Structure and properties of ZrO$_2$–MgO powders

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Abstract. It have been studied magnesia stabilized zirconia (ZrO$_2$–MgO) powders produced by high-frequency decomposition of water salt solutions. It have been shown that due to precursor dissociation powders consist of spherical particles with smooth surface and irregular hollow aggregates resembling foam. An increase in the magnesium concentration in the precursor has an effect on the powder properties, namely, the specific surface decreases significantly and the bulk density increases. Zirconia in the nanostructured state is present only in the powders with 8.6 and 13.9 mole% MgO, with the size of the c-ZrO$_2$ crystallites in them no more than 100 nm. In powder with 43.3 mole% of MgO the magnesia content in c-ZrO$_2$ solid solution corresponds to its solubility limit of 22.2 mole% at temperature 2100°C.

1. Introduction

Plasma spray synthesis is one of the most efficient methods of synthesizing ultrafine powder systems of various chemical compounds [1]. A high dissociation temperature of precursors in plasma and a high cooling rate of reaction products provide a high nucleation rate and low nucleus growth rate, which makes possible the formation of the nanostructured state in the system.

A highly nonequilibrium phase formation in plasma spray synthesis makes this method attractive for the production of solid solution powders with limited solubility of components under normal conditions. This group of solid solutions includes the ZrO$_2$–MgO system, as magnesia is not dissolved in zirconia under normal conditions [2]. Partial substitution of zirconium atoms by magnesium atoms in the lattice ensures the stability of high-temperature β or γ modifications of ZrO$_2$ under normal conditions. The phase transition of high-temperature to low-temperature ZrO$_2$ modifications is accompanied by an increase in the unit cell volume, leading to the formation of a defect structure when the ceramics is cooled down to the sintering temperature of the powder mixture. Owing to this fact, only zirconium ceramics on the basis of β or γ modifications have found practical application.

A characteristic feature of the ZrO$_2$–MgO ceramics is a unique combination of high strength and fracture toughness. The type of the ZrO$_2$ lattice and, consequently, properties of the ceramics depend on the MgO content in solid solution determined by the ratio of components in the precursor. It should be expected that the precursor composition affects not only the phase composition of the powder but also its particle size distribution, which is important for the structure and properties of the ceramics as a material produced by powder technology.

The aim of this paper is to study how the magnesia content in the ZrO$_2$–MgO system influences the phase composition, crystal structure and morphology of powder particles produced by plasma chemical synthesis.

## 2. Materials and experimental procedure

Magnesia stabilized zirconia (ZrO_2–MgO) powders were produced by denitration of aqueous solutions of zirconium and magnesium nitrate salts in high-frequency plasma. The ratio of zirconium and magnesium salts in the precursor was calculated from the magnesia content in the synthesized ZrO_2–MgO powders: 8.6, 13.9, 25.4, 35 and 43.3 mole%.

The powder particle morphology was analyzed using scanning and transmission electron microscopy. The specific surface of the powders was determined by the BET method. The phase composition and crystal structure were analyzed by the results of X-ray diffraction with CuK_α radiation. The ZrO_2 phase content was calculated from the ratio of the integral intensities of diffraction lines in X-ray diffraction patterns.

Powder compaction was analyzed by diagrams in the coordinates $lgV=f(lgP)$, where V is the powder volume and P is the compaction pressure, under quasi-static compression in a steel mould.

3. Results and discussion

Electron microscopic analysis of the particle morphology has shown that the ZrO_2–MgO powders of all studied compositions consist of spherical particles and irregular aggregates that resemble solidified foam (Fig. 1). The spherical particles had a smooth surface, appearing on the fracture surface as spheres with a wall thickness of more than 0.25 μm. Most of the aggregates were transparent to the electron beam even at low 40 kV accelerating voltage of the electron beam in the microscope.


a)   b)   c)
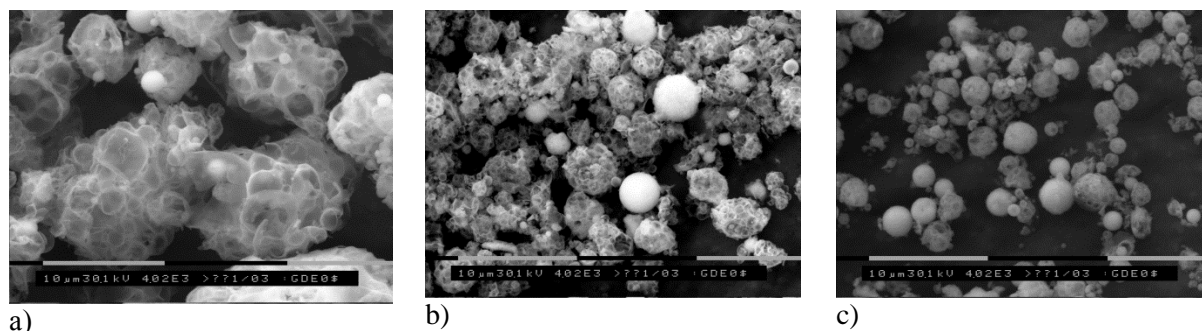
Figure 1. Powders of ZrO_2-MgO with a) 8,6 mol. %; b) 25,35 mol. %; c) 43,3 mol. % MgO

