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NANOSTRUCTURED MATERIALS PRODUCTION- MODELING OF THE PROCESSES AND TEM IMAGE ANALYSIS

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Abstract : In the paper two items are discussed: i) the processes leading to production of nanostructured materials- powders or layers; ii) the analysis of TEM micrographs of glass materials suitable for nanocomposites formation. The considered processes are carried out in thermal plasma (direct current and radio frequency) set-ups. They are related to the production of ceramic materials such as Si-oxide, -nitride, -carbide. Modeling of the processes is made and relations between the process parameters and the products characteristics are found. TEM image analysis is related to immiscible oxide glasses where heterogeneous structures with micro- and nano-sizes are observed. The structure parameters of these structures are obtained.

Introduction : The thermal plasma suggests specific thermal- as well gas-dynamic conditions which make it a perfect medium for nanomaterials (powders, layers) production (see e.g. [1]). The successful production needs information about the relation between the processes, realized in the plasma set-ups and the product characteristics. This can be done by modeling the processes.

In this paper our experience in thermal plasma production of some ceramic nanomaterials such as Si-oxide, -carbide, -nitride is discussed. The stress is put on the modeling of the basic processes, taking place in direct current (DC) and radio frequency (RF) plasma set-ups.

Nanocomposites based on immiscible oxide glasses [2] are studied very actively. The attention is paid to the immiscibility micro- and nano-sized formations, in which suitable nanoparticles are to be involved and nanocomposites with specific functional properties to be obtained. TEM is an appropriate method for studying the structure of the glass matrices.

In the present paper some of our results on TEM image analysis of different tellurite glasses are shown and the evolution of the observed heterogeneities is considered.

i) Modeling the processes in thermal plasma set-ups :

1. Processes in DC arc plasma set-up for silica nanoparticle production

In the Institute of electronics BAS there is a long-term experience in studying the silica nanopowder production in thermal DC plasma set-up. The set-up consists of stationary vaporizer and flow plasma reactor, both working at atmosphere pressure. In the vaporizer the raw material (99.95% SiO₂) is heated and vaporized by Ar plasma (18 - 30 kW). In the flow reactor the vapor is rapidly cooled by mixing with a cooling gas, O₂. The ratio vapor to cooling gas is usually 1:10 or 1:25. During the cooling nanoparticles with mean sizes from some to some tens nm are produced. The processes in the vaporizer, as well as those in the plasma reactor, are modeled and the results are discussed in [3-11]. Here briefly the model assumptions and some of the more important results are presented.

1.1. Vaporization of the raw substance. Thermodynamic modeling

The vaporization is connected with SiO₂ chemical destruction to SiO and O and because of this the vaporization process can be influenced by use of reductors (C or H₂), which react with the oxygen.

The processes (destruction, reduction) are thermodynamically equilibrium since they take place in stationary device. Calculations are made [3, 9] for obtaining the chemical equilibrium contents of the species, the conversion degree of SiO₂ to SiO i.e. vaporization degree as well as the specific energy consumption for the vaporization of the SiO₂. Both parameters – vaporization degree and specific energy consumption are accepted as optimization parameters of the vaporization. Different systems, depending on the mole ratios of the initial components (Ar; SiO₂; C, or H₂), are considered and the optimization parameters are calculated. It is found that the vaporization is influenced by the initial mole ratios of the components; the use of reductor C (in stoichiometric mole ratio to SiO₂ i.e. 1:1) leads to a decrease of the SiO₂ vaporization temperature and also allows the vaporization to be carried out at high conversion rate and low energy consumption. The decreasing of the vaporization temperature plays important role in the processes carried out in the plasma reactor. It is shown [6] that in the cases when carbon is used in SiO₂ production powders consisted of small nanoparticles with aggregation ability.

1.2 Nanoparticle formation. Kinetic and gas-dynamic modeling

Silica nanoparticle formation takes place in the flow plasma reactor. The phenomena, realized in the reactor, are based on several processes (mixing, cooling, chemical reactions and condensation) carried out simultaneously in a very short time (microseconds). All these, time-dependent processes are considered in the model.

Three basic approaches are applied to present the mixing and the cooling processes. The first one [4, 5] simply accepts that the mixing is instantaneous and the cooling rate is a constant with values of 10⁵-10⁶ K/s. The second one is called “gradual mixing” [7]. In it an empirically found function (“mixing function”) is used to present the variation of the cooling gas concentration along the reactor. The other like function but with the opposite sign is used for the temperature evolution. The idea of the “gradual mixing” is continued in the third approach [8, 9] where the influence of the mixing on the temperature variation and on the vapor supersaturation is considered. In this last approach the fluid dynamic equations, as well as

mass- and energy balances, are used for obtaining the flow velocity, the temperature and the species concentration variations.

