Modelling of induction thermal plasma synthesis of iron nanoparticles in oxygen-contaminated gas mixtures

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Abstract: The synthesis of iron nanoparticles in a radio-frequency induction thermal plasma (RF-ITP) system working in a mixture of argon contaminated with oxygen (10-100 ppm) has been modelled considering the iron oxidation reactions both in gaseous and condensed phases. The results show that oxidation occurs mainly in the gas phase where Fe is converted to FeO. As the concentration of oxygen impurities increases, the nucleation region is shifted towards higher temperatures and the resulting nanoparticles are characterized by larger diameters.

Keywords: Nanoparticles synthesis, induction thermal plasma, meso-scale model.

1. Introduction

Nanoparticle synthesis in radio-frequency induction thermal plasmas (RF-ITP) is a widely adopted industrial process which has been also applied to the synthesis of iron nanoparticles [1,2].

Iron nanoparticles have long been known to be extremely reactive and pyrophoric. However, iron at the nanoscale has great potential related to its magnetic and catalytic properties [3].

In this process, the contamination of particles with oxygen should be avoided both for process safety and for preserving the quality of the product. However, a complete understanding of the formation mechanisms of iron nanoparticles and its oxidation in thermal plasmas has not been achieved.

The modelling of the oxidation reactions during iron nanoparticle synthesis has been recently investigated for the gas metal arc welding process [4,5], where oxidant mixture are usually adopted for welding of mild steel.

In this paper, an industrial RF-ITP system has been modelled using a 2D approach to obtain the temperature field and vapour concentration in the nanoparticle nucleation zone. The results of the 2D model, taken on selected streamlines passing through the nucleation region, have been used as input to a detailed 1D model of the synthesis of iron oxide nanoparticles in order to investigate the effects of oxygen impurities (10 and 100 ppm) in the formation mechanism of iron nanoparticles.

2. Modelling of the RF-ITP system

The thermal plasma process has been modelled within a 2D axisymmetric framework in the ANSYS FLUENT environment. The model describes plasma thermo-fluid-dynamics, precursor behaviour (trajectories, thermal history and evaporation) and the vapour transport in the reaction chamber [6]. The domain is composed of a commercial plasma torch (Tekna Plasma Systems model PL-50) and a reaction chamber equipped with a quench gas radial injection. Details on the PL-50 geometry and operating conditions can be found in [7]. Operating gas is pure Ar at 25kW of coupled power. The precursor is solid Fe with 10 μm diameter and it is injected with a feed rate of 1 g/min. The quench gas is pure argon with a flow rate of 250 slpm.

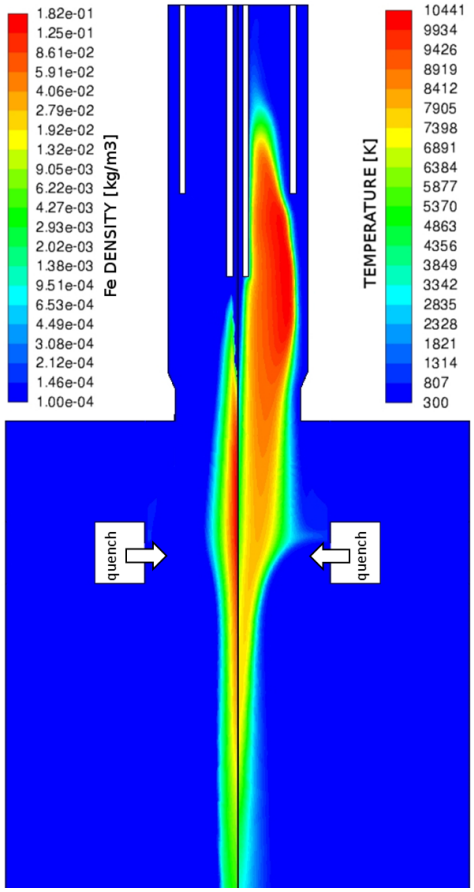

Figure 1 – Temperature field (right) and iron vapour concentration (left) in the RF-ICTP

Relevant results of the modelling of the RF-ICTP system are shown in Figure 1 and 2. In Figure 1 the 2D temperature field and vapour concentration distribution are reported. The high temperature region is mainly confined in the region above the quenching ring, across which a strong temperature gradient is obtained (around 10^6 K/s). The iron precursor is completely evaporated inside the plasma torch and its vapours are transported by convection and diffusion in the reaction chamber.

