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Investigation of the influence of the mode of heat treatment of the initial powder on the efficiency of sintering zirconium ceramics by dilatometry

Using methods of synchronous thermal and X-ray structural analyzes applied to zirconium dioxide powders partially stabilized with yttrium obtained by chemical coprecipitation the processes of dehydration of these powders during annealing in air have been investigated. Using the dilatometry method, the regularities of compaction of powder compacts have been investigated with thermal sintering. It was found that the resulting powders mainly consist of the tetragonal modification zirconium dioxide and are nano-sized. The average particle size was 25 nm. The resulting powders are characterized by a high degree of agglomeration. It is shown that an increase in the thermal annealing temperature from 500 to 700ºC leads to partial baking of individual particles inside the agglomerate, and causes the formation of hard agglomerates, the presence of which complicates the processes of compaction and subsequent sintering. The presence of such agglomerates prevents the production of ceramics with high mechanical characteristics: density and porosity. Thermal annealing temperature increase leads to a decrease in the density of the sintered ceramic and a decrease in its hardness.

Keywords: zirconium dioxide, dilatometry, co-precipitation, chlorides, microscopy, agglomeration.

Introduction

Ceramic materials based on partially yttrium-stabilized zirconium dioxide are increasingly used in various fields of science and technology. High hardness allows the use of zirconium ceramics for the production of cutting and abrasive tools; high melting point and low thermal conductivity are used in thermal insulation and refractory materials. Zirconium ceramics are used for the production of adsorption-semiconductor gas sensors [1, 2], thin-film coatings [3, 4], ion-exchange materials, and chemical reaction catalysts [5–7].

All stages of the technological cycle are important to obtain high-quality ceramics [8]. At the stage of synthesis of initial powders, the features of their structure are formed, such as grain size, interface surface and their state, porosity and other defects [9–14]. Therefore, method of obtaining initial powder play an important role in obtaining ceramics with high values of mechanical properties [15–21].

Currently, a large number of methods for obtaining nanosized zirconium dioxide powders exists [22–25]. Many of these methods allow to obtain high quality powders, but are of little use in conditions of mass production. Among them, the so-called methods of soft chemistry which lead to the formation of a crystalline or semi-crystalline structure without high-temperature treatment, stand out [26], for example, the coprecipitation method [27]. It is applicable in mass production environment, and, at the same time, has a low cost of the finished product. The main disadvantage of this method is a high degree of agglomeration [28].

The purpose of this work is to study of the effect of agglomeration of zirconium dioxide powders, partially stabilized with yttrium, obtained by coprecipitation on the kinetics of the sintering process of powder compacts.

