Scale-Up of Metal Nanoparticle Production

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ABSTRACT

Metal nanoparticles are used in various applications and products nowadays with rising tendency. The demand of the industry for pure metal nanoparticles is hence increasing. The scale-up of nanoparticle synthesis, especially metals, is however very challenging. In this study, a production facility for pure metal nanoparticles is presented. The scale-up approach is the parallelization of multiple transferred arcs, which have been individually optimized for nanoparticle generation. It is shown that the production rate of the process scales successfully with the number of transferred arcs, while the particle size stays on the nanoscale. Copper nanoparticles with a mean size of 79 nm are synthesized with a production rate of 69 g/h. The successful scale-up allows furthermore an estimation of the production rate of other metals, which production has been tested before on a single transferred arc.

Keywords: metal nanoparticles, gas phase synthesis, arc discharge, scale up, production facility

1 INTRODUCTION

Metal nanoparticles are used in various products and applications. Copper nanoparticles are e.g. used to increase the thermal conductivity of nanofluids [1] or in medical applications due to their antimicrobial activity [2]. The demand of pure metal nanoparticles by the industry naturally increases with the field of applications and products. To fulfill this demand increased or scaled up production facilities for metal nanoparticles are required. Scaling up the nanoparticle production of metals is however very challenging. The challenge consists of the formation of pure metals, which means that oxygen must not be present during formation. Hence, well developed nanoparticle production facilities e.g. flame reactors [3] cannot be used for metal nanoparticles, at least not without the usage of reactive additives. The usage of those additives is often avoided by the industry due to their hazardous potential. Further important aspects for the producers of nanoparticles are the efficiency, versatility and the handability of the process. Last but not least it has to be ensured that a scaled-up production facility still delivers particles in the nanosize range, which makes many production approaches of nanoparticles unfeasible.

This study reports about a production facility of metal nanoparticles that is built to produce pure metal nanoparticles economically and ecologically. It bases on a transferred arc synthesis process, which has been investigated in detail on the lab scale before [4]. Nanoparticles are thereby produced by anode evaporation due to a transferred arc between two electrodes. The scale-up is now done, by using multiple electrode pairs (arcs) in parallel to increase the production rate of nanoparticles. The electrode pairs are arranged in one reactor housing, so only one infrastructure (gas supply, cooling, etc.) is required and has therefore not be scaled up with the number of electrode pairs. The scale-up approach by parallelization has the advantage that all process development and optimization can be done on the lab scale, before it is transferred to the production facility. The evaluation of the process and production is done in terms of production rate of nanoparticles, their size and the needed amount of electricity.

