusion mass transfer, which do not require, in the first approximation, the attraction of the effect of electric current on the properties of materials.

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