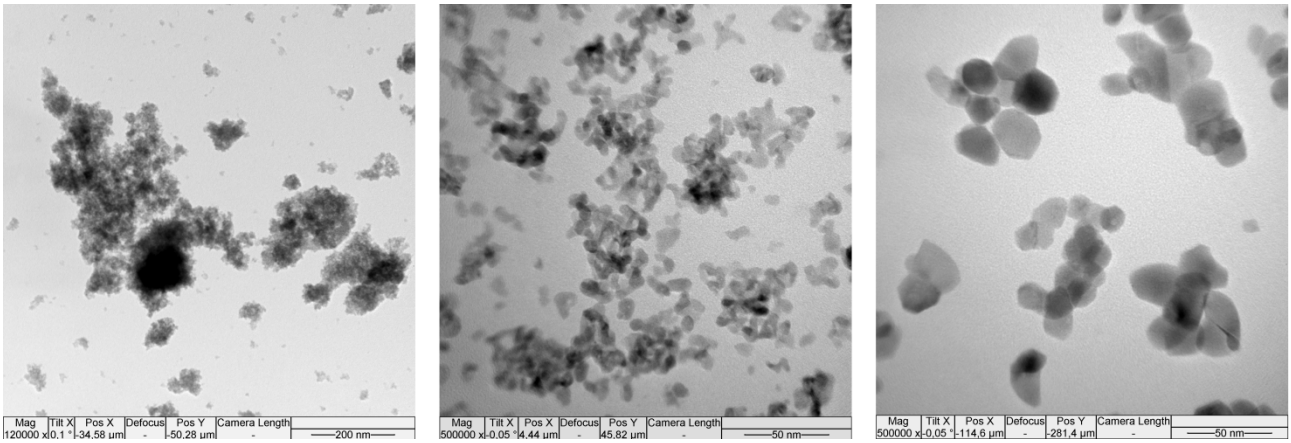
The method of the experiment

For the production of ceramic material based on partially stabilized zirconium dioxide composition (ZrO_2 + 3 mol.% Y_2O_3) a chemical method of co-precipitation of zirconium and yttrium hydroxides from an aqueous solution of zirconium and yttrium salts is used: zirconium oxide-dichloride YCl_3x6H_2O and yttrium chloride 6-water YCl_3x6H_2O by adding a 25 % aqueous solution of ammonia to pH 9.5. The hydroxide mixture is washed, dried at a temperature of 90 °C for 12 hours and then annealed at a temperature of no more than 700 °C. Annealing time is 1 hour. BET analysis of the obtained powders was carried out on the device “Sorbtometer-M” (Catakon, Russia). Studies were carried out for the initial powders obtained by sol-gel technology without annealing (type P1) and for P1 powders subjected to annealing in air at temperatures of 500 °C (type P2) and 700 °C (type P3) at a heating rate of 20 °C per minute isothermal exposure for 60

minutes. Press samples were made by uniaxial static pressing on a hydraulic press PGR-10 (Lab Tools, Russia). The pressing pressure was varied in the range of 70–960 MPa. The ceramics were sintered in a dilatometer furnace DIL 402 C (NETZSCH, Germany) in an air atmosphere. The air purge rate was 20 mm/min. Electron microscopy was performed on a JEM-2100 scanning electron microscope (Japan). X-ray diffraction analysis was performed on an ARL'xtra diffractometer (ThermoFisher Scientific, Switzerland) with a semiconductor Si (Li) Peltier detector using monochromatized CuKα-radiation. The diffractograms were measured in the angle range 2θ = (90–120)° at a speed of 0.02 ° c^{-1}. The phase analysis was performed using the PDF-4+ powder database of the International Centre for Diffraction Data (ICDD). The diffractograms were processed by the full-profile Ritveld method using the Powder Cell 2.4 software package. The density and porosity of the ceramic samples were determined by hydrostatic weighing in distilled water on a Shimadzu AUW-220 D (Shimadzu Corporation, Japan) scale with a special prefix. The microhardness was measured using a Zwick (Germany) ZHV1M microhardness meter. The thermal analysis of the powders was performed on a synchronous thermal analysis device STA-449 combined with a mass spectrometer QMS 403 D (NETZSCH, Germany).

Experimental results and discussion

Microstructure research. The results of electron microscopy of P1-P3 powders are shown in Figure 1. From the analysis of the presented results it can be seen that the P1 powder consists of agglomerates of small primary particles. The small size of the primary particles leads to a significant increase in the surface energy of the powder system. In combination with the close location of individual particles under the action of Van Der Waals forces, the formation of multiparticle clusters of individual particles — agglomerates, the shape and size of which vary very widely [29].



a b c

Figure 1. Electron microscopy of powders (a, b, c are P1, P2, P3 respectively)

In the P2 and P3 powders (Fig. 1b, Figure 1c) separate crystalline particles the size of which increases as the annealing temperature increases are isolated. At the same time, agglomerates of individual particles are also observed in the structure of the powder. Thus, the previously established inheritance of the structure of the initial amorphous xerogels of hydrated zirconium dioxide by nanocrystalline zirconium dioxide is confirmed [30]. At the same time, the heat treatment temperature is sufficient for the initial stage of sintering, which leads to the acquisition of strength by the aggregates and the consolidation of the structure [29].

The diffractograms of the studied powders are shown in Figure 2. As follows from the results obtained, the P1 powder is X-ray amorphous, while the P2 and P3 powders have a crystal structure characteristic of the tetragonal modification of zirconium dioxide. With an increase in the annealing temperature, the peaks narrow, which indicates an increase in the size of the crystallites.

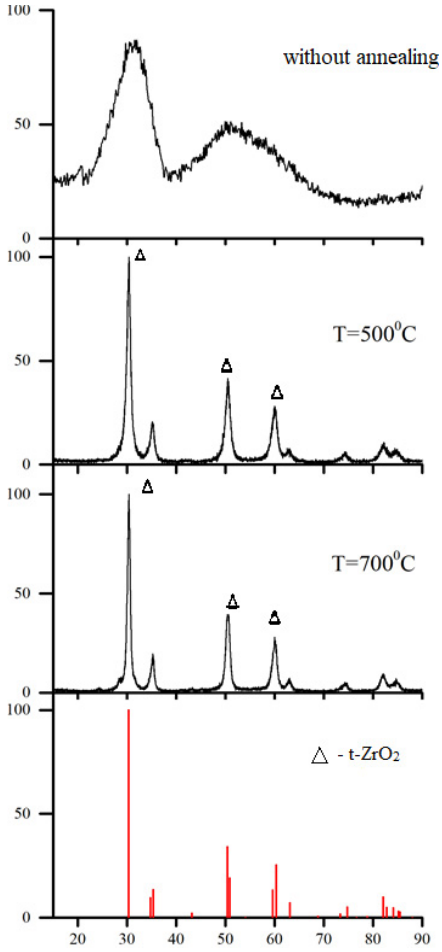


Figure 2. Diffractograms of the studied powders

The results of the thermal analysis of the P1 powder are shown in Figure 3.

