

Advances in synthesis, application and dependence of vaporization of micron sized particles in thermal plasma in SOFC technologies

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Different plasma-chemical methods have been used lately in SOFC technologies form creation of nano-layers by magnetron or laser plasma spaying methods to use of sintering nano sized powders. The use of nano-sized powders obtained by plasma-chemical reactors, as electric-arc plasmatron Vissokov and co-workers used or high frequency inductive thermal plasma reactors (HFI), proves to be efficient and ecologically friendly method. Optimizing the parameters of Fuel Cells using nano powders we achieve higher specific capacity, current density and lower degradation rates of the material, as it is proven by various novel approaches by using plasma-chemical methods for FC production. The process of powder vaporization is limiting for any PCR, so we are looking to optimize the characteristics of the plasma generator in order to obtain nano particles with high purity and the reaction taking place in gaseous phase should modeled to produce the right size uniform size nano powders. There have been considered schemes for vaporization of micron-sized particles in electric arc and high frequency inductive thermal plasma reactors (HFI). Making use of the set of equations (RCF-method), we also performed calculations for the following oxides: Al_2O_3 , CaO , CuO , Fe_2O_3 , MnO_2 , MoO_3 , NiO , SiO_2 , TiO_2 , ZrO_2 , MgO . When modeling the process, one usually consider the most unfavorable case of vaporization taking in account the largest micron particle diameter. Changes in the diameter of micron-sized particles are calculated along the plasma-chemical reactor axis, using the set of equations constructed by the team searching for selection of the optimal parameters. A comparison is made between the calculated literature data and specific research results in thermal plasma.

Keywords: powder vaporization, plasma-chemical methods, (HFI), SOFC, nano powders

INTRODUCTION

Different plasma techniques have been developed and adapted to the specific requirements of efficiency in SOFC fabrication. The nano-particles can be synthesized by a number of synthetic methods, such as co-precipitation method, assembly process, template method, sintering of nano-powders or cost-effective spray process as atmospheric plasma spray ("APS"), vacuum plasma spray ("VPS"), radio frequency plasma spray ("RF"PS), and high velocity oxy-fuel ("HVOF") spray. Solid oxide fuel cells ("SOFC"s) are capable of generating electric power through the chemical reaction between hydrocarbon fuels and oxygen with high efficiency. Their further mechanical reliability can be improved and manufacturing cost can be reduced by reducing cell operating temperature. Therefore, the development of intermediate temperature SOFC technology has attracted a lot of worldwide attention of future energy markets. As relates to SOFC technology,

lower operating temperature requires higher activity of electrodes, high ionic conductivity of electrolytes, low over potential of electrode/electrode, and lower overall internal resistance loss is a goal. It is how to fabricate the thin (<20 μm) electrolyte layer with the full density (>97%) that is required to provide satisfactory gas tightness and internal resistance loss. These requirements can be met by developing new electrode/electrolyte membrane materials, improving cell assembly concepts, and novel fabrication methods using plasma technologies. The theory and practice of heterogeneous catalysis have demonstrated that the activity of solid-phase catalysts is determined by their chemical and phase content, crystal structure and active specific surface. A correlation of slopes is usually observed between the catalysts' active and total specific surface dependencies. On the other hand, it is also known that one can use LTP [6,11] to produce condensed-phase compounds (metals, oxides, nitrides, spinel materials, etc.) that have highly developed specific surface with the size of their ultra-dispersed particles (UDP's) of the order of few tens of nanometers (nanopowders NP). These

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compounds manifest high catalytic activity [1-3,14]. When the plasma-chemical synthesis (PCS) of UDP's is accompanied by chemical reactions, and when an effective quenching of the reaction products takes place at rate $dT/d\tau = 105 - 106 \text{ K s}^{-1}$, then conditions are created for condensation of UDP's with an unusual distribution of the additives [3,9], degenerated crystal structure [3,18,] and numerous defects in the crystal lattice; these also exhibit high catalytic activity in heterogeneous catalytic processes [1-3,9-18,] and low deteriorating rate in high temperature applications. All stated above makes the material obtained by plasma-chemical synthesis extremely suitable for SOFC applications. Plasma processes for sequential fabrication of the multiple layers in a SOFC unit by spraying or sintering are the best offer at present for the fabrication of nanostructured electrodes for high-performance primary and rechargeable lithium batteries are showing a great deal of promise when applied to SOFCs and stacks.

