Sintering of zirconia ceramics using microwave and spark heating techniques

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Abstract. The paper presents the results of an complex study of structural and mechanical properties of zirconia ceramics sintered using different techniques. The samples were sintered via the conventional method of heating, in the field of microwave radiation and spark plasma. The experimental data indicates that a microwave field and spark plasma have a stimulating effect on zirconia ceramics sintering. In contrast to the microwave sintering, spark plasma sintering provides ceramics with improved properties at similar time-temperature annealing modes. Moreover, the properties of the ceramics under spark plasma sintering at T=1300 °C are similar to the properties of the ceramics sintered in a microwave field at T=1400 °C.

1. Introduction

Zirconia ceramics is a promising material that has been widely used in various fields of science and technology. Ultrafine powders (UFP) used in its manufacturing provide high-density ceramics of fine structure with unique physical and chemical properties. This expands the scope of its application, for construction and instrumental purposes in particular.

It is well known that both structural characteristics and physical properties of ceramics are primarily determined by the characteristics of the ultrafine powder medium such as particle size distribution, morphology of particles, their size and degree of agglomeration. Depending on the technique used to synthesize zirconium oxide powder, these characteristics can vary greatly.

Investigations conducted over the years [1–6] aimed at producing zirconia ceramics from UFP synthesized by the plasma chemistry method. This method is based on thermal decomposition of aqueous solutions of yttrium and zirconium nitrates in high-frequency discharge plasma. It features high performance [7, 8].

However, the studies showed that the properties of the ceramics sintered from these powders via conventional technological techniques are not as good as those of the ceramics produced from commercial UFP, the well-proven powder by Tosoh Corporation (Japan) in particular [9,10]. This is due to the reduced efficiency of plasma chemical powders (PCP) sintering which is caused by the presence of a large number of hard particle agglomerates in PHP.

This paper aims to study activation of sintering compacts from PCP through nonconventional techniques such as microwave radiation and spark plasma.

2. Experimental procedure

Zirconia ceramics was sintered from PCP of stabilized zirconium dioxide (in mol%) ZrO_2– 3 Y_2O_3. The compacts were prepared through static compression. Thermal sintering of the compacts was carried in a resistance furnace SNOL. The rate of sample heating and cooling was 10 °C/min.

Microwave (MW) sintering and spark plasma (SP) sintering of ceramics was performed at the Research Center in Karlsruhe (Germany). MW sintering was carried out in a microwave oven made by Gycom (Russia). The setting parameters were as follows: frequency of 30 GHz; power of 15 kW. The sintering mode: the rate of the temperature rise was 50 °C/min; the exposure time was 10 min. For SP sintering, a sintering furnace (HPD 10, FST Systeme Gmbh, Germany) was used. The heating rate was 200 °C/min and the pressure applied was 32 MPa. The bulk density of the ceramic samples was measured through hydrostatic weighing in distilled water using Shimadzu analytical balance supplied with special attachment for this purpose. An X-ray diffraction analysis of the powders and sintered ceramics was performed with ARL X'tra diffractometer using SuK monochromatic X-rays. The obtaioned X-ray diffraction regularities were processed by full-profile analysis with the software package Powder Cell 2.4. The microstructure of the ceramic samples was investigated using scanning electron microscopy (SEM) with the Hitachi TM-3000 electron microscope. The microhardness was determined with the ZHV1 micro Vickers hardness tester (Germany). The indentation load was 200 g, and the time of exposure under load was 10 s. The sample surface was subjected to 10 indentations.

3. Experimental results

The X-ray analysis showed that the phase composition of the zirconia ceramics obtained in different sintering techniques was similar. In all the cases, the diffraction pattern of the samples indicated the lines corresponding to tetragonal zirconium dioxide only.

Studies have been conducted aimed at establishing the optimal regime of thermal firing of ceramics, which results are presented in Table 1.

Table 1. Characteristics of zirconia ceramics sintered at different firing regimes

T (°C)	t (min)	ρ_{rel}	H_v (Гпа)	**T (°C)**	t (min)	ρ_{rel}	H_v (Гпа)
1300	0	0.79	5.9	**1500**	0	0.91	9.7
	30	0.84	7.6		30	0.92	10.4
	60	086	8.1		60	0.92	10.4
	180	0.88	8.4		180	0.91	10.2
1400	0	0.86	8.1	**1600**	0	0.92	10.4
	30	0.91	9.2		30	0.89	10.0
	60	0.92	9.8		60	0.88	9.2
	180	0.93	10.4		180	0.85	9.1

Note: T is the sintering temperature; t is duration of the isothermal stage; ρ_{rel} is relative density; H_v is microhardness.