The temperature profile along the selected streamline is reported in Figure 2 whereas the relation between the iron concentration and the temperature along the same streamline is reported in Figure 3 for the temperature range of interest for the synthesis of nanoparticles (300 - 3000 K). It can be observed that the concentration of iron decreases as the temperature decreases as a consequence of vapour diffusion in the reaction chamber.

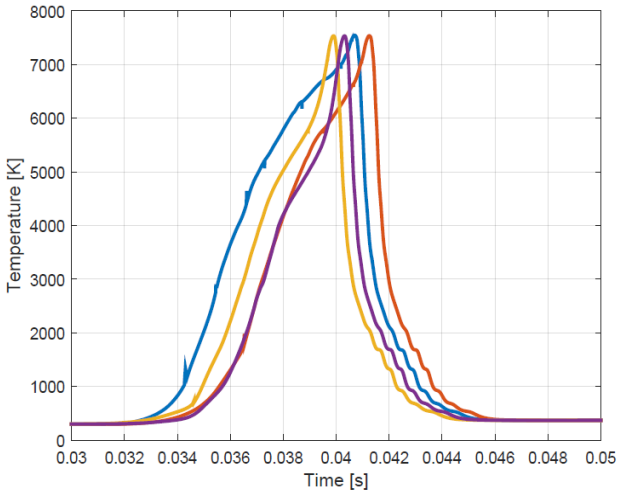

Figure 2 – Temperature profile along selected streamlines

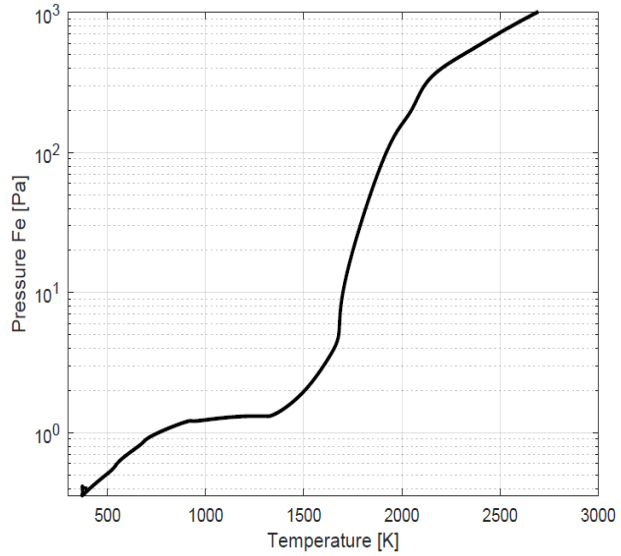

Figure 3 – Iron vapour concentration as a function of temperature along the selected streamlines

3. Modelling of iron nanoparticle synthesis

The modelling approach adopted in the present work is based on a stochastic algorithm developed for the analysis of the synthesis of nanoparticles [8]. This model has been extended in [4] to include the physical and chemical phenomena that describe fume formation in thermal plasmas.

The generation of nanoparticles is simulated tracking the temporal evolution of a control volume V_{ctr}, which is assumed to move with the flow along the selected streamline starting from a high-temperature region (at 3000 K) and ending in the colder region surrounding the plasma (at 300 K).