2. THERMAL PLASMA SYNTHESIS OF NANOSIZED METAL POWDERS -THEORY

Recently metal powders with relatively large sizes of 50 ~ 500 nm are increasingly in demand in various industries as the alternatives to conventional micron-sized ones. For example, Ni powders with sizes of 50 ~ 200 nm are very promising as the attractive electrode materials in high performance or SOFC. However practical applications for most kinds of metals with sizes of <50 nm exhibiting particular properties due to the size effect, are now limited because they are still expensive. The plasma-chemical technique (PCT) thus turns out to be efficient in synthesizing highly active catalysts [1-3, 9-103] Although at present the investigations on the preparation of highly active catalysts are still at the laboratory, pilot-plant, or patenting stage, reports on the item have been found in the specialized literature on the synthesis and activation of catalysts under low-temperature plasma conditions [1-3,6,9-17]. The way of catalyst preparation affects such important properties as its specific surface, porosity, density, mechanical strength, thermal stability, etc. This is why the preparation procedure is sometimes as important as the catalyst's chemical composition. According to Roginskiy's theory of over-saturation [17], catalysts obtained under the conditions of energy over-saturation must possess an increased activity.

The extent of energy over-saturation of a system increases with the increase in the rate of heat

transfer to the system, according to the following equation:

$$dQ/d\tau = \alpha(T_1 - T_2)dF_1 \quad (1)$$

where T_1 is the temperature of heat carrier (plasma in the case considered here) and T_2 is the temperature of the heated substance (micrometer-size particles), dF is the surface separating plasma and particles. If one assumes that the material treated is of spherical shape with radius R , then the specific surface of particles belonging to different fractions will be inversely proportional to their radii

$$F_1/F_2 = R_{12}/R_1 \quad (2)$$

or, the smaller the particles, the higher will be their specific surface. However, decreasing the particles size is only reasonable to a certain limit, defined by Biot's number

$$Bi = \alpha R/\lambda = (R/\lambda)/(1/\alpha) \quad (3)$$

where λ is the particle coefficient of heat conductivity and α is the coefficient of the heat transfer from the heat carrier to the particle.

The numerator in Equation 3 characterizes the resistance to heat propagation from the surface to the centre of the particle, and the denominator, that to transfer of heat from the heat carrier to the particle surface. When R is large, the heat-transfer process is limited by the heat resistance of the particle, and inversely, for small R , by the heat resistance of the phase interface. There obviously exists a value of R for which the two quantities are equal ($Bi = 1$)

$$R = \lambda/\alpha \quad (4)$$

To create the maximal energy over-saturation, the raw material must be pre-dispersed to a particle size as close as possible to that defined by Equation 4. The calculations for the case of catalyst, e.g., elemental Fe or iron oxides yield a value of approximately 50 μm . It is well known that industrial catalysts must comply with the following requirements:

- 1) Activity – the catalyst should provide sufficient reaction rate under the specific technological conditions;
- 2) Stability – the catalyst should not lost its activity over a lot period of time;
- 3) The catalyst should exhibit a lack of sensitivity to catalytic poisons, mostly chlorine and sulfur compounds;
- 4) Selectivity – the catalyst should accelerate the desired reaction only, and not side reactions;
- 5) It should have good mechanical strength;

6) Most of the catalysts are produced as oxides and have to be reduced before use the reduction period should be as short as possible in order to avoid a decrease in the production efficiency.

The assumption for the limiting role of the stage of condensed-phase vaporization in heterogeneous PCR has found wide acceptance. An important consequence of the assumption is that, besides ensuring suitable thermodynamic conditions (temperature, reagents ratio), one has to guarantee also sufficient time of residence of the particles in the PCR so that they are completely vaporized. The presence of these conditions will allow one to synthesize the product desired in gas phase. Following an appropriately fast cooling of the reacting mixture, i.e., at a given quenching rate $dT/d\tau$, the product can be obtained in the ND form needed. The above makes obvious the necessity of modeling the particles vaporization process. One could thus obtain sufficiently accurate data to determine the process' optimal parameters, such as, PCR dimensions, time of residence of the particles in it, temperature profile along the reactor's axis, temperature in the zone near the walls, temperature of the reactor wall, etc. Some researchers (Polack *et al.* [32]) have modelled the process up to the particles' melting point; others (Panfilov *et al.* [30,31]) have applied numerical methods to solve the set of differential equations describing the process - a procedure inconvenient for practical engineering calculations.