Usually the models, describing the nanoparticle formation from vapor of refractory raw substance, accept vapor high supersaturation at the beginning of the condensation. In such case the particle growth is determined by pure collision process (free-molecular coagulation). In our modeling the free-molecular coagulation is also accepted as the main process, responsible for the particle growth. In some works [5, 6, 11, 12] particle fusion process (coalescence) and respectively the aggregation ability of silica nanoparticles is also discussed.

As a result from the model calculations the particle size distribution function (PSDF) and its evolution is obtained. The influence of the different process parameters, such as initial precursor (SiO_2 gas molecule) concentration, cooling time i.e. time on the particle growth, etc. on the PSDF are investigated.

The more important results from our modeling can be summarized in the following :

a) case of instantaneous mixing and constant cooling rate

It is found out that PSDFs have log-normal character. From the integral form of the PSDF (log-probability line) the mean particle size is determined (at PSDF=50%). Figure 1 presents the calculated integral PSDFs for the both cooling rates (10^6 and 10^5 K/s) and for two initial precursor concentrations. The results show that if the processes are carried out with higher cooling rate and/or with lower initial precursor concentration, particles with smaller mean sizes can be obtained.

b) case of gradual mixing

It is obtained [7] that the mixing strongly affects the particle growth process. A delay in the precursor generation, as well as in the establishing of the self-preserving form of the PSDF is observed, due to the mixing.

Both approaches (a and b) accept, a priori, the silica vapor high supersaturation at the beginning of the condensation process. In the last approach (c) it is shown that the high supersaturation of the vapor is reached during the mixing.

c) fluid dynamic modeling of the mixing

It is found [8] that the mixing influences the temperature evolution which on its turn influences the variation of the precursor (SiO_2 gas molecules) concentration. The time for the SiO oxidation to SiO_2 depends on the type of O_2 mixing too. Two mixing functions are applied. At the linear one, the oxidizing time is shorter than that at the non-linear. After the complete SiO oxidation, the vapor saturation is observed. The supersaturation is not reached immediately but its value varies with variation of the temperature in the reactor.

In Figure 2 are shown PSDFs calculated for three different vapor saturations (7.6, 75, 195) reached at temperatures of 3000 K, 2710 K and 2590 K, respectively, in the case of linear and non-linear mixing. It is seen that the mean particle diameter (at PSDF=50%), is smaller in the cases of higher supersaturations, as well as in the case of linear mixing.

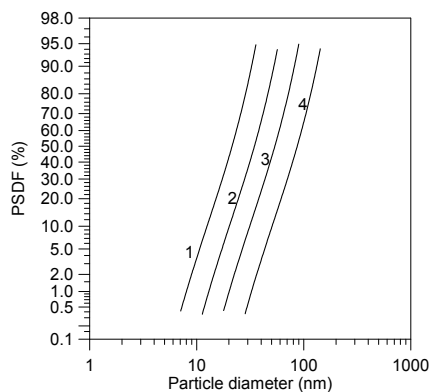


Figure 1 PSDF calculated for initial monomer concentrations $6 \times 10^{16} \text{ cm}^{-3}$ and $2 \times 10^{17} \text{ cm}^{-3}$ at cooling rate of 10^6 K/s (1, 2), at cooling rate of 10^5 K/s (3, 4), respectively

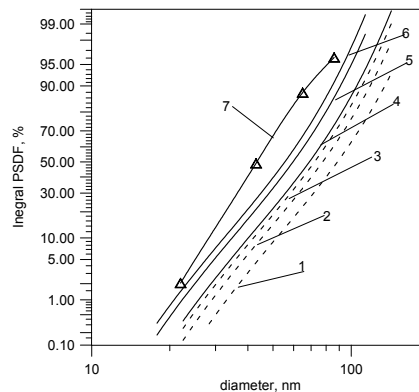


Figure 2 PSDFs calculated by fluid dynamic model, for linear mixing (1, 2, 3) for non-linear mixing (4, 5, 6); experimental PSDF (7).

Conclusions from the modeling of silica nanoparticle production

The modeling of the processes in thermal DC arc plasma set-up is important because: i) it helps the better understanding of the conditions, realized in the set-up, and their influence on the particle growth mechanism; ii) by the modeling optimization parameters for the raw substance vaporization, as well as relations between the process parameters of the flow reactor and particle characteristics (e.g. mean sizes), can be obtained.

2. Processes under the conditions of RF plasma for SiC, Si₃N₄ production

SiC, Si₃N₄ are advanced ceramics interesting because of their well wear-, corrosion-, and high temperature resistance. They can be produced as nanostructured coating by thermal plasma chemical vapor deposition. Radio Frequency Inductively Coupled Plasma (RF-ICP) set-up and liquid precursors - different types of chlorosilanes are applied for SiC and Si₃N₄ production [13, 14].

The processes, carried out in the RF-ICP set-up, and leading to SiC and/or Si₃N₄ synthesis are complex and as a first step of their understanding thermodynamic modeling is made [15]. The thermodynamic calculations are performed for the precursor, CH₃SiCl₃ and plasma gas - mixture of Ar/H₂ or Ar/N₂, taken in different ratios. Ar is used as precursor atomization gas.