2 PRODUCTION FACILITY SETUP & PROCEDURE

A schematic of the production facility is shown in Figure 1. Principally it can be described as a closed circuit and divided in three parts: synthesis, filtration of nanoparticles and the gas reconditioning. A key factor of this process is thereby the gas reconditioning, as the carrier gas is recirculated and re-used. For the production of non-nitride forming metal nanoparticles, nitrogen has been found to be by far the most efficient carrier gas in terms of mass production rate [4]. Since copper nanoparticles are produced in this study, nitrogen is hence used as carrier gas. In order to prevent oxygen contamination, the process is evacuated prior synthesis and refilled with the carrier gas twice. Therefore a vacuum pump (Trivac D65B, Oerlikon Leybold Vacuum GmbH, Cologne, Germany) in connection with a roots pump (Ruvac WA 501, Oerlikon Leybold Vacuum GmbH) is used to evacuate the process to a pressure of 1 mbar. Afterwards the system is filled with nitrogen from the house supply to atmospheric pressure. The process pressure is atmospheric. During synthesis, the roots pump is used to recirculate the carrier gas in the closed circuit of synthesis and filtration unit. The recirculating amount of gas is adjusted by a valve attached to a roots pump-by-pass. To prevent the system from overheating, the gas is cooled in front of the roots pump by a gas cooling unit. Nitrogen can be added or extracted from the process by a valve in combination with the vacuum pump or via a characterization port. The circulated amount of carrier gas is measured by a differential pressure
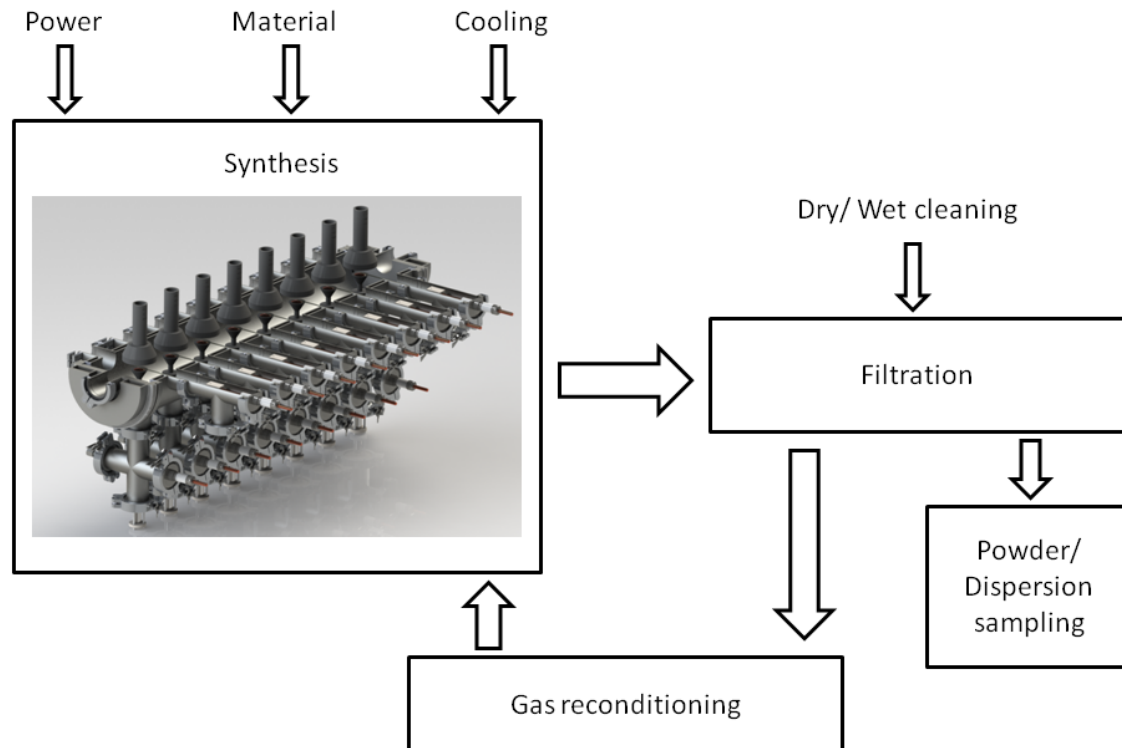
Figure 1: Schematic of the production facility

monitoring over a 40 mm orifice, before it enters the synthesis unit by a gas distribution system.

The synthesis unit consists of two reactor chambers. The reactor chamber is also depicted in Figure 1. Each chamber contains 8 electrode pairs, hence 8 single operating production processes (lab-scale). The lab scale production process has been described in detail elsewhere [4,5]. A transferred arc is ignited by a commercial TIG welder (Stamos S-Wigma 200P, Expondo GmbH, Berlin, Germany) between the electrode pair. The cathode is a tungsten rod, the anode is a graphite crucible, which contains the feedstock material, here copper. The arc strikes directly on the copper, leading to copper evaporation and the formation of a copper vapor. Eventually the copper vapor cools down in dependency of the carrier gas, supersaturates and forms nanoparticles by nucleation, coagulation etc. The lab scale process has received intense investigations and optimizations in terms of production rate, efficiency, long term operation and particle size.

