Characterization of platinum alloy powder - PtRh 80-20 - for additive layer manufacturing

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Abstract

In aerospace new technologies, like additive manufacturing, are widely in discussion and for some components, presently becoming standard. Due to the fact that the quality and properties of the applied powder have an essential influence on the later mechanical properties of the final components, this investigation is engaged with the characterization of platinum alloy powder. Furthermore, this study gives an overview of the manufacturing process of the powder. The analyses show that in terms of quality, the morphology and chemical composition of the platinum rhodium powder can be maintained through successive ALM loops. In conclusion, the performed investigations could demonstrate the maturity of the platinum alloy powder production, for use in ALM manufacturing processes.

1. Introduction

The development of new technologies for applications in aerospace plays an essential role to cope with highest reliability demand, under extreme temperatures and cost pressure. For this reason, new technologies, like additive manufacturing, are widely in discussion and carefully studied. Therefore, the further development of existing and innovative materials becomes a crucial factor to widen its field of application. Noble metals are applied in many aerospace applications due to advantageous properties, like corrosion resistance, high melting point and high temperature strength. Especially platinum group metals feature enhanced characteristics, like superior high temperature resistance and are therefore of particular interest [1, 2].

One of the potential applications is the manufacturing of small bipropellant reaction control thrusters, which combustion chamber are partially based on platinum alloys. Airbus Defence and Space has developed and manufactures small 10 N rocket engines based on platinum alloys material. This engine is widely used for attitude-, trajectory- and orbit-control of large satellites and deep space probes. This application has a long history. Since the early nineties more than 130 spacecrafts were equipped with Airbus Defence and Space's 10 N platinum thrusters [3].

To extend the application area of platinum alloys with improved properties, like higher operation temperatures, new alloy compositions are under development. Thus, additive layer manufacturing (ALM) provides the opportunity to produce new alloy compositions on the basis of platinum powder. Using this additive layer manufacturing technology, parts can be built up layer by layer with almost net-shape geometries. At the same time, it enables to manufacture samples or components with a complex geometry and leads to a reduced amount of scrap [4, 5, 6]. In addition to the used ALM facility and process parameters the quality and properties of the applied powder has an essential influence on the later mechanical properties of the final component. For this reason, the investigation and characterization of powder, which is applied for additive layer manufacturing, is one of the key factors.

The aim of this work is to investigate and characterize platinum rhodium powder for the use in ALM manufacturing processes. Within this study, the morphology of platinum rhodium powder before and after an ALM process was

investigated by means of scanning electron microscopy (SEM) and light microscopy. The chemical composition of the powder was analysed using EDS.

2. Materials and Methods

2.1 Material

For this study a platinum rhodium powder was used. The alloy composition was 80 wt.-% platinum and 20 wt.-% rhodium. In the following chapters the manufacturing process and inspection of the powder are described.

2.2 Manufacturing process and inspection of the powder

An overview of the rationale of the powder procurement and its inspection is illustrated in Figure 1.

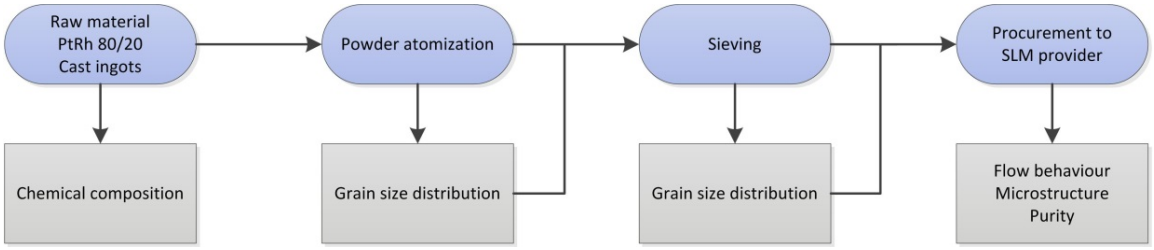


Figure 1: Work and inspection flow of the powder procurement for ALM of PtRh 80/20

In the first step the powder procurement starts with the supply of the solid raw material, which shall be of the same quality than the raw material destined for the conventional manufacturing sequence. This comprises especially the chemical composition of the material, which is given by internal Airbus Defence & Space specification. The same quality is essential for later comparisons of the components and their properties. This raw material is then atomized to an average grain size, which meets the requirements of the subsequent ALM process best. The process has a natural dispersion, which results in a too large or too fine grain size, the powder than has to be sieved and sighted. When the potentially multiple sieving processes result in a grain size distribution, which meets the requirement of the ALM provider, the powder will be procured. The powder then will be characterized according to its microstructure, flow behaviour and purity.