The chemical equilibrium contents of the species in the systems Si-C-H-Cl-Ar and Si-C-H-Cl-Ar-N are calculated. The aim is investigation of the conditions under which the SiC and Si₃N₄ solid phases can be obtained.

For the system Si-C-H-Cl-Ar, 25 different cases are considered. They are determined at constant initial moles of the Ar and the H₂ and for 5 different initial moles of the precursor, CH₃SiCl₃ (0.007, 0.015, 0.017, 0.021, 0.026), and 5 different values of the pressure (10, 20, 30, 40, 50 kPa). The temperature is varied in the range 500-3000 K by steps of 100 K.

The results [15] show that in all cases the equilibrium mixtures contain both solid species SiC and C in a wide temperature range. The variation of the pressure does not influence the

production of the solid species. The variation of the initial CH_3SiCl_3 concentration leads to the variation of C and SiC. Pure SiC can be fixed below 800 K, only.

For the system Si-C-H-Cl-Ar-N the possibility for Si_3N_4 , synthesis by use of N_2 is studied. The N_2 is taken as addition to the plasma gas, Ar. As in the previous system, equilibrium compositions of 25 cases are calculated, depending on initial conditions. Ar and N_2 mole concentrations are kept being constant, the pressure as well as CH_3SiCl_3 concentration values are the same as in the system Si-C-H-Cl-Ar.

The results [15] show that in all cases three solid species (SiC, C and Si_3N_4) are observed in the equilibrium mixtures. Si_3N_4 is formed at temperatures lower than 1300-1400 K, near these temperatures both SiC and Si_3N_4 can be fixed in the most of the considered cases. It is obtained that the pressure, as well as the initial CH_3SiCl_3 concentration, influence the solid species production in the same way as it was observed for the system Si-C-H-Cl-Ar. Difference can be observed in the temperature range, in which SiC is fixed in the system Si-C-H-Cl-Ar, and in the system Si-C-H-Cl-Ar-N. In the last system SiC is fixed in higher temperature range 1400-2400 K. The experimental results also show that the use of N_2 favors the formation of the SiC high temperature phase (α -SiC) [14].

Conclusions from the modeling of Si-based ceramics production

The thermodynamic calculations, which are made, show the influence of the initial parameters in RF ICP set-up on the chemical and phase contents of the produced species. The possibility of SiC and Si_3N_4 solid species production from liquid CH_3SiCl_3 precursor under thermal plasma conditions is presented.

ii) TEM image analysis for studying the structure of glass materials

The TEM has special place among the methods for structure determination of the immiscible oxide glasses. As it is known these glasses are characterized with different types of immiscibility formations. The drop-like heterogeneities can serve as matrices for nanocomposite formation.

The appropriate processing of the TEM micrographs and the interpretation of the obtained results is of great importance for studying the glass structure.

We made TEM image analysis of the micrographs of samples of TeO_2 - GeO_2 [16] and also of TeO_2 - B_2O_3 separately and as a part of three-component systems in which the third glass-former is SiO_2 , TiO_2 , etc. [17]. The aim is to detect and characterize the immiscibility formations. The characteristics are drop area (A), perimeter (P) and circularity C ($C = 4\pi(A/P^2)$). Distributions related to the drop area and drop circularity, as well as average area (AA) and average circularity (AC) are also obtained. The average values- AA and AC are denoted as structural parameters (SPs) of the glasses.

Samples with different compositions are considered for the investigated oxide systems. Here we present the results for some of the systems.

For the binary system $94\text{TeO}_2.6\text{B}_2\text{O}_3$ it is found $AA = 0.051 \mu\text{m}^2$ and $AC = 0.824$, while for the sample $4\text{TeO}_2.96\text{B}_2\text{O}_3$ the metastable immiscibility drops are smaller, AA reach to 0.871nm^2 . The obtained results show that the SP depends on the glass composition.

In the ternary systems two kinds of the immiscibility drops are observed - big and small one. For the sample $60\text{TeO}_2.30\text{B}_2\text{O}_3.10\text{SiO}_2$ the big drops have $AA = 0.659 \mu\text{m}^2$ and $AC = 0.749$. Most of the small drops are connected with each other. For these one that are separated and have perfect spherical shape ($C=1$), $AA = 0.024 \mu\text{m}^2$. For the sample $60\text{TeO}_2.20\text{B}_2\text{O}_3.20\text{TiO}_2$ - the big drops have $AA = 6.074 \mu\text{m}^2$, $AC = 0.728$, the small separated drops have $AA = 0.114 \mu\text{m}^2$.

Conclusions from TEM image analysis of the glassy systems

In many binary and ternary TeO_2 -based glasses exist compositions with uniformly distributed metastable immiscibility formations. The SPs of these glasses are important because on this basis selection of the most appropriate compositions can be made in order to use the considered glasses as convenient matrices for composite materials formation.

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