Influence of Hydrate Moisture on the Sealing of a Nanopowder Dispersed System Based on Zirconia

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ABSTRACT
The present paper is devoted to the problem of sealing zirconia nanopowder. We studied the effect of the water content in zirconia nanopowder on the process of sealing this powder. We found that the shrinkage, specific surface area and weight loss of a nanopowder system based on zirconia during sealing substantially depend from the level of ambient humidity where nanopowder is placed. By optimizing the external conditions of moisture content in a sample, the value of relative shrinkage of a nanopowder system based on ZrO$_2$ under uniaxial pressure can be increased to 6%, while under high hydrostatic pressure sealing it can be increased up to 8%.

CCS Concepts
• Applied computing → Physical sciences and engineering • Applied computing → Physics

Keywords
Zirconia nanopowders; Sealing process; Hydration; High pressure; Humidity.

1. BACKGROUND
One of the most widely-used functional and structural materials in the field of nanotechnology is zirconia. Due to a unique set of physical, chemical, electrical, and optical properties, it has been applied in many branches of science and technology.

An important problem in this area is obtaining nanoceramics with high physical and mechanical properties through the consolidation of nanopowders. During consolidating of nanoparticles the main task is to preserve grain size in nanoscale range with a minimum level of heterogeneity of a structure.

Sealing nanopowders to form compact sets with required shapes is an important stage in the technology of nanoceramics using traditional ceramic technology [1, 6, 11]. The behavior of a sample during sintering depends largely on a quality of a compact set. Usually, a high hydrostatic pressure is applied, providing a spatially uniform mechanical effect on a sample from outside. Nanoscale powders are poorly compacted due to high levels of interaction between nanoparticles [7]. The energy of such an interaction is largely determined by electrical forces that are inversely proportional to the distance between particles (Lennard-Jones potential) [9]. In the case of a chemically-active surface, the degree of surface hydration is a significant factor of interparticle interaction. The ionic atmosphere surrounding nanoparticles affects the distance between particles hydromechanically (by changing the quantitative composition of adsorbed molecules of water). Thus, obtaining uniform compact sets is a problem for nanoscale powders in the case of a chemically-active surface of nanoparticles. This can be solved by varying the quantitative composition of adsorbed moisture.

Nanopowders based on zirconia have a high level of chemical activity on the surface (surface area of nanopowder ~ 120 m$^2$/g). Due to this property, nanoparticles can quickly change in the quantitative composition of the hydration shell at normal physical conditions. So, they are excellent model objects for testing the aforementioned suggestions.

This present research aimed to establish the influence of ZrO$_2$ powder’s initial degree of hydration on the efficiency of sealing.
nanopowders based on ZrO₂ with uniaxial and high hydrostatic pressure (HHP).

2. METHODS
Nanopowder of composition ZrO₂ + 3 mol% Y₂O₃ was prepared using co-precipitation method [8] from a chloride precursor followed by thermal dehydration in a specialized microwave-furnace at 120°C then calcination at T = 700°C for 2 hours. The objects of study were compact sets in the form of tablets made from this powder.

The experimental procedure was as follows. To unify the initial physical conditions and remove physically-bounded water from the powder, the powder was dried in a furnace at a temperature of 120°C for 1 hour. Then, the powder (mass of per portion m = 1g) was placed in a special climatic chamber, which allowed a wide range of adjustments to ambient humidity (η = 10 ± 95% of relative humidity), and maintained at a constant level. The powder was placed in a chamber with a certain level of humidity and fixed temperature T = 21°C for 1 hour. Preliminary experiments had shown that during this time thermodynamic equilibrium of the nanopowder system with the environment is reached and the amount of adsorbed molecules per unit time does not exceed the amount of desorbed. The following values of relative humidity in the chamber were used for each series of samples: η = 20, 30, 50, 70, and 90 % of relative humidity. The measurement error of relative humidity was 5%. After aging in a climatic chamber, uniaxial pressure (P1 = 40MPa) was used to make compact sets in the form of tablets (diameter 20 mm, height varied from 1.52mm to 1.58 mm depending on the physical conditions at which the system was aged before the compaction process). Immediately after compaction, these compact sets were sealed by high hydrostatic pressure (HHP). To determine the shrinkage of samples, a standard micrometer with a dial for outdoor measurements with a measuring range of 0 - 25 mm with a scale division of 0.01 mm (0.005 mm accuracy) was used. Shrinkage after compaction was determined by the height of each tablet and after exposure by HHP by changing the volume of the samples. Experimental results were averaged over a series of 3 measurements.

The mass of each sample was measured (ADS50-type scales were used) after each stage of preparation.

Specific surface area was determined by the BET method (Brunauer, Emmett and Taylor method) on the SORBI-4 unit with a measurement error of 6%.

Spatial structural organization of samples was investigated by SEM images with magnification x500 (Figure 2, a). It is indicates a relatively homogeneous distribution of the material in the volume of samples. At higher magnification pores which are occupied on average half of the sample volume and facilitate easy penetration of moisture are visible. Image with magnification x10 000 shows that microstructure of sample is loose and flake. Aggregates are irregular in shape; their size is 1 - 3mkm.