2.2.1 Procurement of raw material

The characteristics of the raw material have to meet the requirements of the ALM process in agreement with the later application. Since most of the material properties are defined within several manufacturing steps (grain size during atomization, tensile properties during ALM process) the chemical composition of the raw material is its most relevant property to assure before starting the powder manufacturing. The raw material was atomized by NANOVAL GmbH & Co. KG due to their expertise in the atomization of non-standard materials and especially noble metals. A detailed description of the atomization process is given later on in Chapter 2.2.2. The vacuum casted raw material was delivered in small bars. The chemical composition of the material was analysed by X-ray fluorescence (XRF) and glow discharge spectroscopy (GDS). The measurement principle of XRF is the emission of characteristic secondary (or fluorescent) X-rays from a material that has been excited by bombarding it with high-energy X-rays or gamma rays. The glow discharge spectroscopy enables a direct bulk analysis and depth profiling analysis of solids. The measurement principle relies on cathodic sputtering, which is used to remove material layer by layer from the sample surface. Thus, the atoms removed from the sample surface. Afterwards, they migrate into the plasma where they are excited through collisions with electrons or metastable carrier gas atoms. Then, the spectrometer measures the characteristic spectrum emitted by this excited atoms [7].

2.2.2 Atomization process

The powder atomization was performed by NANOVAL GmbH & Co. KG using their internal developed and meanwhile multiple built atomization facility. Figure 2 shows a schematic of the atomization principle by Nanoval.

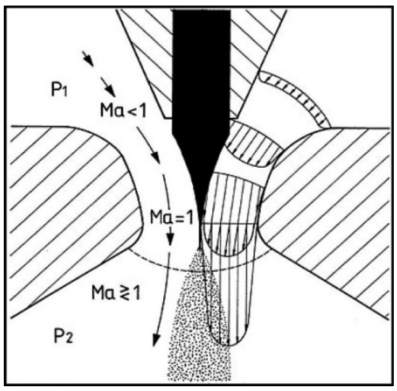


Figure 2: Schematic of the atomization principle by Nanoval [8]

The Nanoval principle uses a Laval nozzle type with a convergent to divergent flow duct. In the nozzle sonic speed is achieved. The melt filament is accelerated and by this it gets thinner until it bursts open. This process generally results in fine powders with a narrow particle size distribution. The raw material is filled in a crucible, which is available in several dimensions. For the atomization of the PtRh powder a crucible with a maximum net weight of 5 kg is used. The material is heated up in a vacuum furnace up to its melt temperature. The average powder size to be achieved can be adjusted by the temperature of the melting pool. This correlation has to be determined experimentally for new materials. When the correct temperature is reached the atomization process is started. The main part of the atomized powder falls into the main collector, only the smallest particles are separated by a cyclone interceptor. After finishing the process the facility is flooded with ambient air and the powder can be taken from the collectors in highly pure condition. A purging of the tubing follows releasing a further portion of powder, which is however contaminated and cannot be further used.
The further investigations of the powder will be given in the following chapters.

2.3 Measurement of the particle size distribution

The measurement of the particle size distribution was performed with a Helos BR/ R3 from Sympatec GmbH. It is a laser diffraction method and is based on the principle of the interaction of a laser beam with the particles. The particle size distribution is determined by measurement of the angle dependence of the intensity of scattered light of a laser beam. Thereby, smaller particles lead to higher scattering angles than bigger particles. The data of the angle dependent scattered light intensity are analysed and the size of the particles is calculated, which is responsible for the diffraction pattern. For this the Mie theory is used [9]. The particle size is indicated as diameter of the volume-same ball. The measurement range was 0.9 - 175 µm and 4.5 - 875 µm. For the measurement a sample portion of 5 g is necessary.

2.4 Manufacturing by additive layer manufacturing (ALM)

The powder machining by additive layer manufacturing was performed with the Concept Laser MLab machine. The used manufacturing process is a powder bed process and a 90 W laser was applied. The process was performed by room temperature and argon was used as shielding gas.

