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Synthesis of Ceramic Oxide Powders in a Microwave Plasma Device

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Abstract

Synthesizing oxide ceramic powders by application of a microwave plasma is of great advantage. The microwave plasma can be used two ways: to act as a source of heat for the pyrolysis of solutions and to excite gas phase reactions to obtain nanosized powders. Both applications are superior to standard methods. A microwave cavity well suited for these experiments and its operating characteristics are described. Using a microwave plasma as a source of heat for pyrolytic decomposition of nitrates in aqueous solutions leads to a fine grained product with particle sizes from 100 to 1000 nm. Crystallite sizes in those particles are in most cases less than 10 nm. This is demonstrated with zirconia-based ceramics, such as ZrO_2 - 3m% Y_2O_3 - 20m% Al_2O_3 . Depending on conditions during pyrolysis, it is possible to obtain a product in which alumina is either dissolved in zirconia or the onset of the phase separation is observed. Energy efficiency for this process is better than 80%. If the reactants are gaseous, e.g., ZrCl_4 , it is possible to produce powders with mean crystallite sizes of about 4 nm. In the case of zirconia these particles are nanocrystalline with a cubic structure. This structure is not in equilibrium under the experimental conditions.

1. Introduction

Pyrolytically prepared powders usually exhibit excellent homogeneity and small grain sizes. This is of importance, as it is nearly impossible to obtain perfect homogeneity when synthesizing complex powders using classical ceramic technologies, such as blending or milling. In the case of chemical precipitation, it is difficult to obtain homogeneous powders, since the different constituents usually precipitate at different pH values. Pyrolytic processes, performed in electrically heated systems usually have a low energy efficiency [1,2]. Energy efficiency can be improved by using a flame as a source of heat, however the process is constrained by chemistry and safety of the flame [3,4]. These problems can be minimized if a plasma is used as the source of thermal energy [5,6]. Certainly, the energy efficiency of a flame process cannot be achieved, as all processes using electrical energy are impaired by the second law of thermodynamics. Direct coupling of microwaves to a mist of a salt solution avoiding a plasma does not lead to a dried and completely reacted product. This is because the coupling of microwaves with frequencies up to 2.45 GHz to the small droplets is not sufficient [7,8].

Other interesting applications of a microwave plasma are gas reactions, where kinetic or thermodynamic inhibitions can be overcome. These obstacles are overcome by the interaction of gas species of the starting material with charged particles like electrons, ions, or radicals. This opens the door to new routes for the synthesis of nanophased ceramic powders. The first experiments in this direction using a frequency of 2.45 GHz in an argon plasma [9] or with a frequency of 0.915 GHz in a argon-oxygen plasma [10] resulted in nanophased powders. The importance of those methods can be found in the fact that all of the previously published methods for synthesis of nanophased powders are non-continuous [11,12]. A new continuous method with low energy consumption would be of great importance.

It is the aim of this paper to demonstrate the experimental possibilities of a microwave plasma in synthesizing ceramic powders with different structures.

2. Device for the Synthesis of Ceramic Powders in a Microwave Plasma

2.1 Basic considerations

Plasma processes for the synthesis of ceramic powders are described frequently. Such processes use either a rf or dc plasma [13,14,15].

Working at ambient or slightly reduced pressure, such a plasma has temperatures of more than $10,000^{\circ}\text{C}$ as well as very high viscosity. This creates nearly insurmountable experimental problems. Working at low pressure (e.g. $\gg 1$ mbar) reduces the temperature and the associated problems, but the production rate is also decreased [9,15].

A microwave plasma is a "non-equilibrium" plasma. In such a plasma, the energy of the electrons is substantially higher than the energy of the ions. The energy of uncharged particles is even lower. This is because the energy transferred to a charged particle in an oscillating electric field is proportional to $E/(m \cdot f^2)$, where E is the electrical field strength, m is the mass of the charged particle, and f is the frequency. As the transfer of energy is inversely proportional to the square of the frequency, the temperature in a microwave plasma is significantly lower than in a rf or dc plasma. Typical temperatures in a microwave plasma are in the range of 400 to 1000°C . The energy transferred in a microwave plasma occurs through the collision of electrons with neutral particles. In this case, the energy transferred is proportional to $E/m \cdot z/(f^2 + z^2)$ [16], where z is the collision frequency between the electrons and the neutral particles. It is obvious that the energy transfer increases with increasing collision frequency for $z < f$ and decreases with the collision frequency for $z > f$. According to the kinetic theory of gases, the collision frequency increases with increasing pressure. The most stable experiments can be performed in the range $z < f$. According to these considerations, at a given frequency two free parameters influence the energy transfer to the plasma: gas pressure and electrical field strength. The power density in the plasma can be controlled to some extent by selected impurities in the gas and increasing ionization density [17,18,19].

