Methods of obtaining and the prospect of using powders based on aluminum magnesium spinel

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Abstract. The prospects of use optically transparent ceramics from aluminum magnesium spinel are considered. Technologies of synthesis of spinel powders for the subsequent application when receiving transparent ceramics are described.

Development of materials with the increased physical and mechanical properties is one of the perspective directions of the modern equipment. Thanks to a number of valuable properties, such as high hardness, durability, thermal stability and high light transmittance, transparent ceramic materials are of special interest optically. Such materials find broad application as arc lamps of high pressure, details of optical systems of navigation, fairings of rockets, etc. The problem of development of new transparent armored materials is relevant.

Effective protection against high-energy weapons of destruction with high penetration – armor-piercing rifle bullets with the heat-strengthened cores – is inconceivable without its use as an element of protective structure of ceramics – highly rigid, but fragile material [1]. And in the field of an individual armored protection and protection of the easy equipment against bullets of small arms, the use of ceramics for the last 20 years has sharply increased in connection with distribution of bullets with highly rigid steel and hard-alloy cores [2].

Transparent antipulse and splinterproof armor is used for production the bullet-proof of windows of cars, planes and helicopters, banks and offices. In the means of an individual armored protection (MIAP) the transparent ceramics is applied to production of visors for helmets and observation ports of armored shields.

The protecting ability of a barrier in relation to action of the shock getting weapons of destruction usually is characterized by its thickness or area density, which provides the standard nature of environmental damage [1].

The mechanism of interaction of bullets and ceramic plate comes down to the fact that for some time the ceramics at the expense of the high hardness does not allow the drummer to get into itself. At the same time the drummer is forced to be deformed or collapsed for barrier surfaces, spending own kinetic energy. It is accepted to call this time penetration delay time. After this time the rest of the core of a bullet gets into a ceramic crumb into which the ceramics in a point of influence manages to turn [2].

Armor, as a rule, has as a part of several layers.
The ceramic layer of multilayered structures is produced from separate ceramic elements with a 50 - 100 mm party size, 10 - 15 mm thick, which paste to an organoplastics or metal substrate. To prevent transfer of cracks to the next elements between them leave a small gap (about 0.5 mm) which is filled with elastomer [1].

Thus, the role of a ceramic layer of a multilayered barrier comes down to destruction of a head part of a bullet, increase in the area of impact on the subsequent layers of a barrier and absorption of a part of kinetic energy of the remains of a bullet in the course of its braking in already destroyed ceramics [1].

Ceramics from aluminum magnesium spinel MgAl₂O₄ (AMSh) is held a specific place among optically transparent ceramic materials. In comparison with other ceramic transparent material (ALON, polycrystalline Al₂O₃) spinel has advantage in the form of bigger availability of input products and smaller temperatures of synthesis.

The optical ceramics from AMSh represents material with an exclusive mechanical durability, wear resistance on attrition, erosion resistance, resistance to unilateral aerodynamic blow, chemical inertness. The material is mechanically stable up to the temperature of 1250 °C (to 1500 °C at short-term influence) [3], is characterized by transparency in the wide spectral range (from ultra-violet (UF) to infrared (IK) area of range).

As a rule, the ceramics from aluminum magnesium spinel is received in three stages: spinel powder synthesis, formation of semi-finished products, sintering in hydrogen or vacuum.

The phenomenon of inheritance is observed by the subsequent phase of the structure of the previous one in ceramics.

Properties optically of transparent ceramics strongly depend on structure, structure and dispersion of powdery precursors therefore when receiving optically transparent ceramic materials much attention should be paid to synthesis of initial powders.

Many researchers meet that for receiving dense transparent ceramics it is necessary to use the nanodimensional crystal powders consisting of weak agglomerates or separate small monodisperse particles with the form close to spherical. Also special attention need to be paid to chemical and phase purity [5].

At production of transparent oxide materials rather low-temperature ways of preparation of initial compositions first of all such as cryochemistry, coprecipitation, heterogeneous methods which provide high degree of uniformity of distribution of components [6] are the most widespread.

Cryochemical method. Four operations are the cornerstone of this method: preparation of the mixed solution of salts, freezing, sublimation drying and heat treatment of powdery products. Physical and chemical bases of a cryochemical method of receiving high-homogeneous powdery materials are based on charts of a state «water-salt» [6]. The cryochemical method allows to receive 0.2 – 0.4 microns united in strong clump [7]. Need of the special equipment, labor input of technological process and also the possible aggregation of particles which is negatively reflected in a ceramics light transmittance belong to the main lack of this method.

Hydrolysis of salts. Hydrolysis of the isoproxide of MgAl₂ (OPri) 8 magnesium-aluminum is most often used for receiving transparent ceramics. The similar method is considered by authors of works [8, 9, 10] and consists in dissolution of magnesium and aluminum in isopropyl alcohol in the presence of activators (chlorides of tin and ammonium). Received thus isoproxide is exposed to vacuum distillation for additional cleaning. The mix of hydroxyls of aluminum and magnesium formed as a result of hydrolysis is calcinated before formation of complex oxide. In a research [11] it is shown what applications of this way has allowed to reduce spinel formation temperature: the formation of a phase of spinel will read at 360 °C, and full crystallization happens at 900 °C. The samples made by this method do not differ in the high level of light transmittance (figure 1) [10]. The high cost of initial materials and complexity of execution belongs to the main shortcomings of this way.