2.5 Surface Characterization

2.5.1 Light microscope

The light microscopic investigations were done for the analysis of the density of the powder. For this purpose, powder particles were embedded, grinded and polished afterwards.

2.5.2 Scanning electron microscope (SEM)

A JEOL JSM-6320 field-emission scanning electron microscope (SEM) was used to characterize the morphology of the platinum rhodium powder. Furthermore, energy-dispersive X-ray spectroscopy (EDS) was performed to analyse the chemical composition of the powder. Additional, to the actual particle size distribution measurement the particle diameter was optically determined by means of SEM.

3. Results and discussion

3.1 Particle size distribution

The particle size distribution results from the atomization process. It was measured after the atomization process to have an overview of the generated powder particle size. Additional, the measurement of the particle size was performed after the sieving to control if the particle size distribution meets the requirement of the ALM provider. The particle size distribution has an influence on the layer deposition and the connection between the powder particles during the fusing process. Furthermore, it can be affected inequalities in geometry and internal stress. For this reason, it is important to analyse the particle size distribution before an ALM process.
The presented results were measured after the sieving process. A diagram of the particle size distribution is given in Figure 3.

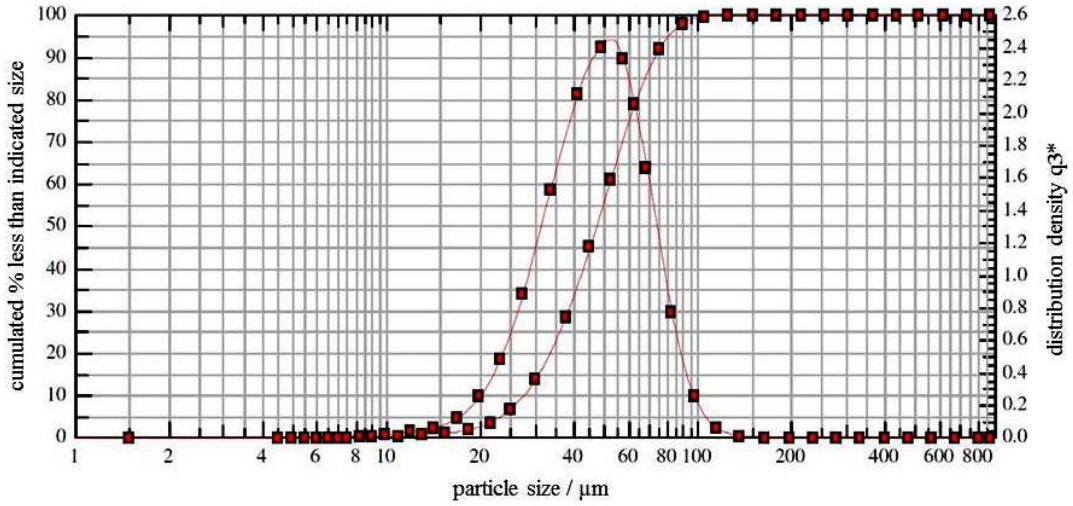
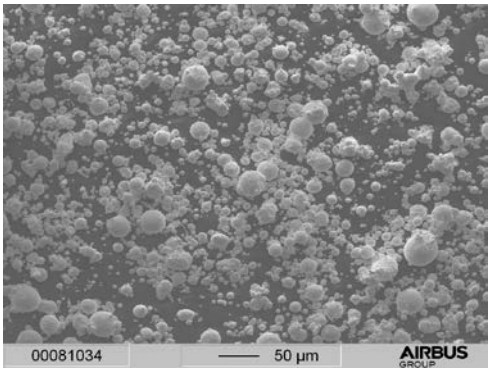


Figure 3: Particle size distribution of platinum rhodium powder after sieving

It can be seen that the average particle diameter d_{50} is 47.32 µm. 10 % of the particle are less than 27.48 µm and 90 % of particles are less than 73.26 µm. Furthermore, it can be detected that 45.03 % of the particles have a particle diameter d < 45 µm. The particle fraction, which was achieved by the sieving process, should be in the range of 20 and 65 µm. The particle size distribution, which is illustrated in Figure 3, shows that the desired particle size range can be obtained.