2.2 Experimental setup

Figure 1 is a sketch of the experimental device. The plasma tube, made of quartz, is located in a TE_{01} waveguide (type WR

975, which is equal to IEC 153 type R9) of a 915 MHz microwave system. This portion of the waveguide is made of stainless steel. The reaction tube is located in a cut-off tube to prevent microwave radiation leakage. A mist of an aqueous solution or a vapor of a metal chloride is introduced into the upper part of the tube. Temperature is measured after the plasma zone, where the gas mixture has achieved an equilibrium temperature. The experiments were performed at temperatures from 450 to 850°C. Powder was collected on a grid heated to 450°C to avoid adsorption of reactive gases on the surface of the powder particles. The microwave system was adjusted by using a sliding short to obtain a standing wave. Tuning of the system is monitored by the ratio of the reflected to input power. Figure 2 shows this ratio as a function of the position of the sliding short for different load conditions. In the case of an empty cavity, i.e., the cavity with quartz tube but without plasma, the power ratio is sinusoidal, reflecting the standing wave in the system. The minimum in the reflected power is at a reflector position of 80 mm. At this position a maximum of the power is absorbed in the walls of the cavity. At 190 mm a minimum of power is absorbed in the cavity. Ignition of an argon plasma under reduced pressure of about 5 mbar is possible for reflector positions from 180 to 210 mm. After igniting the plasma, the tuning of the cavity is changed dramatically. Because of the power absorption in the plasma, the cavity is detuned in such a way that it is possible to maintain a stable plasma from 90 to 270 mm. In the case of the lowest pressure (40 mbar), with the least absorption, the region for a stable plasma was reduced to a range from 110 to 260 mm. The data plotted in Fig. 2 illustrates the increasing absorption of microwaves in the plasma with increasing pressure. As can be seen from the two curves plotted for 90 mbar, the data for the reflected power in a plasma loaded cavity is very reproducible. Additional tuning can be obtained by adjusting the impedance of the system with a triple-stub tuner. The triple-stub tuner allows optimization of a specific set of operating conditions. Small alterations to those conditions will lead to significant detuning of the cavity causing immediate plasma quenching.

Typically a gas volume of about 5 - 10 m³/h STP is passed through the plasma zone. Gas pressure in the system ranged from 70 to 140 mbar. This led to a mean residence time of a particle or gas molecule of approximately 1 ms in the plasma zone. Powder particles were collected approximately 3 to 4 ms after leaving

the plasma zone. During this time the particle cooled from the synthesis temperature to the temperature of the specimen collector.

An important advantage of this process is the low energy consumption. Careful measurements revealed that there is excellent transfer of microwave energy to the plasma. More than 80% of the energy of the electromagnetic field goes into the plasma [5,6]. Energy losses are due in approximately equal parts to ohmic losses in the stainless steel cavity and reflected energy not absorbed in the plasma. Ohmic losses can be reduced by using a copper cavity. A further minimization of the reflected power leads, as indicated in the previous paragraph, to unstable operating conditions.

3. Synthesis of Powders from Solutions

3.1 Aqueous solutions

The pyrolytic preparation of ceramic oxide powders is an important and well established way to obtain homogeneous powders of complex composition. Starting solutions are in most cases nitrates, but the use of chlorides or even suspensions is also possible. The solutions are introduced into the plasma chamber by means of a two phase nozzle. The nozzle delivers a mist of droplets with a mean diameter of about 7 μm [20]. As described previously [1,2,3,4], the nozzle is located in a frit through which a carrier gas flows. This arrangement has the advantage of avoiding vortices besides the nozzle. To demonstrate the facility of a microwave plasma as a heat source for powder synthesis, ceramic powders based on zirconia and alumina were produced using aqueous solutions of the nitrates [5,6]. In a typical run, a gas volume of about 5 to 10 m^3/h STP was passed through the plasma zone. This gas carried a mist of the aqueous solution of the reactants equivalent to a volume from 0.5 to 1.0 l/h.