Primary particles formation by nucleation of vapours in the gaseous phase is predicted, calculating the homogeneous nucleation rate. Primary particles growth is predicted by balancing the surface condensation of vapor against evaporation. A free molecular collisional kernel is used to predict primary particles coagulation to form aggregates. A ballistic algorithm is applied upon collision, to simulate aggregates coagulation and predicts the fractal dimension of the resulting merged aggregate. Sintering and coalescence are considered using the Friedlander-Koch relation for the sintering time [4]. The composition of the gas-phase is calculated assuming chemical equilibrium for given temperature, pressure and atom concentration conditions. The atom concentration in the gaseous phase is tracked by subtracting the vapour converted to nanoparticles. The system is kept at constant pressure.

The temporal evolution of the temperature and the initial concentration of iron are imposed according to the profile obtained from the selected streamlines extracted from the simulation of the RF-ITP system. Two different cases have been investigated in which the oxygen impurities in the argon mixture have been set to 10 and 100 ppm, respectively.

Relevant results are reported in Figures 4, 5 and 6. First, it should be noted that the nucleation temperature of the nanoparticles depends on the initial oxygen concentration: with 10 ppm the nucleation of Fe starts around 1600 K, whereas at higher concentration the nucleation is shifted to 2000 K as a consequence of the increasing importance of the nucleation of FeO. At this higher temperature, also the initial concentration of Fe obtained from RF-ITP 2D simulation is increased from 70 Pa to 150 Pa (see Figure 3). With 10 and 100 ppm of oxygen impurities, the oxidation process occurs mainly in the gas phase, where Fe is converted to FeO. No significant conversion of FeO to Fe_3O_4 and Fe_2O_3 in the liquid and solid phases can be appreciated since all the oxygen available is consumed in the gas phase. The FeO/Fe ratio in the final product is increased from 5% to 30% as the oxygen impurities are increased from 10 to 100 ppm.

The particle size distribution of the nanoparticle ensemble at the end of the synthesis process is shown in Figure 5. The case with higher initial oxygen concentration results in a size distribution shifted towards higher diameters.

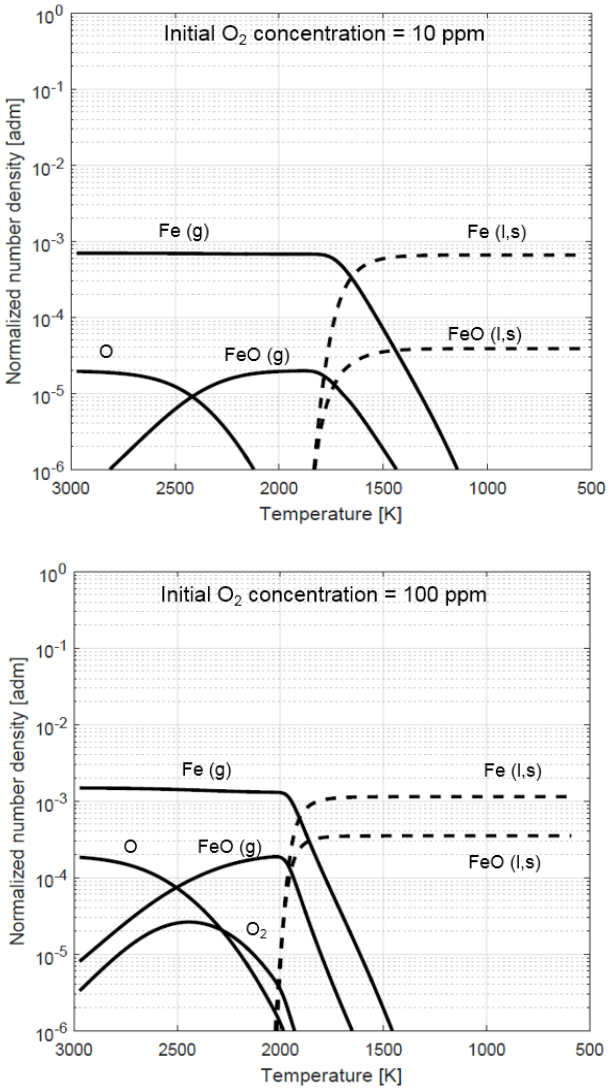

Figure 4 – Normalized number density of gaseous and condensed species at different temperatures during the synthesis process for two different oxygen initial concentrations (10 and 100 ppm)