3.2 Powder morphology

Scanning electron microscope (SEM) micrographs of the platinum rhodium powder was used to make a first assessment of its morphology before an ALM process, to emphasize the potential alteration/ differences between the initial and the post-processed powder. Figure 4 a) shows an overview of the powder particles. It can be seen that there are size distribution of powder particles. In Figure 4 b) and c) details of powder particles are given. The SEM micrographs at higher magnifications, shows imbricated like powder structure. Additional, satellite formations and agglomerations are recognized.



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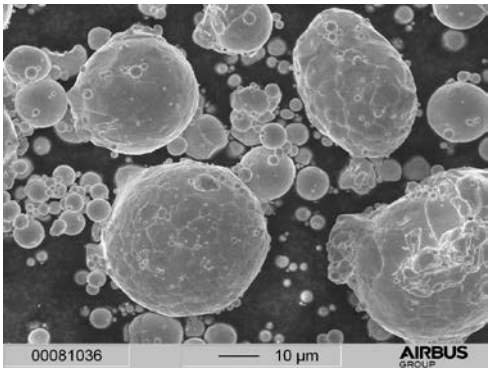

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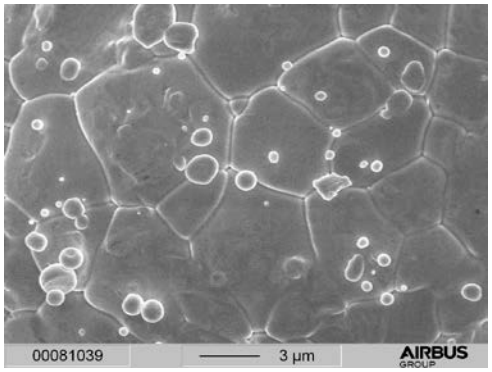

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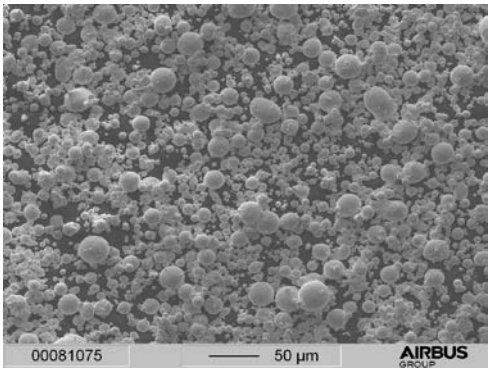
Figure 4: SEM micrographs of platinum rhodium powder before the ALM process a) 200 x magnification, b) 2000 x magnification, c) 5000 x magnification

The SEM micrographs in Figure 5 illustrate platinum rhodium powder after the use in the ALM process. Figure 5 a) shows an overview of the powder. At first view no differences to the powder (Figure 4), which was investigated before the ALM process, are visible. Details of the powder morphology are given in Figure 5 b) and c). The same kind of conglomerations and formation of satellite particles can be observed as before the ALM loop.
At this point, it can be determined that there is no alteration of geometry between the two platinum rhodium powders.

For a direct comparison the two powders were mixed. The SEM micrographs of the mixed powder are given in Figure 6. Figure 6 a) shows an overview of the mixed powder. There are no differences to the SEM micrographs in Figure 4 a) and Figure 5 a). The details of the powder (Figure 6 b) and c)) also illustrate satellite formations and agglomerations.

The investigations of the powder morphology reveal that there are no differences between platinum rhodium, which was investigated before and after the ALM process. Furthermore, the powders show a spherical structure.

Beside the powder morphology also the powder diameter was optically examined by SEM. The results of these measurements are given in Figure 7.



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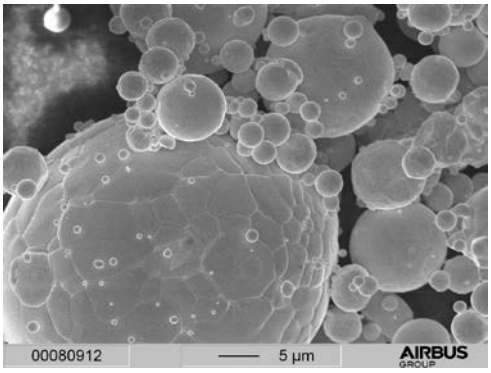