This method was applied to synthesize oxide ceramics of various compositions. To demonstrate the flexibility of this process to produce a homogeneous product in complex systems, the ternary composition ZrO_2 - 3m% Y_2O_3 - 20m% Al_2O_3 was selected. According to the phase diagram [21], a two phase product, where

the majority of the alumina is segregated, is expected. Zirconia is expected to be present as the tetragonal or, in the case of larger grains, the monoclinic phase. The synthesis of this powder from nitrate solution resulted in single phased cubic zirconia. Figures 3 and 4 show the morphology and an electron diffraction pattern from this powder. The starting solution had a concentration of 0.1 mol/l. Argon with 20% oxygen at a pressure of 133 mbar was used for the plasma gas. With a gas flow rate of about 9 m³/h STP, a temperature of 550°C was measured using a thermocouple. Electron microscopy revealed particle sizes in the range of 100 to 1000 nm. Crystallite sizes are less than 50 nm; most of the particles exhibit crystallite sizes of less than 10 nm. The majority of the particles were found to be solid; a few hollow ones were found in addition. Segregation of alumina was not observed. Similar to the case of pyrolysis in a hydrogen flame [3,4], alumina is present as a non-equilibrium solid solution in zirconia.

Using the same experimental conditions except for air instead of Ar - 20 vol% O₂ as a plasma gas, changes the picture entirely. The temperature increases from 550 to 750°C, and the product changes as well. It can be demonstrated by electron microscopy that powder synthesized under these conditions shows indications of separation into two phases. This is demonstrated in Figs. 5 and 6. In Fig. 5 there is a bright seam around the powder particle. A concentration profile obtained by energy dispersive x-ray analysis reveals that this brighter seam consists primarily of alumina. An additional enrichment in alumina can be seen in the center of the particle. This segregated, brighter alumina-rich phase is grown epitaxially on the darker zirconia-rich phase (Fig. 6).

A comparison of the morphology of powder particles obtained by plasma pyrolysis with the morphology of powder particles obtained by flame pyrolysis [3,4] results in no significant differences. In this respect these two processes are equivalent, indicating that the reaction mechanisms for powder formation are essentially the same. Obviously, plasma-enhanced chemical reactions play a minor role. Powders of the same composition, obtained by pyrolysis in a conventional electric furnace with ohmic heating, are amorphous [1,3].

3.2 Organic solutions

Besides the use of aqueous solutions, the use of water free organic solutions of metal halides is beneficial. The basic idea is to use a process consisting of the following steps:

- evaporation of the solvent;
- evaporation of the metal halide;
- oxidation of the metal halide;
- formation of oxide powder particles by agglomeration.

From the process of particle formation, one may expect a very fine, nanophased product. Typical solutions for this type of synthesis are zirconium chloride (ZrCl_4) in acetonitril (CH_3CN), aluminum chloride (AlCl_3) in carbon tetrachloride (CCl_4), or titanium tetrachloride (TiCl_4) in hexane (C_6H_6).

Figures 7 and 8 display typical products obtained by this process. In this experiment a mixture of argon with 20 vol% oxygen was used for the plasma gas. The reaction was performed at a pressure of 90 mbar and a temperature of 800°C . The throughput was about 1 l/h of a 0.7 molar solution of ZrCl_4 in CH_3CN . In Fig. 7, clouds of powder particles with particle sizes of approximately 5 nm are visible. Additionally, there are a few spherical particles with diameters of 40 to 150 nm (Fig. 8). Electron diffraction revealed that the product is cubic zirconia. The observation of a bimodal particle size distribution leads to the assumption of the following mechanisms of particle formation.

- The fine fraction of the powder is produced by the three step mechanism mentioned above.
- It is assumed that with increasing temperature the oxidizing reaction forming zirconia is faster than the evaporation of zirconium chloride. This leads to the formation of the large spherical particles shown in Fig. 8.

To obtain a product with a single-moded particle size distribution, it is necessary to evaporate the mist of droplets well before the plasma zone. Using an azeotropic mixture makes further improvements possible. Doing this it is possible to produce large amounts of oxide ceramic powders with particle sizes below 10 nm.

4. Synthesis of Powders from Gaseous Precursors

Because of the problems in obtaining complete evaporation of droplets, it may be better to avoid the solvent altogether and to introduce the metal containing compound directly as a vapor [10]. This is not too difficult, as the halides of aluminum, titanium, zirconium, etc. have a relatively high vapor pressure. The formation of the powder particles from a vapor of the halides in a microwave plasma can be assumed to follow these steps:

- ionization of the oxidizing gas and dissociation of the halide;
- formation of oxide molecules;
- agglomeration of the oxide molecules by random collisions.

