

Chemical model of Ar/O₂ microwave plasma with nanoparticle formation from metal precursors

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Abstract: A one dimensional chemical kinetic model of Ar/O₂ microwave plasma was developed and a mechanism for the decomposition and oxidation of iron pentacarbonyl was added. The model was applied to low pressure plasmas up to 25 mbar and the size of plasma generated iron oxide nanoparticles was calculated as function of input concentration and residence time in good agreement with experimental data.

Keywords: microwave plasma, particle formation, modelling, particle mass spectrometer

1. Introduction

Nanoparticles can be formed under very different conditions, e.g. at low, ambient or high pressure and temperature. In industrial processes, nanoparticles may arise as unwanted by-products, or, in other cases, as valuable intermediates and products. Due to the variety of conditions and aspects associated with the formation of nanoparticles, there is great interest and need to provide adequate measurement tools and to develop theoretical models which help to understand and predict particle properties.

Commercial nanoparticles are often produced in the gas phase by combustion or other thermal processes, because this appears most economic. However, low temperature processes may be required, if the product material is thermally unstable or if temperature sensitive coatings are to be added in situ [1]. Microwave plasmas operate at comparatively low temperature, around 200 °C, and thus offer a good alternative to combustion. Also, they provide a good laboratory tool to investigate the particle formation in detail. This paper reports about the measurement and modelling of iron oxide nanoparticles formed from iron pentacarbonyl in an Ar/O₂ microwave plasma. The particle size distribution was measured with a particle mass spectrometer. A volume averaged, one dimensional chemical plasma model was developed and plasma properties like refractive index and reflexivity were calculated as function of electron concentration and time. This permits to estimate the energy efficiency of the plasma process. A reaction set for iron pentacarbonyl was used to calculate the decomposition of iron pentacarbonyl and the formation of iron oxide in the plasma. The iron oxide was assumed to form solid clusters of 1 nm diameter, which then coagulate to form larger particles. The final particle diameter depends on input concentration and residence time, but is always below 10 nm at residence

times below 200 msec in agreement with experimental results. The experiments show a slight variation of the particle size with varying microwave power, but this cannot be understood from the chemical model.

2. Experimental

The experiments were carried out in laboratory scale plug flow reactors. The quartz tubes were 2 cm in diameter and up to 1 m long. A mixture of 20 % oxygen in argon was used as carrier gas and gaseous iron pentacarbonyl in argon was added to give input concentrations of iron pentacarbonyl up to 200 ppm. The total gas flow was 4.4 NI/min and the operating pressure was 25 mbar. A 2.45 GHz microwave generator was used to irradiate the gas mixture in the flow reactor over a length of approx. 10 cm. The microwave power was 425 W typically and could be varied from 200 to 600 W. For size measurement, a particle mass spectrometer (PMS) was placed at distances of 50 or 100 cm from the irradiation zone, which corresponded to residence times of 43 and 86 msec, resp.

The particle mass spectrometer has a two stage molecular beam sampling system, so that any gas – particle interactions are readily quenched. Due to the microwave process, a part of the particles is charged electrically, and only the charged particles are detected by the PMS. They pass a capacitor with variable electric field and are separated according to the polarity. Also, they are deflected from passing straight according to the ratio of kinetic energy to charge, and collected at Faraday cups. The intensity signal is proportional to the number density. The particle velocity is measured simultaneously and the mass to charge spectrum is obtained [2]. The mass to charge spectrum often showed two peaks at deflection voltages which differed by a factor of two. This indicates particles of the same mass with single and double charge. Therefore, particle

samples were also investigated by electron microscopy. In this way, the particle size distribution was found to be monodisperse, which confirms the occurrence of single and double charges on the particles [3]. Finally, the mass spectrum can be converted to the size distribution with knowledge of the material density.

