Agglomeration of Ni-nanoparticles in the Gas Phase under Gravity and Microgravity Conditions

S Lösch¹, G N Iles², B Schmitz³, B H Günther¹

¹ Fraunhofer Institute for Manufacturing Technology and Advanced Materials (IFAM), Wiener Str. 12, 28359 Bremen, Germany
² European Space Agency (ESA), ESTEC Nordwijk, The Netherlands
³ Astrium GmbH, Space Transportation, Airbus-Allee 1, 28199 Bremen, Germany

E-mail: loesch@ifam.fhg.de

Abstract. The agglomeration of metallic nanoparticles can be performed using the well-known inert gas condensation process. Unfortunately, thermal effects such as convection are created by the heating source and as a result the turbulent aerosol avoids ideal conditions. In addition, the sedimentation of large particles and/or agglomerates influences the self-assembly of particles. These negative effects can be eliminated by using microgravity conditions. Here we present the results of the agglomeration of nanoscale Ni-particles under gravity and microgravity conditions, the latter provided by adapted microgravity platforms namely the European sounding rocket MAXUS 8 and the European Parabolic Flight aircraft, Airbus A300 Zero-G.

1. INTRODUCTION

Agglomeration phenomena within metal aerosols enable many technical solutions for functional materials and generally occur under the combined effect of Van der Waals, electrostatic, and magnetic interactions [1][2][3][4]. Particularly interesting would be long chains consisting of monosized particles. For ferromagnetic materials, such as Ni, Co, and Fe, the agglomeration process is dominated by magnetic interparticle forces [5] leading to magnetic pearl necklaces, which could be useful, e.g., as functional ingredients in sensor applications. In this paper, such necklaces are synthesized from thermally produced nickel aerosol using the well-known inert gas condensation technique [6] with the clear objective to investigate the relationship between background gas pressure, agglomeration time and size/shape of the resulting Ni-agglomerates under laminar flow conditions. It is expected that the “free-flow” residence time of magnetic particles correlates to the length of the deposited particle chains. The experiments have been conducted under microgravity (µ-g) conditions in order to suppress thermally-induced convection. Several parabolic flight campaigns (PFC) as well as a sounding rocket flight (SR) were used as experimental platforms to extend the time available for Ni-particles/agglomerates on their way from the heating source to the substrate up to the minutes range.
2. EXPERIMENTAL SET-UP

The typical inert gas condensation process with its single stages is illustrated by a simple diagram as shown in figure 1. Hereby the metallic material is heated up above its melting temperature inside an adapted crucible. The inert gas, whose gas volume is variable, carries the particles originated by nucleation and coagulation, and agglomerates upstream within a defined flow chamber until reaching a deposition area where substrates can be removed after each experiment for ex-situ analysis. The left sketch of figure 2 shows a schematic of the Ni evaporation condensation vacuum source made from standard vacuum parts used for agglomeration experiments of metallic materials in laboratory and during parabolic flights. A 5g Ni ingot (purity 99.95%) is heated up to 1850°C using an induction coil rf-heater. The melted Ni is located inside an Al₂O₃ crucible. The inert gas Ar flows through the silica glass tube and carries the Ni-nanoparticles and agglomerates downstream. At the exit of the tube the Ni-agglomerates are deposited on electro-polished substrates made from non-magnetic stainless steel. More technical details and operational procedures about this set-up can be found in [7].

In gravity (1-g) turbulences do not show up at residence times below 8sec. At smaller flow rates thermally induced turbulences within the aerosol prevent a well-defined and reproducible deposition behavior. For example a very limited range of residence times can be used in 1-g, while keeping well-defined flow conditions. Unfortunately the rf-heating equipment could not be used on a sounding rocket due to restrictions in electric power and weight. Therefore the evaporator concept had to be modified as shown in the right-side sketch of figure 2. Approximately 0.1g of Ni-wire (purity 99.99%) was wound on a tungsten filament and evaporated at 1850°C. With this method a steady evaporation of ca.12min could be achieved. The distance between heating source and site of sampling is in both cases 44cm.