Figures 9 and 10 are electron micrographs of zirconia powder synthesized by the process. The starting material was ZrCl_4 . As before, a mixture of argon with 20 vol% oxygen was used as the plasma gas at a pressure of 90 mbar. The reaction temperature was 600°C. Even when the chemical reaction

is thermodynamically possible, it is kinetically thwarted under normal conditions [22]. As the reactive gases are ionized in a plasma, these kinetic obstacles are no longer present.

The product of this reaction is shown in Fig. 9. A very fine powder with a narrow particle size distribution results. The mean particle size is around 4 nm. Large particles were not observed. Note that the particles are single crystals with a cubic structure as shown by the lattice fringes in Fig. 10. Formation of the cubic structure in the particles can be understood by considering Ostwald's rule. Assuming a surface energy of 1 J/m², a hydrostatic pressure, p , caused by surface tension, g , can be calculated by $p=2 \cdot g/d$. Such an estimation leads to a pressure of 4 kbar in a particle with a diameter, d , of 5 nm. Even when a range of uncertainty for g from 0.7 to 5 J/m² is assumed, the monoclinic phase is not stable at the temperature of formation (Fig. 11[23]). From those considerations a transformation to the monoclinic or at least the

tetragonal structure could have been expected. Based on these considerations it is obvious that the cubic structure found experimentally, is metastable.

5. Conclusions

The successful use of a microwave plasma to synthesize ceramic oxide powders has been demonstrated. The microwave plasma can act either as a source of thermal energy or to overcome kinetic inhibitions. For the pyrolysis of sprayed aqueous solutions the thermal effect is predominant. Because of the short reaction time, in most cases the grain size is below 10 nm. Experiments show that in the case of a zirconia - yttria - alumina mixture it is possible to obtain a product where alumina is or is not segregated, depending on the reaction temperature. The particle sizes ranging from 100 to 1000 nm are controlled by the spraying conditions. A comparison of the powder particles obtained by microwave plasma pyrolysis with particles obtained by flame pyrolysis shows that the morphology is essentially the same. As these two processes are equivalent with respect to morphology, one may assume that the mechanisms of powder formation are essentially the same. This implies that microwave plasma pyrolysis uses the plasma solely as a source of thermal energy.

It has also been demonstrated that organic solutions can be used to synthesize nanophased oxide ceramic powders. In this case one obtains powder with particle sizes of less than 10 nm. The difficulty in using organic solutions is to ensure complete evaporation of the metal containing compound before the droplets enter the plasma zone.

If the metal compound is introduced into the plasma zone as a vapor, the reaction results in an oxide powder with mean particle sizes of about 5 nm. In the case of pure zirconia, those particles form in the cubic structure. The fact that these particles are not synthesized in the tetragonal or monoclinic structure can not be explained by equilibrium phase diagrams. In contrast to the plasma pyrolysis of aqueous solutions, the reaction of the chloride vapor to the fine oxide particle is enhanced by the plasma, which helps to overcome kinetic obstacles.

The transfer of energy in a microwave plasma is quite efficient. It has been shown that an efficiency of more than 80% can be obtained for the transformation of microwave to thermal energy.

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Figure Captions

- Fig. 1: Schematic diagram of the experimental device.
- Fig. 2: Ratio of input to reflected power for the plasma loaded cavity at different pressures of argon as a function of the position of the sliding short.
- Fig. 3: Particles of a ZrO_2 -3 m% Y_2O_3 -20 m% Al_2O_3 powder synthesized at 550°C in an argon-20 vol% oxygen plasma.
- Fig. 4: Electron diffraction pattern of the powder shown in Fig. 3.
- Fig. 5: Concentration profile across a particle of ZrO_2 -3 m% Y_2O_3 -20 m% Al_2O_3 powder synthesized at 750°C in an air plasma. The bright seam and the center are rich in alumina.
- Fig. 6: Lattice fringes of the transition range zirconia-alumina rich phase. There is a continuous transition to the lattice planes.
- Fig. 7: ZrO_2 powder particles obtained from a ZrCl_4 solution in CH_3CN in an argon 20 vol% oxygen plasma.
- Fig. 8: ZrO_2 powder particles from the same batch as shown in Fig. 7. Besides the fine particles a few large spherical particles are visible.

- Fig. 9: ZrO_2 powder particles obtained from a ZrCl_4 vapor in an argon-20 vol% oxygen plasma. A very narrow size distribution results; large particles were not found.
- Fig. 10: High resolution electron microscopy of ZrO_2 powder particles from the same batch as shown in Fig. 9. The particles are observed to be single crystals from the lattice fringes.
- Fig. 11: P-T diagram for zirconia according to Ref. 21. Most of the phase boundaries are tentative.

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