Thermal synthesis from initial salts. The method is rather simple performed by and consists in calcinating of mix of the initial components taken in a certain ratio. The similar way is considered by
authors of work [12]. Use of such way leads to emergence of defects in material and to receiving spinel with various degree of a frontage that can adversely affect transparency of ceramics.

Spray drying. Raspylitelny drying. The method consists in dispergating of initial solution in a heat carrier gas stream. As a rule, as the heat carrier air is used. Speed of evaporation of solvent and extent of supersaturation of solution depend on temperature of the heat carrier and speed of his giving. The main shortcomings of a method are considerable losses of material and the violation of its chemical homogeneity connected with redistribution of components in particles of a synthesizable powdery sample during process [7].

Sol-gel process. The principle sol-gel of process consists in transition of liquid solutions of alkoxide, esters or halogenides and also organic compounds to gel at hydrolysis and polycondensation which then in the course of heating at rather low temperatures is powdered [13]. The sol-gel technology has a number of advantages such as: a possibility of receiving dense amorphous bodies at lower temperatures; a possibility of receiving materials with adjustable distribution of particles by the sizes; possibility of obtaining high dispersion (0.1-0.05 microns) and purity; achievement of high uniformity of material [14]. This technology was used by authors of works [14] and [15]. Synthesis of spinel and particles up to 1 micron size happened to a faultless crystal lattice at 950-1000 °C, however, the ceramics on the basis of such powders had no high values of mechanical durability [15].

![Ceramic samples before (upper) and after (lower) annealing, synthesized by hydrolysis of isopropoxides in the slow (1) and rapid heating mode (2) [10].](image)

The Pechini method is one of modifications of a sol-gel way of receiving powders. The method is tolerant to water presence, does not demand the special atmosphere and careful control of the course of reaction. At the same time gel with ideally homogeneous distribution of atoms of metals turns out. Initial reagents at synthesis of complex oxides are served by water solutions of nitrates of metals which mix in a stoichiometric ratio. Organic compounds (lemon, wine, amino acetic, ethylene diaminetetra-acetic acids) are added to the received solution. Initially in the Pechini method as a complexing compound citric acid was applied. Synthesis by Pechini method can take place in two directions. Citric acid (saturated water solution) can be added to solution of nitrates and after to evaporate. There is an ignition of mix under heat treatment and amorphous carbon-bearing primary particles of compound oxides are formed. After cooling mix is frayed and annealed at more high temperature. In other case after formation of metal complexes polyatomic alcohol (ethylene glycol) into system is added. Solution is evaporate before formation of polymeric gel, which is subjected to heat treatment. In the course of synthesis ions of metals and carbonic acid form chelate complex. These complexes have free hydroxyl groups at the expense of which there is a polyetherification of
chelates to polyatomic alcohol. At the same time, ions of various metals will be evenly distributed in polymeric gel. At polymer decomposition formation of primary particles of plain oxides and their reaction with the subsequent formation of a single-phase high-disperse difficult oxidic product at the same time proceeds [16].

The main problem from the point of view of transparent ceramics production is that the particles as a result form strongly agglomerated powders. It is quite problematic to make a high density pore-free product of such powders. Besides, owing to a high non-equilibrium of process it is difficult to receive powders with strictly set parameters of an elementary cell and geometry of particles.

Heterophase methods. The method consists in receiving the low-hydrated slightly soluble connection by interaction of solid soluble salt of the main component with solution of the basis or acid. The amorphous hydroxides or oxalates received as a result of chemical interaction have high ability to absorption of ions from solutions in the “firm phase solution” system. Features of this method are that at transfer of solid salt of any element to slightly soluble connection an inheritance of structure of initial salt happens [6].

Coprecipitation method. Coprecipitation of the components which are a part of ceramics is reached in the form of slightly soluble hydroxides, carbonates or oxalates. Use of the concentrated solutions of salts and solution of the precipitator with various temperatures provides high dispersion of particles and also possibilities of regulation of the size of particles in very wide limits. Application of the return order of a coprecipitation provides course of all process at considerable excess of solution of the precipitator that allows to carry out simultaneous crystallization of components with formation of solid solutions of connections [6]. Often as the precipitator ammonia solution is used (an intermediate product in case of synthesis of oxides) the smaller size as the precipitator apply the bases which are at the same time well adsorbed on the surface of the stabilizer to receiving particles of a deposit. For example, applying tetraalkylammonia hydroxide as the precipitator, it is possible to receive particles of hydroxides of metals about 10-nanometer size [16].