The production facility now contains not one electrode pair, but 16 in parallel. Two reactor chambers are used each containing 8 electrode pairs. At each electrode pair an arc current of 45 A (900W) is applied, the gas flow per electrode pair is roughly 80 l/min. There is no separating wall between the electrode pairs in one chamber, but each electrode pair has its own gas inlet and outlet, power supply and electrode feeder. The carrier gas is distributed to each electrode pair by a carrier gas distributor. The distributor divides the carrier gas flow equally on each of the 16 electrode pairs inside the two reactor chambers. Particles formed by arc evaporation are carried away by the carrier gas out of the reactor chambers through a product flow joiner. The product flow joiner combines first the aerosols of the 8 arcs of one reactor chamber and in the following the product flow of the two reactor chambers. The joined product flow enters subsequently a filtration unit for particle deposition.

A characterization port is arranged between the synthesis and filtration unit where a part of the product flow can be excluded for characterization. At that port offline as well as online characterization devices can be attached. A mass flow controller is used to refill the extruded amount of carrier gas back into the circuit. Particle characterization is here done based on gravimetric measurements of deposited particles on a PTFE filter with a pore size of 5 µm in order to determine the production rate. The deposition time is 5 minutes. BET analysis of the sampled particles allows furthermore the determination of the primary particle size.

The filtration unit consists of two independent filter housings. Two filter housings are used so that the synthesis can be kept running in a second filter, when the first one is loaded with particles and needs to be cleaned. Particle loading is monitored by differential pressure measurement before and after the filter. Each filter housing contains 4 PTFE filter cartridges to increase the filtration surface and thereby decrease the filter face velocity for better

cleanability. Two cleaning mechanisms are applied to each filter; dry pulsed- and wet cleaning. Prior cleaning the deposited particles can be passivated on the filter cartridges by a controlled addition of oxygen into the filter housing. The filter outlet is again connected to the gas recirculation setup, where the closed loop begins again.

3   RESULTS

Figure 2 shows an image of one of the two reactor chambers during production. Through the 8 viewports, the green light (excited copper atoms) from the 8 running arcs is visible. The arcs run stable and show no kind of disruptive interactions with each other. In order to determine the scalability of the process, the production rate (PR_{total}) and the specific electricity consumption (SEC) have been measured for different numbers of running arcs. This is shown in Figure 3. As depicted, the production rate increases almost linearly with the number of electrode pairs. When one electrode pair is used a copper nanoparticle production rate of 3.6 g/h is reached. 5 electrode pairs in parallel production lead to a production rate of roughly 23 g/h, 10 electrode pairs to 48 g/h. Due to a failure of one electrode pair only 15 electrode pairs have been used as a maximum number of parallel running electrode pairs. With this 15 electrode pairs a maximum production rate of 69 g/h has been measured. Small deviations from the linear scaling behavior are a result of changing process conditions, e.g. changing electrode distances due to evaporation and re-feeding of the crucible. This variation is also visible, when calculating the production rate of each electrode pair. Each electrode pair produces roughly 4.17 g/h ± 0.48 g/h. The lab scale version of this process delivers with the same parameters (gas flow, applied power) a production rate of 4.1 g/h, which is in very good agreement with the scaled up results and hence an indication that the scale-up approach is working. The specific electricity consumption stays almost constant (~170 kWh/kg), which is again in good agreement with the lab scale version of the process. As only one pump and one cooling method are applied, the overall energy consumption in terms of kWh/kg is expected to be decreasing in

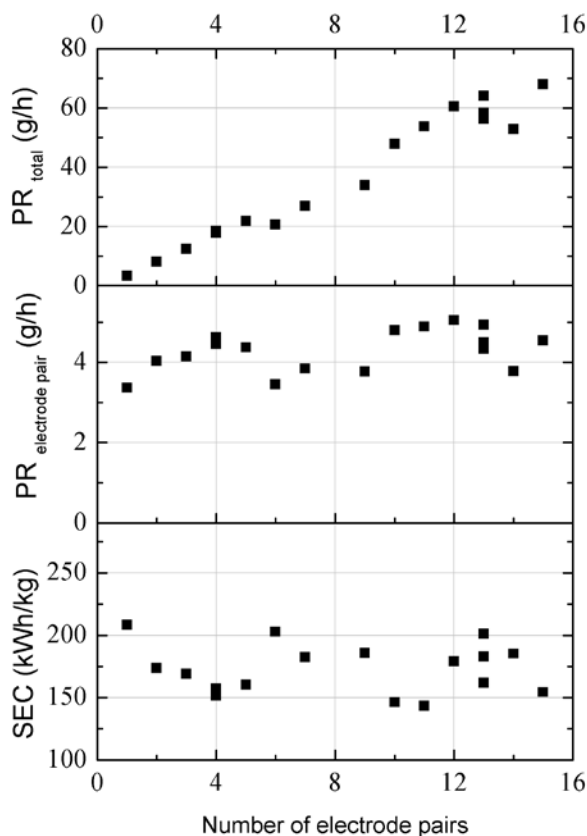Figure 2: Multi-electrode reactor during production