Variation in the ratio of the precursor components had an effect on the powder particle size distribution. The proportion of spherical and irregular particles in the studied powders was different. The fraction of spherical particles in the powders increased with a growing magnesia content in the precursor. For example, in the ZrO_2 – 8.6 mole% MgO powder the amount of spherical particles did not exceed 20%, and in the powder with the largest MgO content 43.3 mole% the amount of spherical particles exceeded 70% (Fig.2).

In powders synthesized by pyrolysis of aqueous salt solutions in low-temperature plasma some particles inherit the shape of aerosol droplets sprayed into the plasma (spherical particles), while other particles are fragments of spheres broken by the release of overheated intradroplet gas. The observed increase in the amount of spherical particles in the ZrO_2–MgO powders can be related to a decrease in the surface tension of aerosol droplets at a growing concentration of magnesia in the precursor, due to which the release of reaction gases was facilitated and the amount of unbroken spherical particles increased.
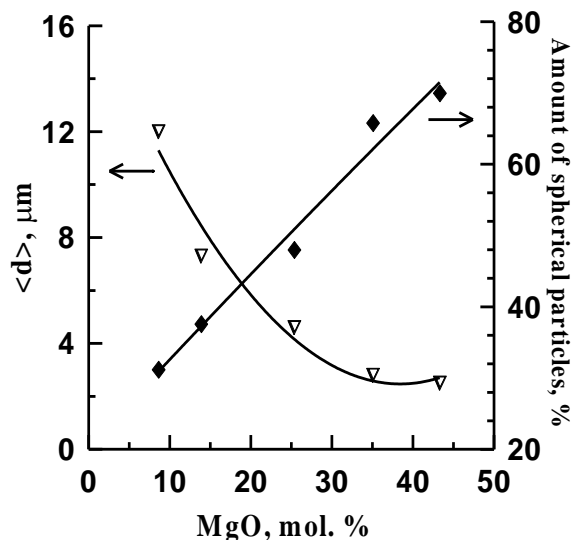
Figure 2. Mean size of grains and amount of spherical particles in ZrO_2 –MgO

Changes in the precursor composition influenced the average powder particle size <d> that was significantly reduced with the growing concentration of magnesia. The average particle size in the powder with the smallest MgO content 8.6 mole% was 12 μm, and in the powder with 43.3 mole% MgO it was 25 μm (Fig. 2). In this case, the average size of spherical particles did not depend on the precursor composition, being the same in all studied powders, while the size of aggregates was reduced.

Naturally, the powder particle geometry variation with increasing MgO content exerted an effect on the powder properties, [3, 4] (Fig. 3). An increase in the amount of spherical particles with smooth surface led to a decrease in the specific surface S_a of the ZrO_2–MgO powders. The powder with the smallest MgO content 8.6 mole% had the largest value S_a=15 m²/g. The specific surface of the powder with 43.3 mole% MgO was 5.5 m²/g. The growing amount of spherical particles and, correspondingly, the reducing amount of hollow aggregates led to an increase in the bulk density of the studied powders (Fig. 3).

Variation in the particle size distribution of the ZrO_2–MgO powders also had an effect on their compaction. The growing MgO content in the powders led to an increase in the parabolicity coefficient of the compaction equation (Fig. 3) determined as the slope of the compaction diagram in the coordinates *lgV=f(lgP)*. Indirectly, the parabolicity coefficient of the compaction equation of a dispersed system reflects the reduction rate of its volume in the mould under increasing pressure. The observed compaction rate growth for the studied powders is related to a decrease in interparticle friction due to an increase in the amount of spherical particles with smooth surface in them.

According to X-ray diffraction results, zirconia in the powders with the magnesia content less than 35 mole% was in the cubic (c-ZrO_2), tetragonal (t-ZrO_2) and monoclinic (m-ZrO_2) modifications. In this case, the c-ZrO_2 fraction in these powders was more than 90%. In the powders with 35 and 43.3 mole% MgO zirconia was only in the cubic modification. Along with the ZrO_2 reflections in the diffraction patterns of the powders with the MgO content above 13.9 mole% there were intensive reflections corresponding to magnesium zirconate $Mg_2Zr_5O_{12}$ and less intensive reflections corresponding to MgO. The integral intensity of the diffraction lines of $Mg_2Zr_5O_{12}$ increased with the growing MgO content in the ZrO_2–MgO system.