Regulation of pH value allows to control phase composition of the received powders also. At coprecipitation of salts of magnesium and aluminum difficulties because of an essential difference in pH precipitation of hydroxides of magnesium (pH = 12) and aluminum (pH = 7,5) can arise water solution of ammonia, the probability of violation of the set stoichiometry of synthesizable connection is high [17]. In a research [12] it is shown that increase pH from 9 to 11 at coprecipitation with the subsequent heat treatment already at 400 °C is formed a phase of spinel and completely phases of hydroxides disappear. Also, according to data of work [18] sedimentation begins at pH = 4 and comes to an end at pH = 9, and at pH = 9 the stoichiometric ratio of cations in draft is reached [19].

Precipitation from water solutions is the most productive and simple method which does not demand the increased temperatures and pressure, organic solvents. Also advantage is rather short time of reaction [16].

The method of coprecipitation is most often applied at synthesis of powders of aluminum magnesium spinel. As initial components various salts of aluminum and magnesium are applied to synthesis of a precursor of AMSh. Are most often used Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O [20, 21, 22, 23, 24], Mg(CO₃)₃(OH)₂·4H₂O, Al(OH)₃ [25], NH₄Al(PO₄)·12H₂O, MgSO₄·7H₂O [12].

Important technological parameter for receiving spinel is synthesis temperature.

With temperature increase above 1000 °C the compound of spinels are significantly changed. There is a so-called γ- nonstoichiometry: aluminum magnesium spinel is beneficiates with quite considerable surplus of Al₂O₃. Any violation of a stoichiometry is followed by emergence of a disorder in a crystal – emergence of vacancies in knots of a lattice or settling of interstices [26] that can have an adverse effect on transparency and strength characteristics of material. It is established that process of a spinel formation depends on many factors: dispersions of initial components, their nature and a type of impurity, specially entered additives, annealing conditions, etc. Formation of spinel begins at 397-497 °C. However, the formed spinel is at the same time in extremely high-disperse, almost amorphous state. Good crystallization of spinel is observed at a temperature of synthesis of 697-897 °C [27].
For the purpose of decrease in temperature of agglomeration and also improvement of physical and mechanical characteristics of transparent ceramics from spinel use such method as introduction of the cementing additives LiF, B₂O₃, Y₂O₃, act as such connections.

For the purpose of increase in transparency of ceramics lithium fluoride into powders is added. Additive of LiF in quantities 0,5 – 3,0 % by weight promotes receiving ceramics with the porosity close to zero. At the same time presence of LiF leads to the intensive growth of crystals of spinel in the course of agglomeration that causes moderate sizes of microhardness and durability on a bend and negatively affects a light transmittance [8].

The similar effect is caused by spinel powder processing by boric acid (figure 2) [28]. Oxides of rare-earth elements often apply for receiving ceramic materials with the set properties as activators of process of synthesis of the main matrix. Along with B₂O₃ oxide of yttrium is considered to be one of the best mineralizers of a spinel formation. In a research [29] it is established that yttrium oxide introduction in number of 2 and 4% exerts strong impact on intensity of reaction of a spinel formation by method of solid phase synthesis in the air atmosphere is optimum for a combination of processes of synthesis and sintering. A spinel yield in this case at 1300 °C makes 100 and 99,7% respectively.

Perspective is an introduction of the additives promoting hardening of a matrix of spinel because of increased requirements to mechanical properties of armored ceramics [30].

![Figure 2](image)

**Figure 2.** The effect of temperature on the crystal size for various powders: 1 - spinel powder, 2 - powder with the addition of lithium fluoride (1% by weight), 3 - powder with the addition of boric acid [28].

Using boron as oxide modifier is effective. Experimental results have shown that presence of B₂O₃ not only reduces precursor powder sintering temperature, but also suppresses ceramics grain growth that provides high optical transparency. Optimum concentration of B₂O₃ at which the high coefficient of transmission (80% is reached at a thickness of 1 mm) makes 0.15 % by weight [31]. It should be noted that the way of introduction of B₂O₃ to powder exerts strong impact on the ceramics grain size. So, during the use of solution of boric acid and removal of powder from solution before drying the intensive growth of grain [28, 32] while drying and sintering of the powder which is not separated from solution allows to receive fine-crystalline structure [31] is observed.

The positive effect gives introduction to a nanocomposite spinel matrix of nanoparticles of Si₃N₄. The received samples have high value of a light transmittance (>70%), the value of impact strength has increased up to 85% [33].
At sintering of transparent ceramics such methods as the hot pressing (HP), isostatic pressing in the hydro / gasostats – cold (HIP) are often applied (GIP), the spark plasma sintering (SPS) [34] more hotly.

These methods provide good caking of material and allow to receive ceramics with high value of a light transmittance and mechanical properties. However, difficulty is represented by the complex equipment and high cost of processes. The method of vacuum sintering is the easiest way when receiving transparent ceramics and also allows to receive samples with high operational properties [22, 33].

The ceramics on the basis of aluminum magnesium spinel meets requirements imposed to modern means of an individual armored protection and is perspective material for production of transparent armor.

Now when receiving ceramics from spinel the special attention is given to synthesis of initial powder. There is rather large number of the methods allowing to synthesize fine-crystalline powders with the set form and the size of particles. The universal method of receiving spinel does not exist. At the choice of a route of synthesis it is necessary to consider all technological chain in general and especially the mode of the subsequent heat treatment. However, preference to low-temperature heterophase methods is given.

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