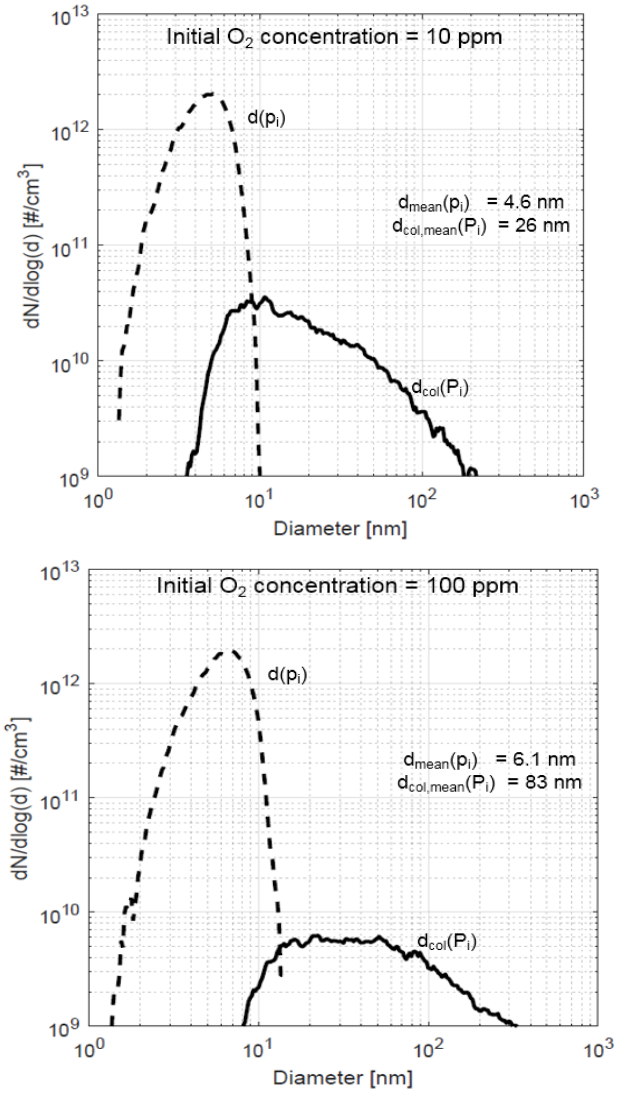

Figure 5 – Particle size distribution at the end of the synthesis process (T=300K) for two different oxygen initial concentrations (10 and 100 ppm)

4. Conclusions

The modelling investigation proposed shows that oxygen impurities play a significant role in the synthesis of iron nanoparticles. Oxidation occurs mainly in the gas phase where Fe is converted to FeO. As the oxygen concentration increases from 10 ppm to 100 ppm the following phenomena can be observed in the RF-ITP system considered:

- the nucleation region is shifted towards higher temperatures (from 1600 K to 2000 K)
- the concentration of iron at the nucleation region is increased (from 70 Pa to 150 Pa)
- the resulting nanoparticles are characterized by larger primary diameters (from 4 to 6 nm) and collision diameter (from 21 to 83 nm)
- the FeO/Fe ratio in the final product is increased (from 5% to 30%)