Likewise the Joule-heating set-up could not be used on parabolic flights due to the limited evaporation time of the nickel and the risk of loosing Ni-drops from the tungsten filament during the hypergravity
phase of each parabola. In both set-ups Ni-agglomerates were collected in the same principle as shown in figure 3. Hereby the substrate is fixed on a sampling rod which is located in a horizontal stainless steel tube with an opening for aerosol exposure. For sampling the rod moves the deposition section of the substrate over the small opening and the aerosol comes in contact with it. After sampling for several seconds the opening becomes closed by moving the rod until defined position is reached. When in this defined position, the deposited section is protected against further deposition. After one full side of the substrate has seen aerosol exposure, the rod is turned 180°, and the same process occurs on the reverse side of the substrate which has more sampling sections. The morphology of the deposited agglomerates was observed ex-situ via Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

The residence time is derived from the Ar gas velocity assuming laminar flow with a parabolic velocity profile (figure 4). At Reynolds numbers less than 2300 the gas velocity can be solved by the law of Stokes:

\[ v(r) = \frac{\Delta p_V \left( \frac{d^2}{4} - \frac{r^2}{4} \right)}{4 \cdot \eta \cdot l} \]  

with the pressure difference \( \Delta p_V \) between entrance/exit port of flow tube with diameter \( d \) and length \( l \) and the dynamic viscosity \( \eta \) of the carrier gas.

By using the law of Hagen-Poisouille \( \Delta p_V \) can be found:

\[ V = \int_{r=0}^{d/2} v(r) \cdot 2\pi \cdot r \, dr = \frac{\Delta p_V \cdot \pi \cdot d^4}{128 \cdot \eta \cdot l} \]  

Now the minimal residence time can be calculated with:

\[ t_{res} = \frac{l}{v_{\text{max}}} \]  

In 1-g the calculated residence time can be used at least as a “figure-of-merit” to correctly compare the agglomeration results by neglecting any effects from convection and sedimentation. In \( \mu \)-g (parabolic flights) the maximum residence time is limited to 22 sec during each parabola, where ca. 6s must be subtracted as sampling time. Extension of this value is possible by using the sounding rocket \( \mu \)-g platform. With the ESA-operated MAXUS a maximum residence time of up to 12min can be realized.
3. EXPERIMENTAL RESULTS

3.1 AGGLOMERATION OF Ni-PARTICLES IN NORMAL GRAVITY CONDITIONS (1-g)

Figure 5 shows typical Ni-agglomerates obtained in 1-g conditions. There is no obvious difference in morphology of particles obtained with Joule-heating and rf-heating. However, we observed an increase in agglomerate length up to 10µm at longer residence times up to 8sec (figure 6). Large argon gas flow rates resulting in short residence times result in short Ni-chains of just several 100nm.

![rf-heater](image)

![Joule-heater](image)

**Figure 5:** Ni-agglomerates obtained in 1-g with rf-heater and Joule-heater (upper and lower image, resp.)

**Figure 6** Ni-agglomerates obtained in 1-g at residence times <1sec and ca. 8s (upper and lower image, resp.)

To define the particle size distribution of the Ni-particles within the agglomerates, individual measurements were taken at different gas pressures and velocities. Up to 700 single particles had been used for each measurement, which was performed by an adapted computer program. The intra-agglomerate size distribution of the Ni-particles made in 1-g is rather broad, see figure 7. A plot of particle sizes, shown in figure 8, indicates that inside one agglomerate Ni-particles between 10 and 150nm can be found. This observation most likely results from convection effects close to the heating source, where a mixing of particles occurs having seen different growth histories. In general no significant dependency between the gas pressure and the particle size distribution could be detected. While with decreasing the aerosol velocity the particle size distribution becomes more normally distributed as shown in figure 8.
Using transmission electron microscopy, it was possible to visualize the Ni atoms. Figure 9 shows that individual particles are surrounded by an oxide layer which is to be expected once the samples are removed from the chamber. The TEM image indicates that this oxide layer is approximately 2.5 nm thick. Furthermore, the Ni atoms are clearly arranged in a crystalline structure with an atomic spacing of 0.2 nm.