3. EXPERIMENTAL RESULTS

Primarily Vissokov and co-workers used to solve the set of equations for the case of an iron particle. Metal iron (radius 5 μm and 30 μm) in electric-arc plasmatron LTP (cathode-anode distance of 10 mm and diameter of the anode-nozzle channel of 5 mm) is used as a raw material in the production of catalysts for ammonia synthesis. To perform the calculations, one needs to know the values of c_p , c_p , J/kg.K; T_{p0} , T_{g0} , T_{pb} , T_{pv} , K; L_{pb} , L_{pv} , J/K; ρ_g , ρ_p , kg/m³; M_g , M_p ; G_{p0} , G_{g0} , kg; g_g , g_p , kg/s; V_{g0} , V_{p0} , m/s, which can easily be found in the specialized reference literature; other parameters are set a-priori: plasma forming gas (argon) with consumption in the range 2.6.10⁻⁴ kg/s (~0,5 m³/h Ar) - 9,93.10⁻⁴ kg/s (~2 m³/h Ar); metal powder consumption (fraction 1 - 50 μm) (1,39 - 4,17).10⁻⁵ kg/s (50 - 150 g/h); plasma temperature 8 000 K.

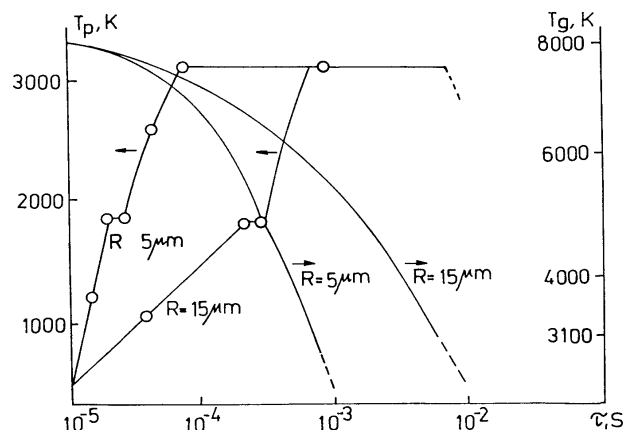


Fig. 1 .Variation of the particles (T_p , K) and gas (T_g , K) temperature as functions of the time of contact (τ , s) and particle radius (τ , s).

As one can see in Fig.1 particles with diameter below 30 μm are fully vaporized in the PCR, which is an important practical fact for the efficient quenching of the vapor-gas mixture in the production of nano-dispersed catalytic mass. The data obtained (Fig.1) concerning the temperature, time of particles melting and vaporization and the gas temperature as functions of the time of contact between the gas and the particles, and between the gas and the PCR walls, are in good agreement with the experimental data. the equations can also be employed to find preliminary values for the coefficients of heat-exchange between the gas and the particles and between the gas and the reactor walls.

The set of equations is solved by means of the RKF 45 program . The Runge-Kutta-Felberg technique is applied to solving sets of ordinary differential equations. When modeling the process, one usually considers the most unfavorable case of vaporization, namely, the largest particle diameter. In order to account more precisely for the influence of the vaporization kinetics on the product transformation degree, it is suitable [39] to introduce the quantity of relative (dimensionless) time of residence (τ_r) obtained by dividing the time of residence of the particle in the reactor (τ_p) to the time necessary for its total vaporization (τ_v) for the same average mass temperature in the reactor:

$$\tau_r = \frac{\tau_p}{\tau_v}, \quad (5)$$

To determine τ_p , the set of equations (2.10 - 2.17) is solved for the following boundary conditions: $d_p - d_{p0}$, 0; $S - 0$, S_0 ; $T_g = T_{g0}$, where S_0 is the length of the plasma chemical reactor, m ; T_{g0} is the average mass temperature of the plasma-chemical reactor, determined by making use of its energy balance, K. To determine τ_v , we apply the