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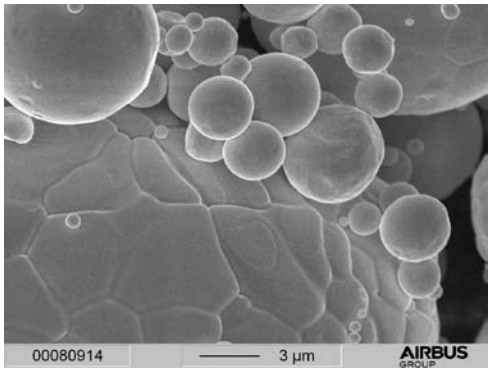

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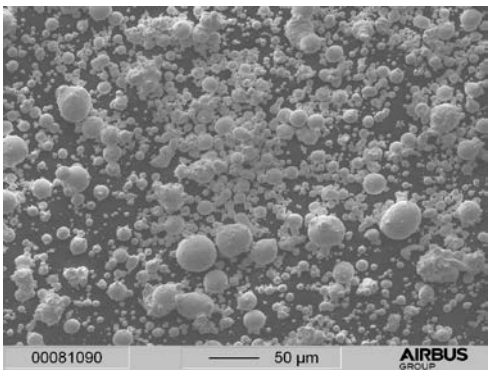
Figure 5: SEM micrographs of platinum rhodium powder after the ALM process a) 250 x magnification, b) 2000 x magnification, c) 5000 x magnification



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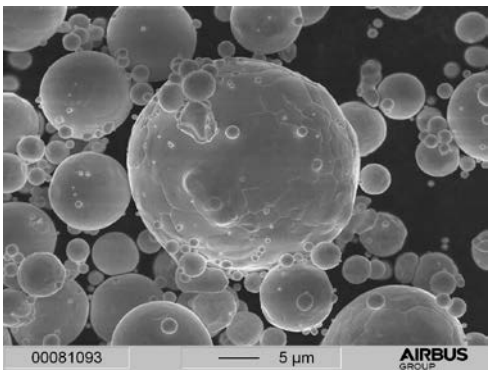

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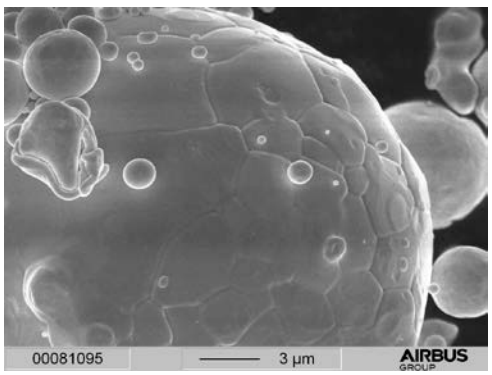

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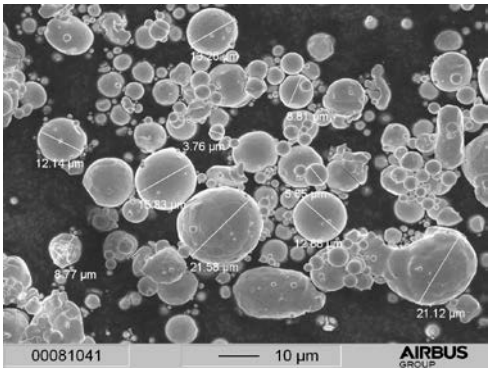
Figure 6: SEM micrographs of mixed platinum rhodium powder before and after the ALM process a) 250 x magnification, b) 2000 x magnification, c) 5000 x magnification



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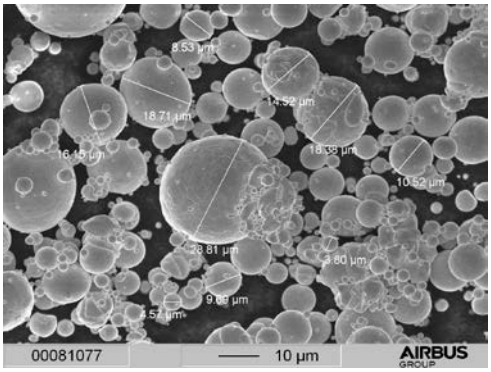