3. Model Calculation

Consider a cylindrical plug flow reactor with radius R and the incident microwave power P_{MW} being applied along the length L , then the power absorbed per unit volume, P_{abs}/V , is given by

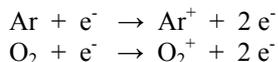
$$\frac{P_{abs}}{V} = \frac{P_{MW}}{\pi R^2 L} \cdot (1-r) \quad (1)$$

with the reflexivity r being a function of the refractive index n , $r = (n - 1)^2/(n + 1)^2$. The refractive index is a function of the ratio of plasma frequency ω_p to microwave frequency ω_{MW} with ω_p being a function of the number density N_e of free electrons such that

$$n = \sqrt{1 - \frac{N_e \cdot e^2}{m_e \cdot \epsilon_0 \cdot \omega_{MW}^2}} \quad (2)$$

where e is the elementary charge, m_e the electron mass and ϵ_0 the electric field constant. By combining eqs. (1) and (2), the actual P_{abs}/V becomes a function of the actual electron number density N_e .

Free electrons are generated in the plasma reactor in an avalanche type manner by ionization reactions of the kind

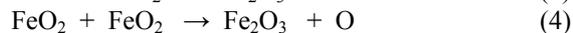
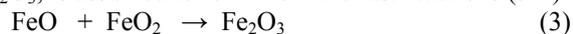


but because of eq. (2) the maximum value for N_e is $7.45 \cdot 10^{10} \text{ cm}^{-3}$ at a microwave frequency of 2.45 GHz. At this electron number density, the reflexivity r becomes one and the electrons do not absorb further energy, until their concentration drops due to recombination with positive ions, attachment to neutral molecules or loss to the wall. According to the energy balance given in [4], the absorbed microwave power is distributed between raise of the electron temperature T_e , excitation and ionization of the gas molecules and some loss of ionic species to the reactor walls. The corresponding differential equations for dN_e/dt and dT_e/dt given in [4] were adopted in the present model, but in addition, differential equations for dn/dt and dr/dt were introduced from eqs. (1) and (2) in order to calculate the actual n , r and P_{abs}/V from the applied microwave power at any instance. The incident microwave power (or dose rate), P_{MW}/V , is modelled as almost rectangular time profile with smooth edges. The present approach gives a good estimate of the governing plasma chemistry despite its crude assumptions [5] and avoids to merely estimate the absorbed energy.

The chemical reaction model in the Ar/O₂ system comprises ionization and excitation by electrons, electron attachment, ion molecule reactions, ion recombination reactions and reactions of molecules with radi-

cals and excited species. In the case of oxygen, a well studied reaction set is available from the literature [5, 6] and only two excited species, O(¹D) and O₂(¹Δ_g), need to be considered beside ground state and ionic species. In case of Ar, numerous excited states may occur (beside ground state and ionized Ar atoms) and according to a previous proposal [5] it appears sufficient to consider only three of them, the metastable Ar^m, radiatively coupled levels Ar^r, and Ar(4p). The mechanism was taken from [5] and [7]. Care was taken to include a comprehensive set of ion recombination reactions and, if not available, the rate constants were estimated according to previous listings [6]. The diffusive loss of electrons and ions to the reactor walls was calculated according to the expressions given in [4, 5] using the proton mass as a rough average between the masses of electrons and ions. The radial loss of reactive neutral species to the reactor walls was assumed to be first order with a rate constant $k_{wall} = D/(0.16 R)^2$, where D is the diffusion coefficient.

The mechanism for the decomposition of iron pentacarbonyl and oxidation to iron oxide comprises the neutral reactions in the Fe/O₂ system [8, 9], ion molecule reactions as they occur in the upper atmosphere [10] and ion recombination reactions. The final product, Fe₂O₃, is assumed to form from the fast reactions (3-4):



with $k_3 = k_4 = 1.66 \cdot 10^{-10} \text{ cm}^3/\text{sec}$ [8]. These reactions were assumed to initiate nucleation to small clusters of 1 nm diameter which contain approx. ten monomers. The clusters then grow by coagulation which can be described by a simple second order rate law in the free molecule regime with a rate constant in the range $1 - 10 \cdot 10^{-10} \text{ cm}^3/\text{sec}$.

4. Results

Fig. 1 shows example time profiles of applied dose rate, electron concentration and reflexivity. When the gas enters the irradiation zone, the concentration of electrons rises sharply with increasing dose rate, and the reflexivity quickly reaches several tens of percents. When the gas leaves the irradiation zone, the electrons are consumed by recombination and the reflexivity drops.