following boundary conditions $d_p - d_{p0}, 0; S - 0, S_0; T_g = T_{g0}$. Besides the relative time of residence, let us now introduce with the same purpose the quantity of degree of vaporization (β):

$$\beta = \frac{G_p^0 - G_p}{G_p^0} \cdot 100, \% \quad (6)$$

where G_p^0 is the initial mass of the particle, kg; and G_p is the mass of the particle at the moment τ_p at the reactor's exit, kg.

The set of equations constructed can be used in the selection of the optimal parameters (PCR dimensions, minimal necessary time of contact between the plasma jet and the particle, place of quenching agents' introduction, as a result of determining the temperature profile along the reactor axis, the temperature strength of the reactor material, etc.) of processes taking place in high-temperature jets with the participation of a vaporizing phase, including the preparation of NDP. Considering the least favorable case, namely, the radius reduction of an iron particle due to vaporization for initial radius of 50 μm as a

function of the plasma-forming gas (argon) consumption and of the particle's location along the PCR axis (Fig. 2). As one can see, due to vaporization, the iron particle's radius at the PCR exit is reduced to approximately 1 μm ; while an iron particle with initial diameter of 20 μm is fully vaporized when the temperature of 8 000 K is reached (Fig. 3). Of course, in the cases of PC preparation of complex compounds (e.g., catalysts, amorphous alloys, composite materials), one can also add in the system of ingredients compounds (oxides, salts, elements) with boiling temperature lower than 3 000 K. For example, one can see in Fig. 4 that, for initial diameter of 20 μm , the particles of all elements considered (Mg, Al, Si, Ca, Ti, Mn, Fe, Ni, Co, Cu, Zn, Zr, Mo) are fully vaporized in the PCR. Returning to the least favorable case (vaporization of particles with diameter of 50 μm), one sees that the Mg and Ca particles are fully vaporized, while the degree of vaporization of the other elements is negligible.

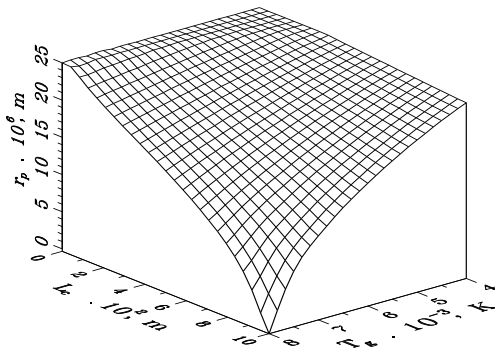


Fig. 2. Variation of the radius of an iron particle with initial diameter 25 μm depending on the plasma jet temperature and on the particle location along the PCR axis.

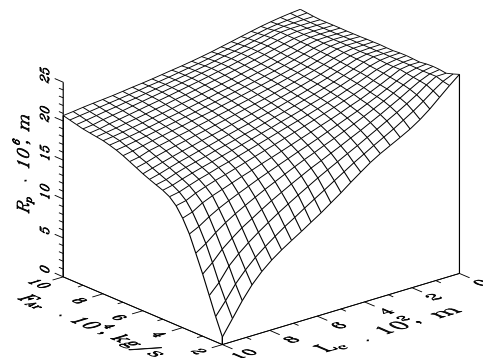


Fig. 3 Variation of the radius of an iron particle with initial diameter 20 μm depending on the plasma-forming gas (argon) consumption and on the particle location along the PCR axis.