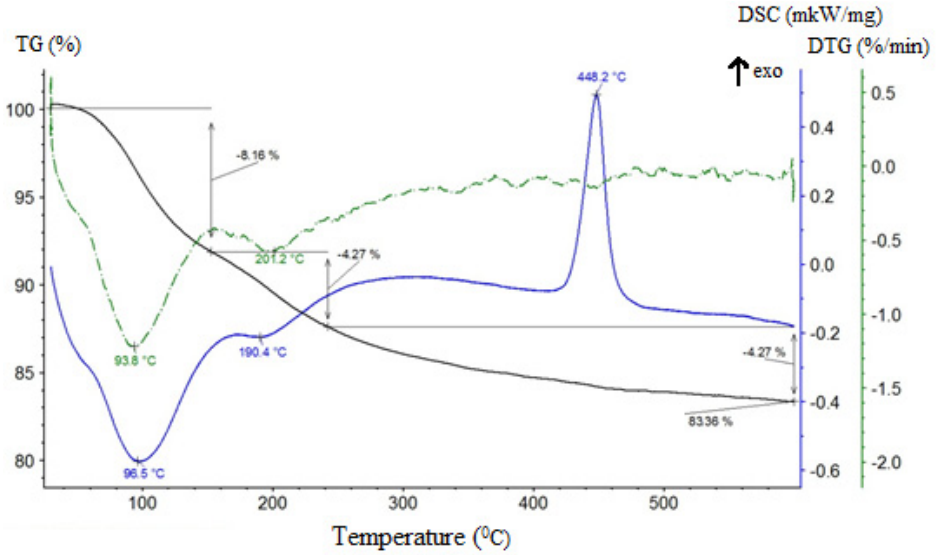


Figure 3. TG, DTG, and DSC curves for P1 powder

When the powder P1 is heated, its dehydration occurs, accompanied by the absorption of heat. The DSC curve shows two endothermic peaks caused by the removal of water present in the test substance in different states. The first and more pronounced peak (96.5 °C) is associated with the removal of physically adsorbed

[31], and the second (190.4 °C) is due to the removal of chemically bound water. Both peaks of the DSC curve are accompanied by a significant decrease in the sample mass (extremes at 93.8 and 201.2 °C on the DTG curve). The total weight reduction when heated to a temperature of 600 °C was 16.6 %. At a temperature of 448.2 °C, a sharp exothermic peak is observed on the DSC curve. This thermal effect is not accompanied by a noticeable change in the mass of the sample, which allows it to be associated with the crystallization process of partially stabilized zirconium dioxide. This conclusion is confirmed by the previously presented results of the XRD.

From the consideration of Figure 4, it follows that that the nature of the compaction depends on the type of powder (P1, P2, P3). For a sample obtained from powder P1 already at the initial stage of heating, there is a noticeable shrinkage of the sample, accompanied by a peak at temperature approximately equal to the crystallization temperature of the tetragonal phase of zirconium dioxide, obtained from the results of thermal analysis. Also, at the final stage of the process, there is an expansion of the sample, apparently a consequence of the transition part of the tetragonal phase into monoclinic. For samples obtained from powders P2 and P3 there are practically no differences in the nature of the shrinkage process.

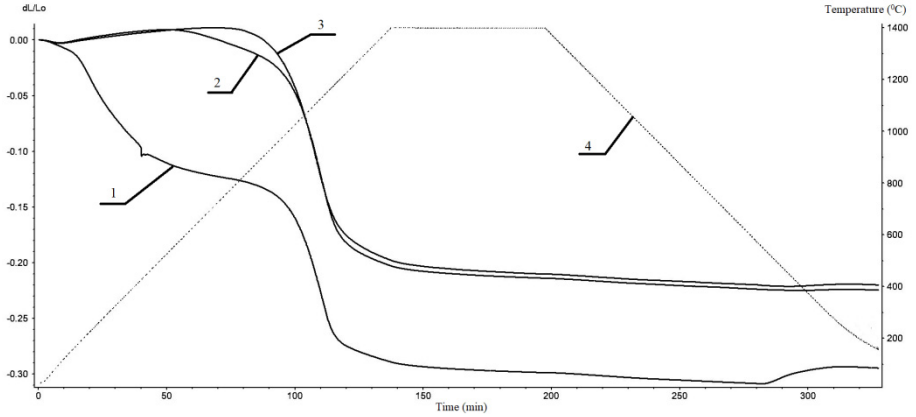


Figure 4. Dilatometric curves of powder compacts P1,
P2 and P3 (curves 1–3, respectively), 4 is thermal annealing mode.