Figure 1. TEM images of the powder ZrO₂ + 3 mol.% Y₂O₃ with magnification of 10 000 (a) 70 000 (b) and the characteristic pattern of the electron diffraction (c).

Figure 2. SEM images of fracture of compact sets (500 MPa) of the powder ZrO₂ + 3 mol.% Y₂O₃ with magnification of 500 (a) and 10 000 (b).

Figure 3 shows the dependences of linear shrinkage after the influence of uniaxial pressure and volume shrinkage after HHP exposure (Figure 3a and Figure 3b, respectively). Dependences are nonmonotonic.

The maximum level of shrinkage after uniaxial compaction was reached at a level of relative humidity of η = 50%. With further increasing of the humidity, the level of shrinkage decreased monotonically.

More interesting is the dependence of volume shrinkage after the influence of HHP. As can be seen from Figure 3b, two critical points can be distinguished: the maximum shrinkage at low relative humidity (η = 30%) and the minimum at η = 70%. Relative shrinkages were 26.4% and 19.1%, respectively. That is, under HHP influence, the level of maximum shrinkage shifted from η = 50% to η = 30%.

According to thermogravimetry analysis, under such conditions (η = 30%), an amount of powder (700°C, 2 g) contained about 2.86% moisture.

The dependencies of weight loss after uniaxial compaction and after HHP were similar (Figure 4). Three situations regarding changes of weight were identified:
- does not take place (humidity values 30≤ η <50%) and change was about 1%;
- has positive dynamics (values of humidity 50≤ η <80%, maximum losses at η = 70%);
- has a negative trend (η> 80%).

3. RESULTS AND DISCUSSION
Investigation of composition of the powder ZrO₂+3mol% Y₂O₃ by TEM methods are shown on Figure 1. It can be seen that the powder is relatively well distributed spatially with individualized particles (Figure 1, b). The volume of the sample contains only solid nanoparticles with diameter 17 nm, and the gas phase. Shells around the particles are visible on Figure 1, b. It is formed as a result of contamination of the surface of nanoparticles of pairs of vacuum oil. This item directly indicates high chemical activity of nanoparticles and can indirectly indicate the presence on surface of nanoparticles of adsorption atmosphere, which probably does not create an electronic contrast and not visible in TEM images.

Homogeneous microstructure can be seen on SEM images with magnification x500 (Figure 2, a). It is indicates a relatively
Obviously, in these situations the mechanisms of moisture desorption from the sample were different.

First was observed at a low humidity level (30%), while the second was observed under elevated moisture content (70%).

Table 1 shows the thermogravimetry data that demonstrated the content of water in the samples during its aging at a chamber with different levels of a relative humidity. The relationship is linear.

Table 1. Water content in samples saturated at different humidity levels for 1 h

| η, %  | 20  | 30  | 50  | 70  | 90  |
|-------|-----|-----|-----|-----|-----|
| Δm, % | 1.99| 2.86| 6.25| 6.96| 9.56|

Figure 3. Dependences of the shrinkage of samples from nanopowder ZrO$_2$-3% Y$_2$O$_3$ after sealing the humidity level of ambient air: a - linear shrinkage after exposure to uniaxial pressure (P$_1$ = 40 MPa); b - relative shrinkage after exposure to HHP (P$_2$ = 200 MPa).

The dependence of specific surface area of the samples after the influence of HHP (Figure 5) on air humidity has two minima. The first was observed at a low humidity level (30%), while the second was observed under elevated moisture content (70%).

Figure 5. Dependence of specific surface area of the ZrO$_2$ + 3% Y$_2$O$_3$ system after sealing, using HHP (200 MPa), the humidity level.

4. RESULTS INTERPRETATION

4.1 Process of Sealing in Ceramic Technology

According to modern concepts, the beginning of sealing nanopowders is accompanied by the compaction of nanoparticles by the convergence and displacement of particles relative to each other [2]. At this stage, any air and moisture present in the nanopowder is expelled through pores between particles. With further compression of the compact set, the sealing of surface layers occurs and the distance between particles decreases; accordingly, pore sizes are reduced. As a result, the removal of gas from the compact set becomes more difficult. Therefore, air in pores and water vapor [10], as well as interparticle interactions, largely reduce the effectiveness of the sealing process. On the termination of the pressing force and the release of the compact set from the mold, elastic expansion is caused by the expansion of pressed air.

The micropowder compaction stage, accompanied by the deformation of particles according to BET- analysis [5], is realized in a more-or-less severe form [10]. Due to increasing particle size, the contact surface between them decreases. According to this, moisture is condensed from a gaseous state to a liquid.

At the same time, depending on the nature of the material of nanoparticles and external influences (level of pressure) on the system, moisture will have a different effect on the nanopowder system.