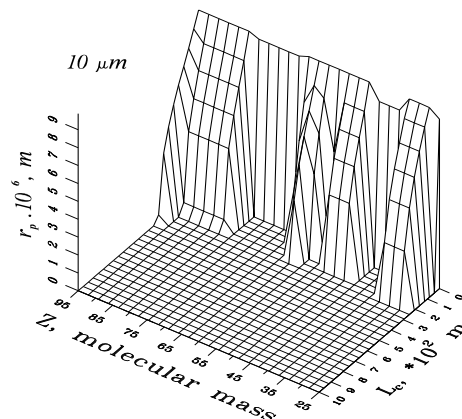
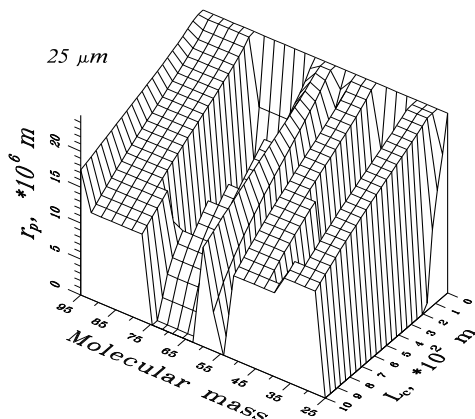


Fig. 4 Variation of the radius of a particle with initial diameter 50 μm and 20 μm depending on the molecular mass of the respective element and the particle location along the PCR axis.

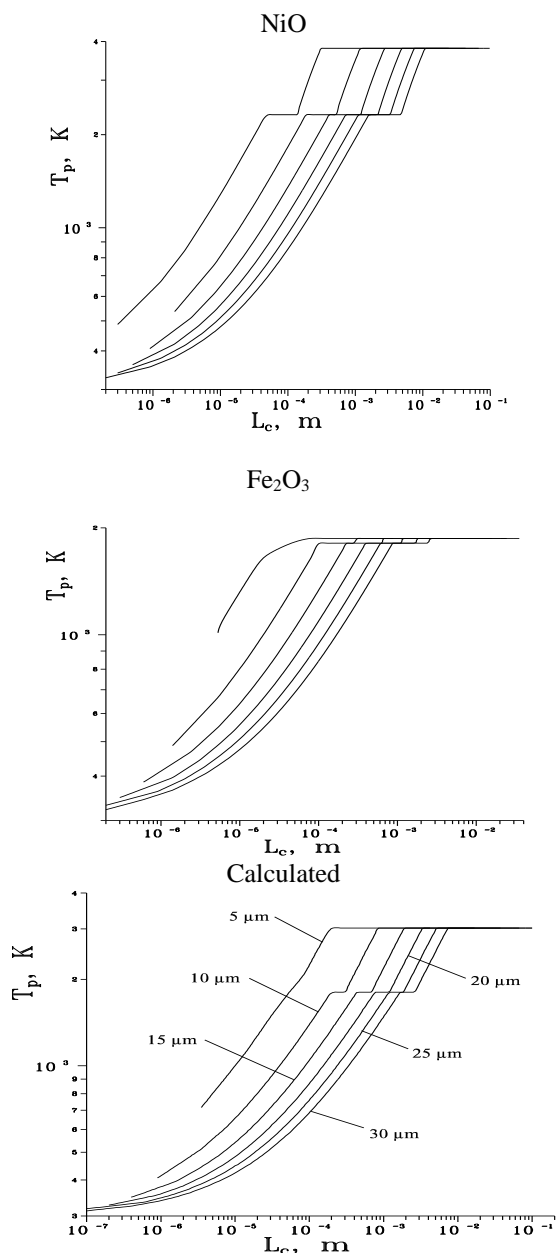


Fig.5a. Variation of oxide particles' temperature (T_p , K) as a function of their location along the PCR axis initial diameter from left to right :5, 10, 20, 25 and 30 μm .