The regularities of sintering zirconia ceramics from UFP PCP in thermal heating were studied in [1]. The dilatometric analysis of the densification kinetics of the samples revealed that during isothermal exposure at high temperatures T>1400 °C, they are observed to expand and their density decreases.

This effect can be attributed to the formation of a large number of gas-filled closed pores, which are very difficult to remove even at high temperatures and long isothermal exposure. At higher sintering temperatures, gas pressure in the closed pores increases. Since zirconium dioxide is characterized by high-temperature superplasticity, this factor may contribute to sample swelling during isothermal exposure, which negatively affects its properties. An optimum mode of thermal sintering of zirconia ceramics (T=1400 C, 3 hour annealing) was found. The characteristics of the ceramics obtained under these conditions are presented in Table 1.

As seen from Table 1, zirconia ceramics is characterized by high porosity. As is known [11], increased porosity typically reduces the ceramic hardness. Therefore, the sintered ceramic samples were of insufficiently high microhardness. Thus, thermal sintering zirconia ceramics from PCP does

not allow production of the material that satisfies the requirements of the product for constructional and instrumental purposes.

The results of the complex study of structural and mechanical properties of the zirconia ceramics sintered by different techniques are summarized in Table 2.

Table 2. Structural and mechanical properties of zirconia ceramics produced by thermal (T), microwave (MW) and spark plasma (SP) sintering

Sintering technique	Sintering mode	L (nm)	$\Delta d/d \cdot 10^3$	ρ (g/cm^3)	Θ (%)	$R_з$ (nm)	H_V (GPa)
T	T=1400°C, t= 180 min	101	0.2	5.6	7–8	340	9.5
MW	T=1200°C, t=10 min	-	-	5.26	13–14	148	8.3
MW	T=1300°C, t=10 min	15.5	0.7	5.65	6–7	206	10–11
MW	T=1400°C, t=10 min	44	0.7	5.86	3–4	220	12.6
MW	T=1500°C, t=10 min	108	0.8	5.3	12–13	455	8.4
SP	T=1100°C, t=10 min	64	0.8	4.3	30	-	4.0
SP	T=1200°C, t=10 min	38	1.0	5.52	9–10	-	10.5
SP	T=1300°C, t=10 min	50	0.6	5.8	4–5	200	11.8
T (Tosoh)	T=1400°C, t= 180 min	95	0.3	6.03	1.0	270	13

Note: L is the size of the coherent X-ray scattering region; $\Delta d/d$ is the value of the crystal lattice microstrain; ρ is pycnometric density; Θ is porosity; H_V is microhardness; $R_з$ is the mean value of the grain size.

A comparative analysis of the results presented in Table 2 indicates the following. MW heating of the samples does not change the optimum temperature of sintering; however, it essentially reduces the duration of the annealing process. This forms the ceramic structure of increased density, hardness and smaller grain size.

In contrast to MW sintering, SP sintering allows production of ceramics with improved properties at the same temperature-time annealing modes (Table 2). Moreover, the properties of the ceramics in SP sintering at T=1300 °C are similar to the properties of the ceramics sintered in the MW field at T=1400 °C.

The obtained experimental data shows that the microwave field and spark plasma have a stimulating effect on zirconia ceramics sintering. A theoretical basis of the activation of the oxide powder sintering under above heating conditions is reported in [12,13]. According to the concepts developed in these studies, high-energy action activates the diffusion mass transfer in heterogeneous structures. This is due to the formation of temperature gradients in the region of particle-particle contacts, which in turn causes thermal diffusion flows of the substance.

The data in Table 2 show that non-conventional sources of material heating such as microwave radiation and plasma spark provide the properties of the zirconia ceramics sintered from PCP close to those of the ceramics thermally sintered from the commercial powder by Tosoh Corporation.

4. Conclusion

The results obtained indicate the use perspectiveness of the considered techniques of activated PCP sintering to produce ceramics with improved properties compared to those obtained in thermal sintering.

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