In general, water in a sample can be separated to chemically- and physically-bounded water. In turn, chemically- and physically-bounded water can be divided into two categories: capillary-mobile and capillary-fixed water [4]. In the first case, water can transmit hydrostatic pressure and can move in a material structure in liquid form. Capillary-fixed water, as in the case of microcrystalline analogs, does not transmit hydrostatic pressure, but does determine the interaction energy between nanoparticles. In particular, if the surface of nanoparticles is hydrophilic, the interaction energy between nanoparticles increases; in contrast, in the case of hydrophobic surfaces, the interaction energy is reduced.

Based on the presence of a minimum in the range of η < 50%, as shown in Figure 1, the surface of the investigated nanoparticles was hydrophilic. Increasing the intensity of physical and chemical interactions between particles / interparticle adhesion led to decreased sealing efficiency.
It is possible to find the boundary moisture content in the material, in which water molecules acquire the property of continuity in the space between particles. At this level of capillary-mobile water, the maximum density, structural mechanical and thermophysical properties are achieved in the system. With a further increase in the amount of moisture in the system, the thickness of the liquid layer increases, measuring the interaction between the particles decreases.

It is precisely the finding of such an optimum moisture content of the powder that is technologically interesting. According to the maximum values of structural and mechanical properties at a certain level of humidity, it can indirectly judge the optimum moisture content in the nanopowder.

Based on Figure 3a and Figure 3b, capillary-fixed water dominated up to 50% moisture at a pressure of 40 MPa and up to 30% and above 70% at a pressure of 200 MPa. Figure 3 shows that practical interest has capillary-mobile water. In Figure 3a, the range of relative humidity is 50-90%. In Figure 1b, the range is 30-70%.

Figure 4 shows that at air humidity over 50%, the water under pressure began to be actively squeezed from the sample; at this range, the weight loss was maximal (about 1.5%). Therefore, it entirely filled pore volume. Thus, as Figure 3a shows, at a pressure of 40 MPa, shrinkage increases. Consequently, water that was present in a sample at η > 50% exerted counterpressure; it stayed in a condensed state, i.e., it was a capillary-mobile type. Increasing the compaction degree, according to Nigmatulin [12], can occur only in the case of the homogenization of the material of compact sets by reducing interparticle adhesion. Probably, the moisture squeezed out of the enclosed volume of interporous space under the influence of external pressure destroys nearby coagulation contacts, acting as a homogenizing agent.

Comparing Figure 3a and Figure 3b it reveals that, at higher pressures, the best compaction required less relative humidity (water content in a sample). The optimal amount of moisture is likely determined by pore volume. At low pressures, pore volume was large and improving sealing efficiency required more adsorbed moisture compared to high pressures, wherein pore volume was less.

Figure 3 shows that when the amount of water greatly exceeds the volume of pores present in a sample at a specific level of pressure, the sealing efficiency decreases. The mechanism of this effect is likely, as in case of micropowders, caused by the emergence of a liquid interlayer in pores, which creates counterpressure and tensile stresses and, as a result, the formation of bundle cracks in the material of the compact set [13]. As can be seen from Figure 4, at a high (η > 80%) moisture content in a sample (about 7% of weight), the sample is practically unchanged compared with its initial content; at high pressures, there is a tendency of adsorbing additional water. First, this is in good agreement with previous findings regarding the reduction of the effectiveness of the sealing process when excess moisture is present in a sample. Obviously, blocking moisture in a sample can be a consequence of resealing its surface layers due to substantially nonuniform compaction. Second, this can be associated with changes in the physical and chemical properties of the hydration surface of nanoparticles at high pressures.

Thus, for a specific material of nanopowder and range of pressure, there exists an optimum content of adsorption moisture at which efficiency of sealing is maximal.

As can be seen from Figure 3a, for the pressures used in the formation of products from nanopowders (uniaxial pressure of 40 MPa), optimal water content is achieved by the pre-exposure of annealed powder at a humidity level of 50-60% and a temperature of T = 21°C for 1 hour. This is a normal condition for industrial premises in the autumn - summer period in south-eastern Ukraine. In contrast, the efficiency of hydrostatic sealing, as shown in Figure 3b, is maximal at a humidity level of 30-40%, which is normal for more arid regions.

5. CONCLUSIONS

It is shown that shrinkage values and masses of nanopowder systems based on zirconia during compaction process is depend significantly on the humidity of the ambient air. This fact is explained by the presence a certain amount of moisture in a sample of. The optimum conditions in which the system should be aged in order to achieve the maximum level of sealing were determined. Optimal water content is achieved by the pre-exposure of annealed powder in a chamber with a humidity level of 50-60% and a temperature of T = 21°C for 1 hour. By optimizing the external conditions of moisture content in a sample, the relative shrinkage of a nanopowder system based on ZrO2 was increased to 6% under uniaxial pressure and up to 8% at high pressure.

By monitoring the humidity in the production rooms during operations with ZrO2 nanopowders, it is possible not only to improve the efficiency of compaction of nanopowder oxide systems, but also to achieve the repeatability of the mechanical properties of samples.

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