

Plasma-chemical method for producing metal oxide powders and their application

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Abstract. Structure and properties of ZrO_2 and Al_2O_3 powders produced using plasma chemical technique were studied in the framework of this research. Obtained Al_2O_3 powder was used for reinforcement of Al alloy. Improvement of mechanical properties of Al alloy associated with introduction of alumina particles into the melt was demonstrated.

1. Introduction

Micro- and nanoparticles of Al_2O_3 , ZrO_2 , AlB_2 , SiC etc. are used as reinforcing ones providing reduction of development of dislocations in accordance with Orowan's mechanism [1] in the process of alloy deformation which improves strength characteristics. Nowadays, the most promising methods of production of oxide nanopowders with high capacity are plasma chemical method. Plasma-chemical systems are characterized with high energy intensity of the heat flux: the temperature of plasma heat transfer media comprises $\sim 10^4$ K while their enthalpy comprises $(1-2) \times 10^2$ kCal/mol [2], which provides high specific production capacity of equipment.

It is known that morphology, particle size distribution, phase composition and structure parameters of powders are determined by the method of production. Thus, properties of the powders used for alloy reinforcement are to be studied carefully in order to provide target properties of materials produced on their basis.

The objective of this research is to study structure and properties of ZrO_2 and Al_2O_3 powders produced using plasma chemical technique and their use for modification of properties and structure of Al alloys.

2. Experimental

Alumina and zirconia powders were produced from sprayed water solutions of salts in air flow heated to low-temperature plasma state using a 70 kW high-frequency unit. The diagram of the unit is given in Figure 1. Sprayed solution is supplied to plasma jet of the heat transfer medium generated by plasmatron 3 in the plasma chemical reactor 2 via nozzles 1. The powders produced are separated by filter 5 and supplied to collector 9. Vapor-gas flow after cooling down in apparatus 6 is separated from the liquid (condensate is collected in tank 10) and prior to emission to atmosphere is cleaned in scrubber 7. In order to obtain metal oxides initial nitrate solutions of corresponding metals of these compounds were prepared with stoichiometric ratios of components and optimal temperature mode of the reactor of plasma-chemical unit was selected. The plasmatron was remotely activated 3-5 seconds



after application of voltage to ignition electrode from the inductor at the pressure level in discharge chamber close to atmospheric pressure or higher. The principle of operation of plasma chemical unit consists in the following: the prepared initial solution with specified composition is sprayed by a spraying device – a pneumatic atomizer – forming a gas-droplet mix spray cone which is supplied to cylindrical reactor with gas (heat transfer medium) flow, in our case it is air heated up to 5000-6000K in a low-temperature plasma generator (plasmatron). Droplet size comprises 50-100 μm . Gas droplet mixture is heated by a plasma jet generated in induction plasmatron powered by a high-frequency generator. Heating process takes place in the plasma chemical reactor having a direct-flow cylindrical scheme, which provides reliable, steady and safe operation in various modes. Solvent is evaporated here from solution droplets with subsequent decomposition of nitrates of Zr, Al etc. to oxides. Powders produced are separated in containers.

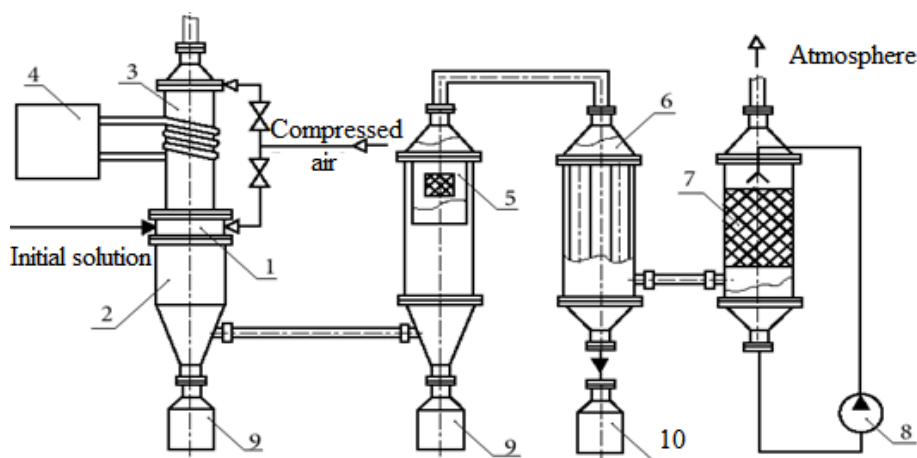


Figure 1. The diagram of plasma chemical powder synthesis unit

The structure of powders was studied using a Philips SEM 515 scanning electron microscope (SEM). The average size of powder particles was measured using the random linear intercept method [3]. The study of the phase composition and structural parameters of powders was performed using an X-ray diffractometer with $\text{CuK}\alpha$ radiation. Calculation of coherent scattering region (CSR) and microdistortion of the crystal lattice $\langle \epsilon^2 \rangle^{1/2}$ was performed using Williamson–Hall method [4] where all broadenings in the X-ray diffraction (XRD) profile were used for calculation. Phases were identified by comparing peaks of X-ray spectra with ASTM (American Society for Testing and Materials) card file. Specific surface area of powders was measured by BET method using a Sorbi analyzer with the measurement error not exceeding 3%.