Figure 3: Production rate (PR_{total}), production rate per electrode pair ($PR_{electrode\ pair}$) and specific electricity consumption for copper nanoparticle arc synthesis with different numbers of electrode pairs

comparison to the lab-scale version.

The particle size of the produced copper particles is with 79 nm slightly smaller than of the single arc process (86 nm). The decreased particle size is a result of an increased gas flow per electrode pair. Smaller particles can be adjusted down to 14 nm with this process by varying the carrier gas composition, applied power or gas flow [4]. The size reduction is however on the expense of the production rate. The scale-up approach is independent of those parameters, so that even increased production rates of smaller particles can be realized with this process. The quality of the produced particles in terms of composition and oxidization seem to be conform with the quality of the lab-scale process, which has been proven before [4,5].

As these results show that the scale-up of the single arc process by parallelization works for copper, an estimation can be given about the production rates of the present setup also for other metals. This is summarized in Table 1. Assuming a production 24h/day, 1.6 kg of copper nanoparticles with a mean size of 79 nm can be produced. For zinc, this value is with 8.6 kg/day even higher, due its higher vapor pressure. In a nitrogen atmosphere zinc evaporates even at low input power (375 W) intensely,

leading to particle sizes out of the nano range. In nitrogen, the production of copper exceeds the one of silver. With the present process 0.35 kg/day silver nanoparticles can be produced. The particle size of silver is with 98 nm still in the nano range. For aluminum, argon has to be used as carrier gas, as it is a nitride forming metal. The use of argon decreases the particle size as well as production rate significantly. 11.5 g/day of 9 nm aluminum nanoparticles can be produced with the present setup. These values are based on the goal of a maximized production rate. The setup allows indeed also the detailed adjustment of particle sizes for all metals.

Material	PR_{single} (g/h)	d_P (nm)	PR (g/day)*
Copper	4.17	89	1601
Silver	0.9	98	346
Zinc	22.3	180	8563
Aluminum*	0.03	9	11.5

Table 1: Production rate and primary particle size of different metal nanoparticles synthesized by the process. *Estimated for 16 electrode pairs. Aluminum synthesized with argon as carrier gas.

4 CONCLUSION

Metal nanoparticle production by transferred arc synthesis has been successfully scaled-up from a lab scale version to a production facility level. It is shown that the production rate of copper nanoparticles multiplies with the number of electrode pairs, without losing any of the particles properties. A production rate of 69 g/h of copper nanoparticles with a mean primary particle size of 79 nm has been achieved. As the scale-up approach is therefore proven successfully, an estimation for the production rate of other metals is given based on the results of a lab-scale version of the process.

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REFERENCES

[1] J.A. Eastman, S.U.S. Choi, S. Li, W. Yu, L.J. Thompson, Appl. Phys. Lett., 78(6), 718-720, 2001
[2] J.P. Ruparelia, A.K. Chatterjee, S.P. Duttagupta, S. Mukherji, Acta Biomaterialia, 4(3), 707-716, 2008
[3] K. Wegner, B. Schimmoeller, B. Thiebaut, C. Fernandez, T.N. Rao, Kona Powder and Particle Journal, 29, 251-265, 2011
[4] M. Stein, D. Kiesler, F.E. Kruis, J. Nanopart. Res., 15(1), 1400, 2013
[5] M. Stein, D. Kiesler, F.E. Kruis, Aerosol Sci. Technol., 47 (11), 1276-1284, 2013