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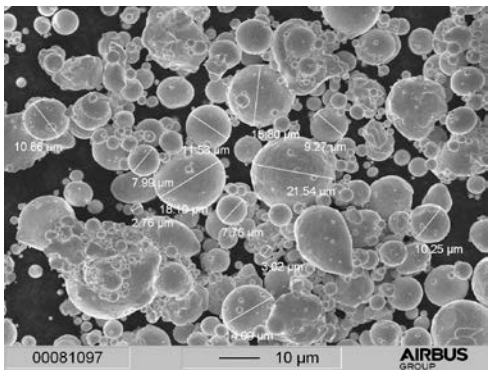
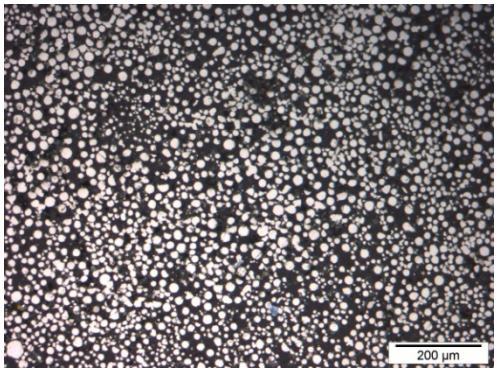


c)

Figure 7: SEM micrographs of platinum rhodium powder with measurements of the powder particle size a) powder before the ALM process, b) powder after the ALM process, c) mixed powder

The particle diameter of the powder, which was investigated before the ALM process is 12.40 ± 5.9 µm. The measurement of the particle diameter, which was analysed after the ALM process, is around 15.4 ± 7.9 µm. The mixed powder shows an average particle diameter of 11.1 ± 5.6 µm. The powder diameter measurements of Figure 7 show that there are no significant differences between the particular powder samples. On average the powder diameters are in one range. All three powders show that the powder diameter varies strongly between 3 and 30 µm. The three images, given in Figure 7, are exemplary for the powder diameter measurements. There are SEM micrographs of the powder diameter measurement, which show powder particles with a diameter of 40 µm. In comparison with the particle size distribution measurements by laser diffraction, it can be seen that there are deviations. The laser diffraction methods determined a higher average particle diameter. The differences between the two measurement methods can be constituted by the fact that the laser diffraction is determined of the angle dependence of the intensity of scattered light of a laser beam and a higher amount of the powder can be analysed.

Additional, metallographic investigations were accomplished to analyse the density of the powder particles. The results of the investigation of the density of the powder are given in Figure 8. The analysed powder was investigated before the ALM process.



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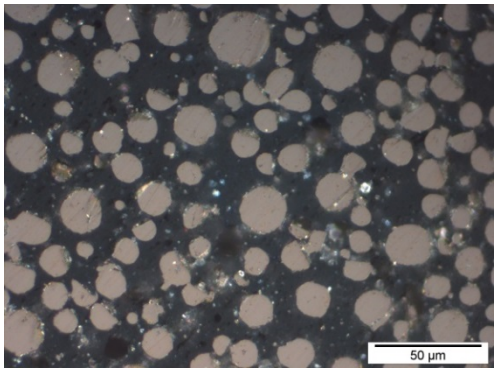

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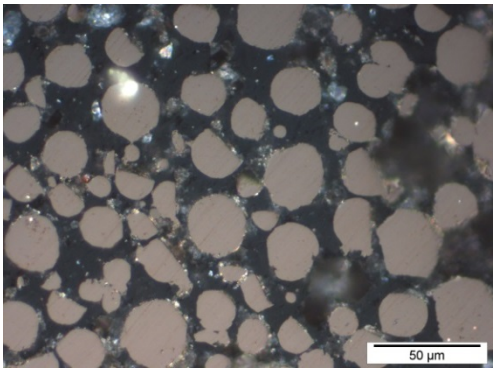

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Figure 8: Light microscopic images of the investigations of the powder density a) overview, b) and c) at higher magnification

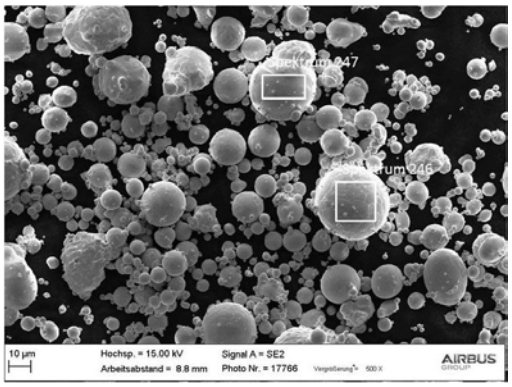
The investigations of the generated powder show full density. Furthermore, the results show that the powder is homogeneous and pore free.