**Figure 9:** TEM image of 2 Ni-particles with single-crystalline structure; the oxide layer is 2.5 nm thick

3.2 AGGLOMERATION OF NI-PARTICLES IN MICROGRAVITY CONDITION (µ-g)

3.2.1 Parabolic flight platform (PF)

Typical agglomerates of Ni-nanoparticles which have been aggregated in µ-g-conditions are shown in figure 10 and figure 11. In contrast to agglomerates produced in 1-g conditions, here the particle chains are stretched much more perfect. Additionally, with increasing “free-flow” residence time the mean length of the agglomerates increases. The longest agglomerates which could be found had a length of ca. 30 µm.

**Figure 10:** typical deposit of Ni-chains obtained from microgravity experiment (parabolic flight) at p=100 mb, \( t_{res}=8 \text{ sec} \)

**Figure 11:** Ni-agglomerates from microgravity experiment (parabolic flight) at p=100 mb, \( t_{res}=16 \text{ sec} \)
The intrachain particle size distribution, shown in figure 12, depicts how \( \mu \)-g experiments can produce more consistent particles throughout the chains as compared to those obtained from 1-g produced particle chains (figure 7). This probably results from the absence of convection effects close to the heating source, where a non-mixing of particles occurs.

Figure 12: agglomerate of Ni-nanoparticles obtained from parabolic flight experiment at \( p=100\text{mbar} \)

The dependency between the mean length of the Ni-agglomerates and different residence times is shown in figure 13. Thus for each parameter, 100 Ni-chains had been measured on the SEM-images via an adapted computer program.

Figure 13: mean length of Ni-agglomerates obtained during parabolic flights as a function of “free-flow” residence time. The straight line is just a guide to the eye.

3.2.2 Sounding rocket campaign MAXUS (SR)

Regarding the results from the parabolic flight experiments the intention of the agglomeration experiments on-board a sounding rocket (MAXUS 8) was to increase the residence time into the minute range. There was microgravity time for running experiments with two different background gas pressures – 100 and 300mb. At each pressure 4 different residence times were set at 13, 40, 70 and 100sec. During the flight the \( \mu \)-g quality was approx. \( 10^{-5} \)\-g, guaranteeing ideal conditions for particle agglomeration excluding any sedimentation or convection effects. This was proven by recording the aerosol with a CCD-camera. The quality of the Ni-aerosol flow at different time intervals during the 300mb experiment is shown in figure 14.

Figure 14: CCD-images of Ni-aerosol at 300mb Ar during MAXUS 8 flight taken close to sampling area; (a) \( t=10\text{s} \) – immediately after switching on the evaporator – turbulent flow due to gravitational effects, (b) \( t=15\text{sec} \) – beginning of \( \mu \)-g conditions, but still turbulent flow, (c) \( t=22\text{sec} \) – steady and well-defined aerosol, (d) \( t=80\text{sec} \), (e) \( t=150\text{sec} \) and (f) \( t=250\text{sec} \); the arrow indicates the width of the aerosol plume; Note: the slit on the tube has a length of 8mm
Surprisingly, no chain-like agglomerates were found in the Ni-deposits. Instead the particles aggregated as fractal structures as well-known from aggregation of non-magnetic materials. In addition we could not find a tendency regarding residence time and mean size of agglomerates as expected (figure 15).

Figure 15: SEM images of Ni-agglomerates produced on sounding rocket MAXUS 8 flight at 300mb and residence times 13s, 40s, 70s and 100s for samples #1,3,5,7 resp.

Furthermore no pressure dependence of the agglomerates’ morphology could be detected (figure 16 and figure 17), whereas the size distribution of the primary particles is similar to those obtained in parabolic flight experiments (figure 18, figure 19).