3. Result and discussion

Preliminary study of kinetics of thermal decomposition using the method of derivatography was performed for Zr nitrates [5]. It was found that the process of decomposition has 8 stages with different kinetic characteristics. Results of this study are given in Table 1.

As it can be seen from the Table 1 water solutions of Zr nitrates are decomposed to Zr oxides at the temperatures higher than 1053 K. The study of Zr nitrate decomposition in a plasma chemical reactor show that the process of oxide formation from nitrate solutions at temperature levels in plasma chemical reactor is complete.

Table 1. Characteristics of the process of thermal decomposition of Zr nitrates.

Temperature range (K)	Mass reduction, (g.)	Chemical formula of the sample at the end of the process
353-443	0.030	$\text{Zr}(\text{NO}_3)_4 \cdot 8-9\text{H}_2\text{O}$
443-583	0.052	$\text{Zr}(\text{NO}_3)_4 \cdot 7\text{H}_2\text{O}$
583-738	0.075	$\text{Zr}(\text{OH})(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$
738-813	0.140	$\text{Zr}(\text{OH})_2(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$
813-893	0.180	$\text{Zr}(\text{OH})_3 \cdot \text{NO}_3 \cdot \text{H}_2\text{O}$
893-913	0.200	$\text{Zr}(\text{OH})_3 \cdot \text{NO}_3$
913-973	0.222	$\text{Zr}(\text{OH}) \cdot \text{NO}_3$
973-1053	0.268	ZrO_2

Powders represented a structure formed by individual spherical particles and bulk aggregated loose substance consisting of particles having irregular form (Figures 2, 3). According to the results of XRD and electron microscopic studies the powders represent an loose micro-aggregate system. Multiple morphology of powder particles produced using plasma chemical methods can be explained by the following circumstances. As the drops of solution come into contact with a heat transfer medium which has a high temperature intensive evaporation of solvent from droplet surfaces takes place, this leads to a sharp saturation of surface layer of the liquid relative to the salt dissolved in it. As a result the shells are formed on the surface of droplets with liquid solution or vapor-gas mixture inside. Under the influence of internal pressure the vapor-gas mixture breaks through these shells which harden after quick cooling down in reactor chill zone producing hollow porous spheres as well as fragments of broken shells [5]. The BET surface of plasma-chemical powder has been measured to amount $60 \text{ m}^2/\text{g}$. Phase analysis has indicated that alumina powder is in a highly nonequilibrium state and contains 5 structural modifications: rhombic (α), cubic (γ), tetragonal, hexagonal (ϵ) and monoclinic (θ). According to XRD analysis data the size of coherent scattering regions of alumina powder is approximately 30 nm. The crystal lattice micro-distortion is 5×10^{-3} .

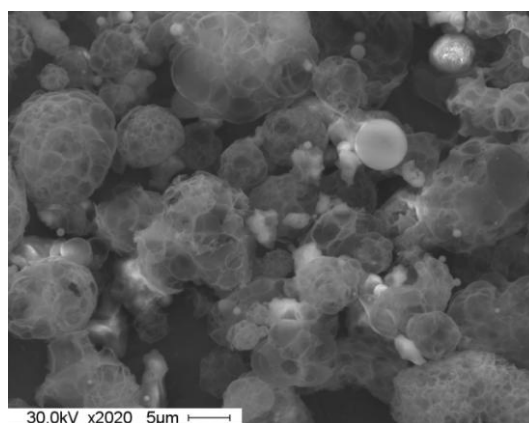


Figure 2. SEM image powder Al_2O_3

Electron microscopic studies have indicated that the average sphere size(diameter) comprises $1.2 \mu\text{m}$, grain size (grain size is considered equal to CSR size) comprises 20nm. As zirconia powder was obtained using a modifying additive(yttrium oxide), the powder contained tetragonal and monoclinic phases of zirconia, Figure 3b.