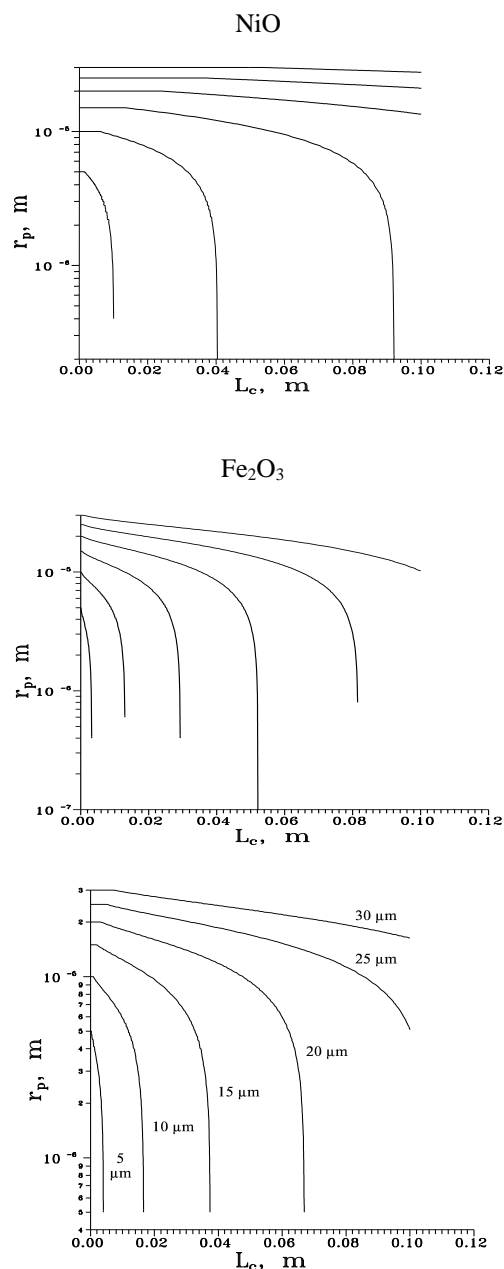


Fig. 5b. Oxide particles' radius (r_p , m) variation as a function of their location along the PCR axis (L_c) initial diameter from left to right :5, 10, 20, 25 and 30 μm .

The particles with $d_p = 20 \mu\text{m}$ reach the boiling temperature within the first 1/3 - 1/5 of the PCR length while those with the largest diameter $d_p = 50 \mu\text{m}$ are heated up to the boiling.

Making use of the set of equations, we performed calculations for the following oxides: Al_2O_3 , CaO , CuO , Fe_2O_3 , MnO_2 , MoO_3 , NiO , SiO_2 , TiO_2 , ZrO_2 , MgO . These are used as raw materials for various types of syntheses of NDP. We plotted the variation of the particles' radius of the respective oxide as a function of their location

along the PCR axis and illustrated the variation of the temperature of the oxide particles depending on their location along the PCR axis giving example with NiO and Fe_2O_3 . PCR parameters are set *a-priori*: plasma forming gas (argon) with consumption in the range $2,6 \cdot 10^{-4} \text{ kg/s}$ ($\sim 0,5 \text{ m}^3/\text{h Ar}$) - $9,93 \cdot 10^{-4} \text{ kg/s}$ ($\sim 2 \text{ m}^3/\text{h Ar}$); metal powder consumption (fraction 1 - 50 μm) $(1,39 - 4,17) \cdot 10^{-5} \text{ kg/s}$ (50 - 150 g/h); plasma temperature 8 000 K.

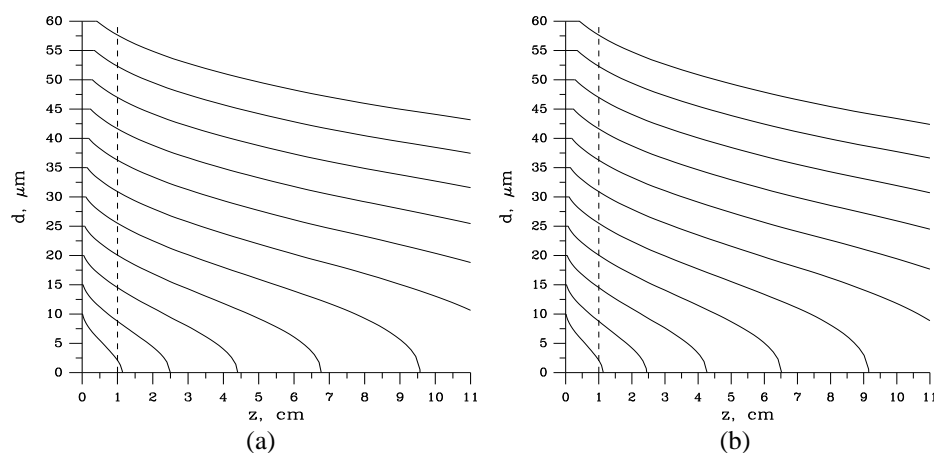


Fig. 6. Variation of Fe_2O_3 particles diameter along the axis of a CW PCR (a) and WW PCR (b)