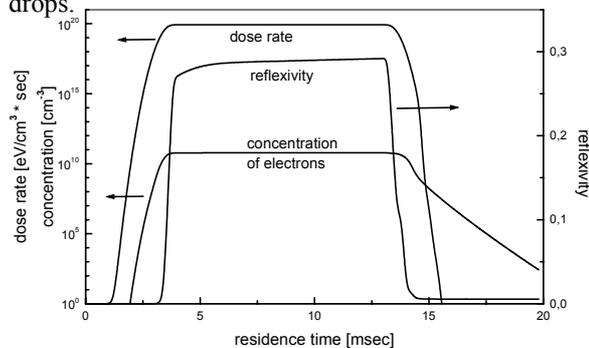


Fig. 1 Example time profiles of applied dose rate, electron concentration and reflexivity.

For an independent comparison, a model calculation was performed for the conditions of Agarwal et al. [11], who measured the O atom concentration in an inductively coupled plasma at pressures ranging from 0.033 – 0.27 mbar and for different Ar : O₂ ratios. They report a continuous increase of the O atom concentration with increasing pressure for 20 % oxygen in argon. Under these conditions, the calculated O atom concentrations are close to the measured results (Fig. 2) which is a good confirmation of the present model.

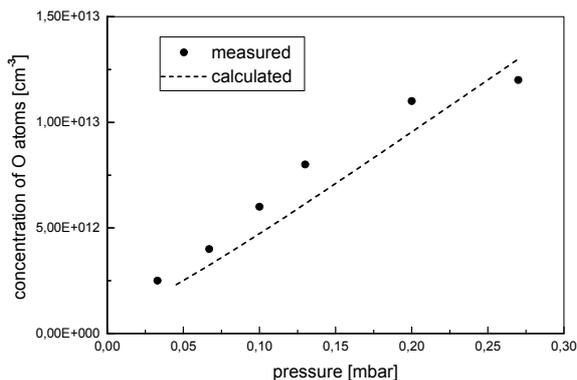


Fig. 2 Comparison of measured [11] and calculated O atom concentrations in Ar/O₂ plasmas with 20 % oxygen.

The formation of nanoparticles from iron pentacarbonyl in microwave plasmas was investigated at a much higher pressure, around 25 mbar, and only particulate species were measured in the gas leaving the plasma zone. Fig. 3 shows a typical result for positively charged nanoparticles sampled at a residence time of 43 msec. The two peaks occurring at deflection voltages

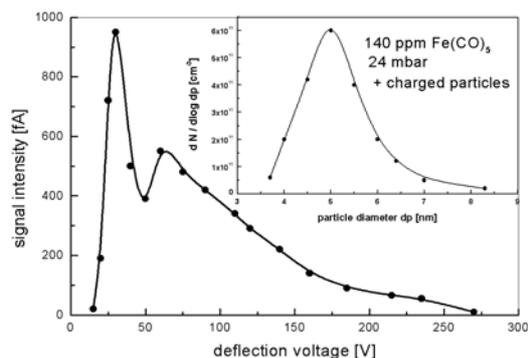


Fig. 3 Signal intensity vs. deflection voltage measured with the particle mass spectrometer and resulting particle size distribution.

30 and 60 V correspond to particles of single (60 V) and double (30 V) charge with a diameter of 4.8 nm. Note that the particle diameter is not a linear function of the deflection voltage, hence the size distribution is rather narrow and extends only to about 8 nm on the

large side.

Fig. 4 shows results of the model calculation for the experimental conditions of Fig. 3. It can be seen that iron pentacarbonyl decomposes rapidly upon entrance to the plasma zone and the number density of iron oxide particles rises steeply to maximum values around 10^{11} – 10^{13} cm⁻³ which is a typical phenomenon for particle formation from gas phase reactions. In parallel, the par-