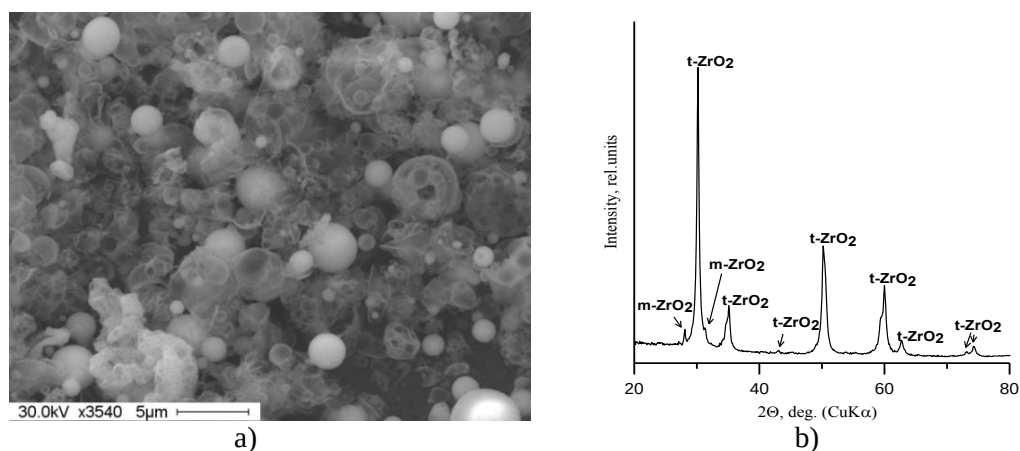
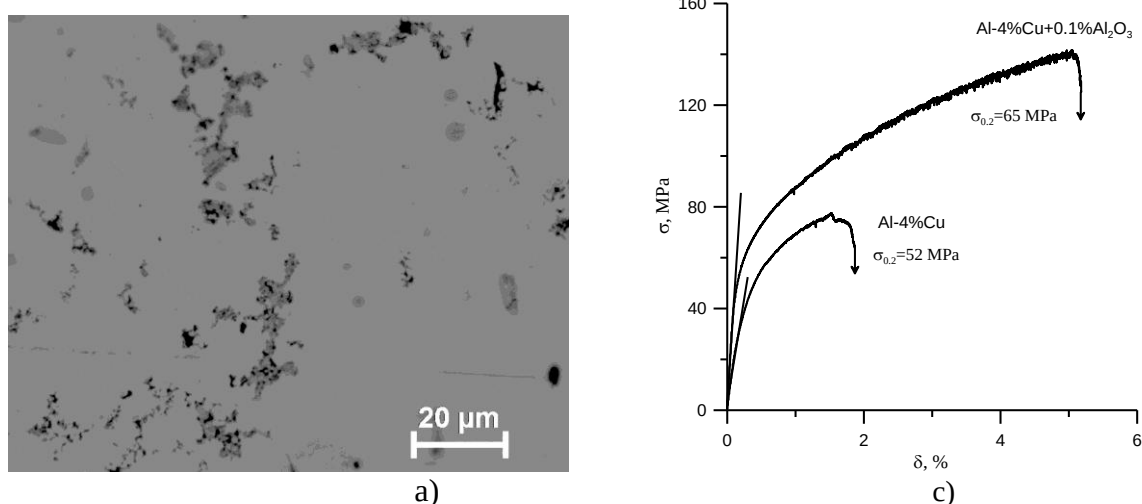
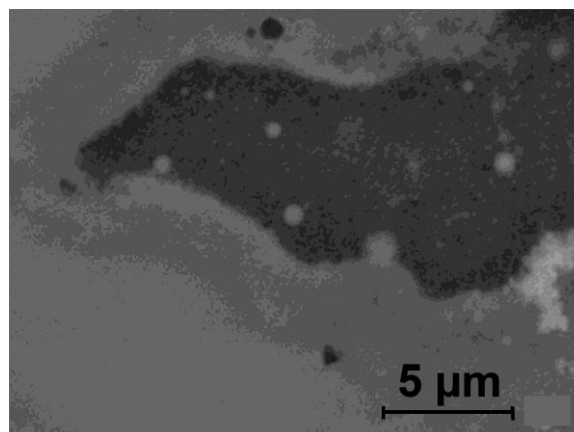


Figure 3. Powder $\text{ZrO}_2(\text{Y}_2\text{O}_3)$. SEM image (a); X-Ray pattern (b)

The tetragonal phase of zirconia prevailed, its share in the powder being 90%. The crystal lattice micro-distortion value was 2.4×10^{-3} ; and the lattice parameters were: $c = 5.1749 \text{ \AA}$, $a = 5.1028 \text{ \AA}$. The comparison of ZrO_2 tetragonal phase lattice parameters with the values given in work [6] showed that the values of lattice parameters for zirconia powder correspond to the values reported for tetragonal phase in the powders composed of $\text{ZrO}_2 + 3 \text{ mol. \% Y}_2\text{O}_3$.

Al_2O_3 - particles were used as reinforcing particles for introduction into an Al alloy. Densely compacted master alloy containing 10 wt% of nanoparticles was introduced into the Al melt with simultaneous ultrasonic processing. The microstructure of an Al-4 wt% Cu-0.1 wt% Al_2O_3 alloy is given in Fig. 4. The stress-strain tensile curves for produced samples are given in Figure 4b. As it can be seen, the introduction of 0.1% Al_2O_3 nanoparticles into the alloy leads to simultaneous improvement of yield strength, ultimate tensile strength and ductility. Moreover, alloy hardness also increases from 570 to 710 MPa.





b)

Figure 4. Microstructure of the as-cast composite material Al-4 wt% Cu+0.1 wt% Al₂O₃ (a, b) and stress-strain diagrams of this composite material in comparison with the matrix (c).

4. Conclusion

It was found that morphological structure of zirconia and alumina powders produced using plasma-chemical technique is a microaggregate system consisting of hollow spherical particles. Possible application of plasma chemical technique for production of metal oxides to be used for improvement of properties of Al alloys was illustrated using the example of alumina powders. Authors plan to synthesize AlN powders using plasma-chemical technique in order to use them as modifiers in nonferrous metallurgy and production of ceramics.

Acknowledgments

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