In order to select appropriate experimental conditions (PCR length and diameter, ingredients' granulometry) for PC preparation (activation of spent samples) of nano-dispersed catalysts for steam conversion of hairdo carbons (natural gas reforming), we calculated the motion, heating, melting and vaporization of micron-sized particles ($d_{eq} = 10, 15, 20, 25, 30$ и $35 \mu\text{m}$) of Ni, NiO, Al, Al_2O_3 , CaO, Fe_2O_3 Mg and MgO in CW and WW PCR.

CONCLUSIONS

The results of the calculations performed agree well with the results of the synthesis and/or regeneration of catalysts for natural gas reforming (steam conversion of methane) and all experimental data received of nano powder obtained. Depending on the features of the target materials and employed plasma torches, various synthesis routes have been analyzed In order to select appropriate experimental conditions for PC preparation of nano-dispersed powders. In-flight treatment of solid precursors may be preferable in the preparation of nano-sized glass powders and single phase oxides, such as, ZrO_2 , NiO, SiO_2 , Al_2O_3 and TiO_2 . Among them, single phase oxides can be prepared by reactive thermal plasmas synthesis. However, their reproducibility and stoichiometry problems should be solved for practical applications with the use of proper computational methods. Depending on the physical properties of ceramic materials, such as melting points, enthalpy, evaporating rate and quenching the treated products can become a metal core – ceramic shell structured particle or a metal catalyst dispersed on ceramic supports. For the ceramic powder of BaTiO_3 with relatively low melting point, the mixed Ni metals can be buried into BaTiO_3 droplets and reformed into Ni core -

BaTiO_3 shell structured nano-composite. We can conclude that the advantages of thermal plasmas, such as, high enthalpy flows combined with a rapid quenching rate, can be very promising in the synthesis of not only a single phase material but also binary or higher nano-materials useful for SOFC production. Nanosized powders in the range of 10–120 nm have been prepared by introduction and evaporation of coarse-grained commercially available powders of chemical elements, oxides or salts in radio-frequency nitrogen, oxygen or air plasma as well as electric arc plasmatron. The necessary conditions for preparation of nanosized powders include evaporation of precursors, control of particle growth and elimination of formation of precursor particles or extra phases and promotion of formation of product particles. Evaporation of mixture of raw powders in the inductively coupled plasma creates good conditions for preparation of multicomponent, highly homogeneous nanoparticulate composites Main advantages of plasma technique are relative high production rate, production ability of several composite powders with high definite specific surface area, phase and chemical composition. The main drawbacks of the plasma technique relate to high energy consumption and wide particle size distribution. Nanostructural materials from prepared powders are manufactured by using conventional pressureless sintering, hot pressing and spark plasma sintering.

The knowledge accumulated and production experience convinces that nano-sized powders produced by ICP plasma technique can be applied successfully for manufacturing advanced ceramic materials.

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НАПРЕДЪК В СИНТЕЗА И ОПРЕДЕЛЯНЕ НА ЗАВИСИМОСТТА ОТ ИЗПАРИЕНИЕТО НА ЧАСТИЦИТЕ С МИКРОННИ РАЗМЕРИ В ТЕРМИЧНА ПЛАЗМА -ПРИЛОЖЕНИЕ ВЪВ ВИСОКОТЕМПЕРАТУРНИ ГОРИВНИ ЕЛЕМЕНТИ

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(Резюме)

Направена е обширната литературна справка ,проучване и оценка на съвременното ниво на развитие на проблематиката при приложение на плазмените технологии в производство- то на твърдо оксидни горивни елементи (SOFC). Направена е оценка на синтезираните нано дисперсни прахове от проф. Високов и колектив. Оценена е зависимостта на изпарение на тринадесет химични елемента е, а също на различни оксиди като циркониев оксид явяващ се основен материал при изработката на мембрани твърдо оксидните горивни елементи ,както и специфичните физикохимични характеристики на полученият материал. Вземайки под внимание екологичния импакт, можем да отнесем плазмените методи на синтез към щадящи екологията производства.