5. References

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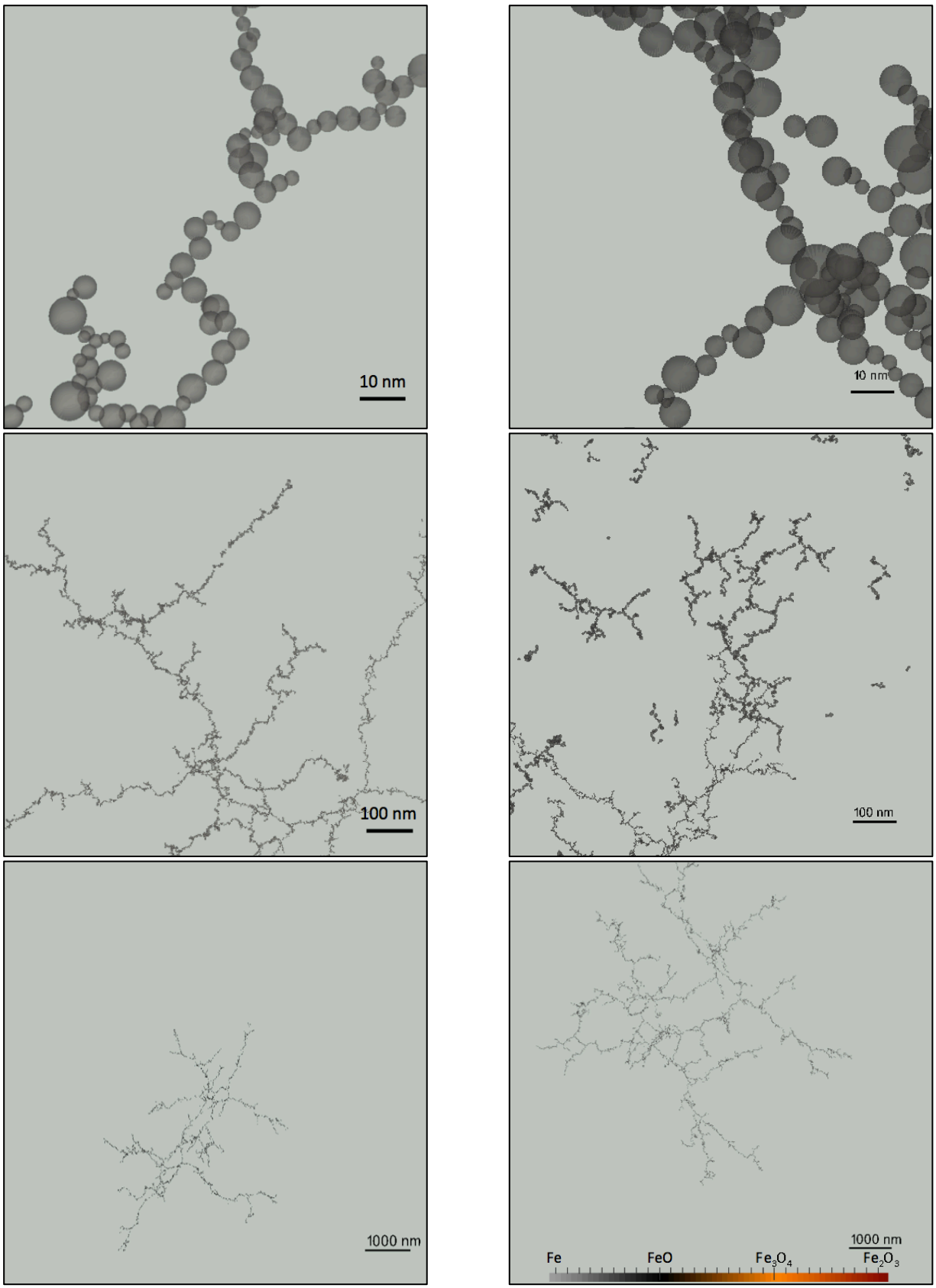

Figure 6 – TEM-style representation of the nanoparticles obtained at the end of the synthesis process with three different zoom levels. Cases with 10 ppm (left) and 100 ppm (right) of oxygen.