Table 1 presents the results determining the density of compacts ρ_{pr}, density of ceramics sintered from them $\rho_{hydrost}$, porosity Θ and microhardness H_y for different types of samples.

Table 1

Physical properties of compacts and sintered ceramics

Sample type	ρ_{pr}, g/cm^3	$\rho_{hydrost}$, g/cm^3	Θ, %.	H_v, GPa
P1	2,44	4,98	16,0	9,1
P2	2,53	5,21	10,8	9,4
P3	2,62	5,18	12,3	8,2

Table 1 shows that when using powders P2 and P3 the characteristics of the sintered ceramics are significantly higher than when using P1 powder. Highest density and lowest density of sintered ceramics is achieved by using P2 powder.

Conclusion

Thermal analysis methods were used to study the processes occurring when the powder P1 is heated in an air atmosphere, obtained by coprecipitation from chloride starting components. The processes of compaction and sintering of powder compacts, made from initial powders P1 and after their annealing at temperatures of 500 and 700 °C (powders P2 and P3, respectively). At the same time, the following was established.

The heating of the P1 powder was accompanied by dehydration, the main part of which ends at a temperature of about 200^{0}C. Total mass yield when heated to 600 °C is 16.6 %. P3 powders obtained by annealing the initial P1 powder at a temperature of 700^{0}C are characterized by a nanoscale crystal structure. The average crystallite size according to the results of XRD and microscopy was 25 nm.

The highest density of ceramics obtained when sintering a sample of powder P2, which is most likely due to a lower density of agglomerates than in P3 powder.

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С. Шевелев, Е. Шевелева, О. Старый

Бастапқы ұнтақты термиялық өңдеу режимінің циркония керамикасын дилатометрия әдісімен біріктіру тиімділігіне әсерін зерттеу

Химиялық тұндыру әдісімен алынған иттриймен жартылай тұрақтандырылған циркония ұнтақтарына қатысты синхронды термиялық және рентгендік құрылымдық талдау әдістерін қолдана отырып, ауада өңдеу кезінде осы ұнтақтардың дегидратация процестері зерттелді. Дилатометрия әдісін қолдана отырып, термиялық күйдіру кезінде ұнтақты компактілердің тығыздау заңдылықтары тексерілген. Алынған ұнтақтар негізінен цирконийдің тетрагональді модификациясынан тұрады және наноөлшемдері бар екендігі анықталды. Бөлшектердің орташа мөлшері — 25 нм. Бұл ретте алынған ұнтақтар агломерацияның жоғары дәрежесімен сипатталады. Термиялық күйдіру температурасының 500-ден 700 ºС-қа дейін жоғарылауы агломерат ішіндегі жеке бөлшектердің ішінара пісірілуіне әкеліп соғатындығы көрсетілген және қатаң агломераттардың пайда болуына әкеледі, олардың болуы ықшамдау және кейінгі синтездеу процестерін қиындатады. Мұндай агломераттардың пайда болуы тығыздығы мен кеуектілігі жоғары механикалық сипаттамалары бар керамиканы алуға кедергі келтіреді. Термиялық күйдіру температурасының жоғарылауы күйдірілген керамиканың тығыздығының төмендеуіне және оның қаттылығының төмендеуіне әкеледі.

Кілт сөздер: цирконий диоксиді, дилатометрия, тұнба түзу, хлоридтер, микроскопия, агломерация.

С. Шевелев, Е. Шевелева, О. Старый

Исследование влияния режима термической обработки исходного порошка на эффективность спекания циркониевой керамики методом дилатометрии

С использованием методов синхронного термического и рентгеноструктурного анализа применительно к порошкам диоксида циркония, частично стабилизированного иттрием, полученных методом химического соосаждения, исследованы процессы дегидратации этих порошков при отжиге на воздухе. При помощи метода дилатометрии изучены закономерности уплотнения порошковых компактов при термическом спекании. Установлено, что полученные порошки состоят преимущественно из тетрагональной модификации диоксида циркония и имеют наноразмеры. Средний размер частиц – 25 нм. При этом полученные порошки характеризуются высокой степенью агломерации. Показано, что увеличение температуры термического отжига с 500 до 700 ºС приводит к частичному припеканию отдельных частиц внутри агломерата, и вызывает формирование жестких агломератов, наличие которых затрудняет процессы компактирования и последующего спекания. Наличие подобных агломератов препятствует получению керамики с высокими механическими характеристиками: плотностью и пористостью. Повышение температуры термического отжига приводит к снижению плотности спеченной керамики и снижению ее твердости.

Ключевые слова: диоксид циркония, дилатометрия, соосажение, хлориды, микроскопия, агломерация.

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