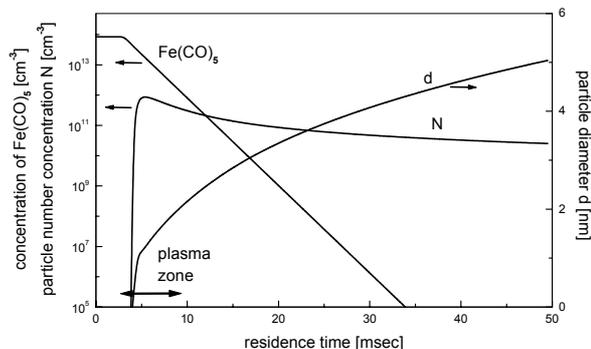


Fig. 4 Iron pentacarbonyl, particle number density and particle diameter calculated as function of residence time (140 ppm Fe(CO)₅, 25 mbar, 425 W).

ticle diameter increases continuously with residence time and reaches a value close to 5 nm after 50 msec, which is in good agreement with the above given experimental result.

Beside residence time, the input concentration of the precursor is an important parameter for the final particle size. Fig. 5 shows the measured and calculated particle size as function of input concentration for otherwise similar conditions as in Fig. 4. The particle size increases with increasing input concentration and finally reaches a plateau at constant residence time.

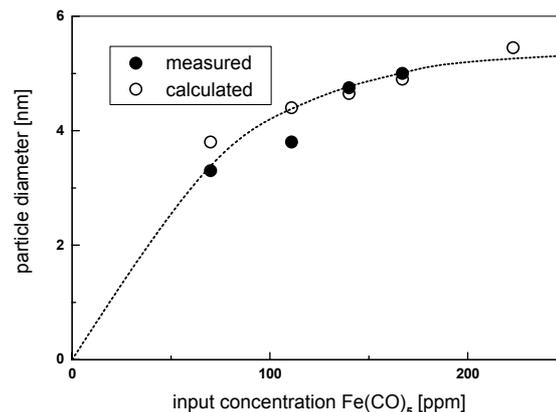


Fig. 5 Diameter of iron oxide particles as function of input concentration Fe(CO)₅ (23 – 25 mbar, 43 msec).

Particles sampled at the double residence time of 86 msec had a 30 % larger diameter. This increase is also reproduced by the model calculation and can be explained the coagulation of the particles.

5. Discussion

Under the microwave plasma conditions discussed here, free electrons are the major link between the energy provided and the particulate product obtained. However, the relationship between electron production and product formation appears to be complicated and non-linear. Fig. 1 shows that the electrons are produced faster upon entrance to the plasma zone than they are consumed when they leave the plasma zone. This indicates that the energy provided is much higher than the energy required to establish the plasma. Moreover, 25 % and more of the applied energy are merely reflected and not used for product formation. Also, as seen from Fig. 4, the major particle formation steps are complete after passage of only about one third of the plasma zone. Hence, there is great need and potential to operate the microwave plasma process with better energy efficiency. Experimentally, we have varied the microwave power between 200 and 600 W with little changes of product quality, but the particle size tended to increase somewhat at low input power.

According to the model presented here, the formation of nanoparticles from iron pentacarbonyl can be described by the gas phase decomposition and oxidation of the precursor and by a simplified nucleation term which assumes the formation of small primary clusters and their subsequent growth by coagulation. The electrical charge of the particles is not considered in this simplified approach and probably, it is not an important factor for particle growth. The calculated numerical ratio of the number density of gas phase ions to the number density of particles is around 5 in the plasma zone and as further experimental result, approx. 30 % of the particles were found to carry electrical charge. This may not be enough to enhance the coagulation rate significantly above the value for neutrals. Therefore, the electrical charge of the particles does not appear to be an important factor for particle growth. Input concentration and residence time were identified as important parameters to control the particle size. Due to the high material density of iron oxide, however, the particles tend to remain small and it appears impractical to obtain particles with diameters over 10 nm at realistic residence times.

6. Conclusions

A simplified volume averaged chemical kinetic model has been used to describe and investigate the chemistry in Ar/O₂ microwave plasmas and the formation of nanoparticles from iron pentacarbonyl added to the main gas. The model is in good agreement with laboratory measurements of O atoms in inductively coupled plasmas and with measurements of particle sizes in microwave plasmas. Input concentration and residence time were identified as major factors which determine the particle size. The energy efficiency of the process offers future challenges.

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