The calculation of average crystallites by X-ray reflection broadening for each phase showed that zirconia in the nanostructured state was present only in the powders with 8.6 and 13.9 mole% MgO. The size of the c-ZrO_2 crystallites in them did not exceed 100 nm. The average size of $Mg_2Zr_5O_{12}$ crystallites in all powders was less than 25 nm.
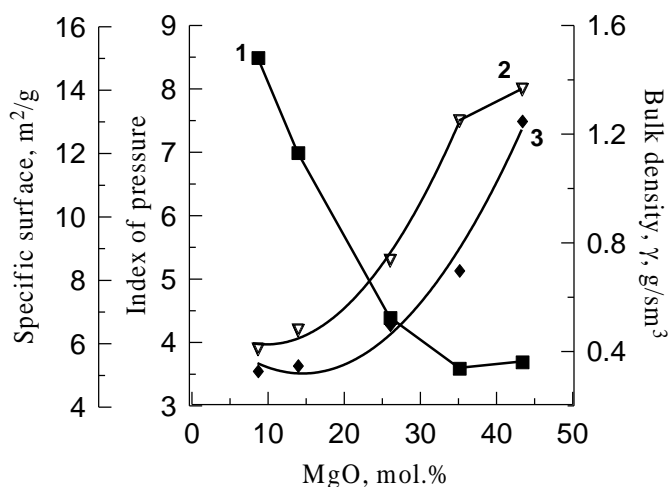
Figure 3. The raw powder density, specific surface and mould ability vs. magnesia content in system

The magnesia content growth in the studied ZrO_2–MgO powders was accompanied by a decrease in the cell parameter a_c of the cubic ZrO_2 modification, which can be, first of all, a result of substitution of Zr^{4+}(r=0.8) cations by Mg^{2+}(r=0.72) cations of smaller radius. Comparison of cell parameters a_c in the studied powders with the data provided in [5] for known MgO concentrations in a solid solution on the basis of cubic zirconia showed that the amount of magnesium cations substituting zirconium cations is less than it could be at complete dissolution of magnesia present in the studied powders. For example, for the powder with 8.6 mole% MgO the magnesia content in solid solution was 7.9 mole%, and for the powder with 35 mole% MgO its content in solid solution did not exceed 16 mole% (Fig. 4). However, in the ZrO_2 – 43.3 mole% MgO powder the magnesia content in c-ZrO_2 solid solution corresponded to its solubility limit of 22.2 mole% at 2100°C, according to the phase diagram given in [2].
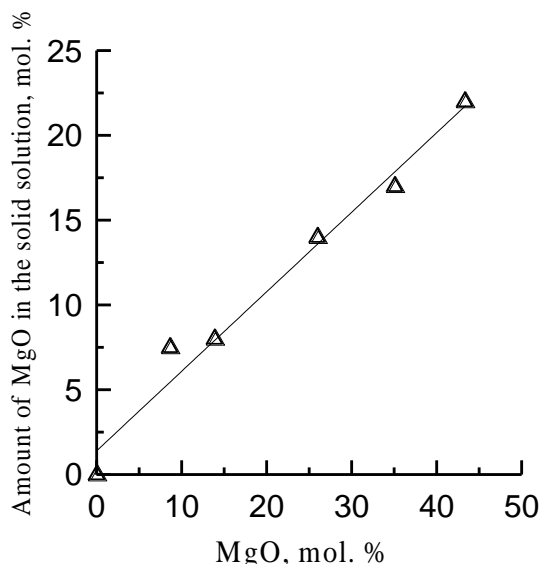
Figure 4. MgO content in a powder solid solution vs. magnesia content in system

Calculation of unit cell parameters a and c for $Mg_2Zr_5O_{12}$ showed that their value increases with the growing MgO content in the ZrO_2–MgO powders, which is related to the closeness of $Mg_2Zr_5O_{12}$ to the stoichiometric composition corresponding to the 28 mole% magnesia content in the system. In the

powder with 43.3 mole% MgO the parameter values for $Mg_2Zr_5O_{12}$ correspond to those given in the ASTM cards (Nos. 41–185): a=0.94445 nm and c = 0.87450 nm.

4. Conclusion

- The magnesia stabilized zirconia (ZrO_2–MgO) powders produced by precursor dissociation in a high-frequency plasma consist of spherical particles with smooth surface and irregular hollow aggregates resembling foam. As a result of increasing magnesium salt nitrate concentration in the precursor, the amount of aggregates decreases and the amount of spherical particles grows.
- An increase in the magnesia concentration in the precursor has an effect on the powder properties, namely, the specific surface decreases significantly and the bulk density increases.
- Zirconia in the nanostructured state is present only in the powders with 8.6 and 13.9 mole% MgO, with the size of the c-ZrO_2 crystallites in them no more than 100 nm.
- The amount of magnesium cations substituting zirconia cations is smaller than it could be at complete dissolution of magnesia present in the studied powders. However, in the ZrO_2 – 43.3 mole% MgO powder the magnesia content in c-ZrO_2 solid solution corresponds to its solubility limit of 22.2 mole% at temperature 2100 $^{\circ}$C.

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