Figure 16: SEM image of Ni-agglomerates produced on sounding rocket at 300mb and t_{res}=13sec

Figure 17: SEM image of Ni-agglomerates produced on sounding rocket at 100mb and t_{res}=13sec

Figure 18: typical Ni-particles agglomerate obtained from MAXUS 8 experiment

Figure 19: size distribution of Ni-particles inside agglomerates made during MAXUS 8 flight for different gas pressures and residence times, i.e., p=300mb at 13s (S1), 40s (S3), 70s (S5), 100s (S7); p=100mb at 13s (S9), 40s (S11), 70s (S13), 100s (S15). The total number for each curve is about 1000 particles.
4. DISCUSSION

Performing an evaporation experiment with permanent gas flow on ground leads to turbulent aerosol conditions driven by thermal effects as shown in the left sketch of figure 20. However, the investigation of the agglomeration of magnetic nanoparticles, i.e., in the gas phase requires ideal aerosol conditions without any disturbing side effects (right sketch of figure 20). This could be provided by using suitable microgravity platforms. The formation of extended chains of nanoparticles is a well-known phenomena observed as a result of agglomeration within magnetic aerosols. Usually the magnetic dipole–dipole interaction is considered responsible for this type of self-organization (see, e.g., [5]). Li et al. [9] observed morphologies of Ni-agglomerates depending on the presence and strength of an external magnetic field (figure 21), i.e., applying stronger magnetic fields results in straighter and longer particle chains. Unfortunately in all these experiments the domain structure of the individual nanoparticles is unclear. However, it can be reasonably assumed that multi-domain particles would not align as perfectly in linear chains as single-domain particles do, if the magnetic interaction between particles dominates the agglomeration process. However, in our experimental set-up external magnetic fields are involved, too, a) due to the W-heater coil in the case of the MAXUS-setup and b) due to the Earth’s magnetic field.

In total we have tested 4 experimental situations (µ-g, 1-g both with rf- and Joule-heating set-up) and only in a single case, i.e., via Joule-heating on sounding rocket platform, no chain-like aggregates have formed (figure 22). We had performed several pre-tests before the MAXUS 8 flight in order to prove if the strong impact of the payload during the reentry into the atmosphere and the landing on ground could modify the deposited Ni-agglomerates. Therefore we had deposited substrates with Ni in a lab and analyzed them via SEM. Subsequently we made vertical drop tests (ground material: ceramic; distance: 1,5m) and vibration tests (amplitude: 1mm, frequency: 50Hz) with these deposited substrates. The SEM studies did not show any changes. In addition we had analyzed the deposit (1-g, µ-g) on the sintered filter which was located at the top of the flow chamber to verify if the design of the sampling module and the procedure to sample the Ni-agglomerates can affect the shape of the agglomerates. Again, the SEM examinations showed no changes to the Ni-structures deposited on the substrates. Due to these tests we could determine the strong adhesion of the Ni-agglomerates on the substrates. To elucidate the possible reason for the non-chainlike Ni-aggregates, we need to figure out the main differences for particle interactions during the agglomeration process. These are

- strength and direction of Earth’s magnetic field
- competition between thermal fluctuation of the direction of the particles magnetic moment (decreasing with particle size) and the dipole-dipole-interaction (increasing with particle size for single domain particles)
- convection effect.

We assume that Earth’s magnetic field being unstable in size and direction during the agglomeration period is responsible for the fluffy morphology of the Ni-aggregates obtained during the MAXUS 8 flight. The apogee of this SR-flight was at an altitude of approx. 720km. During the ascent to and descent from the apogee combined with a slow spin (<0,1Hz) of the rocket payload the magnitude and direction of the earth magnetic field relative to the flow tube axis varies during agglomeration (figure 23).

![Figure 20: typical behavior of an aerosol inside a flow chamber with an evaporator on the bottom; turbulent characteristic due to convection and sedimentation effects under gravity (1-g); ideal gas flow conditions under microgravity (µ-g)](image-url)
5. CONCLUSIONS

With this work we have presented new results on the agglomeration behavior of Ni-nanoparticles in aerosols under earth gravity and microgravity conditions by using the inert gas condensation technique. In general, necklace-like chains are obtained with primary Ni-particles being larger than about 20 nm. Agglomerates obtained in µ-g during parabolic flights are similar in morphology with those obtained in 1-g, but tend to be much longer, if the time available for agglomeration is increased. Further the intra-chain particle size distribution is much narrower compared to those obtained in 1-g conditions. In contrast, the results from a sounding rocket campaign (MAXUS-8) do not fit into this scheme: no particle chains were found even with Ni-particles much larger than 20 nm. This might be due to a different (multi-domain) magnetic structure of the nanoparticles. This will be part of future investigation on the particles’ magnetic properties.

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