3.3 Chemical composition of the platinum rhodium powder

The chemical composition of the platinum rhodium powder was analysed by energy-dispersive X-ray spectroscopy (EDS). Here, only the chemical compositions before and after the ALM process are regarded. The results for the powder before the ALM process are given in Figure 9.

Figure 9 a) gives an overview of the measurement points for the EDS spectra. Two measurements were conducted on the indicated particles in Figure 9 a). The results of the two spectra are shown in Figure 9 b) and c). The spectrum 236 identifies 83.3 wt.-% Platinum and 16.7 wt.-% Rhodium. 83.8 wt.-% Platinum and 16.2 wt.-% Rhodium can be detected in spectrum 247. There is a little deviation to the actual alloy ratio of 80 wt.-% platinum and 20 wt.-% rhodium, which results from the 15 % relative error of the EDS measurement.

Figure 10 shows the EDS results of the powder, which was investigated after the ALM process. An overview of the measurement points for the EDS spectra is given in Figure 10 a). Spectrum 251 (Figure 10 b)) shows 81.6 wt.-% platinum and 18.4 wt.-% rhodium. In Figure 10 c) a platinum content of 82.2 wt.-% and a rhodium content of 17.8 wt.-% can be detected. The deviation of the chemical composition also results from the relative error of EDS.



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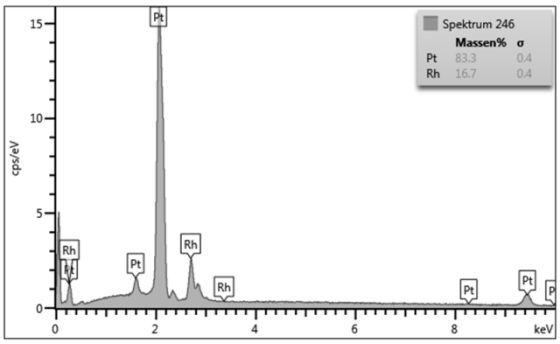

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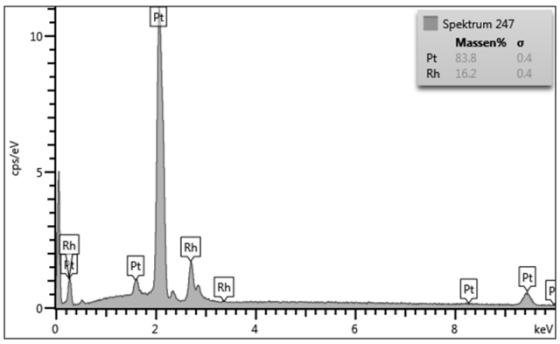

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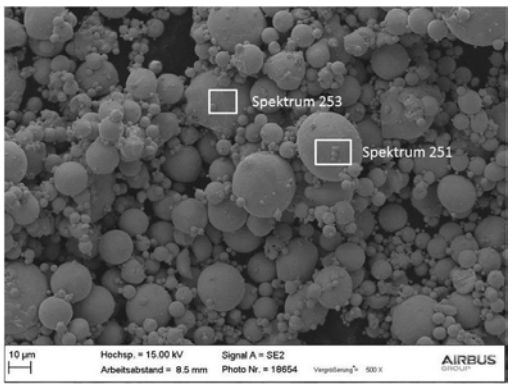
Figure 9: Results of the EDS analysis of platinum rhodium powder before the ALM process a) SEM micrograph overview with the measurement points, b) EDS spectrum 246, c) EDS spectrum 247



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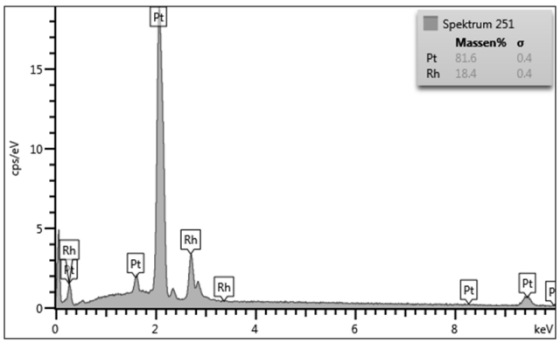

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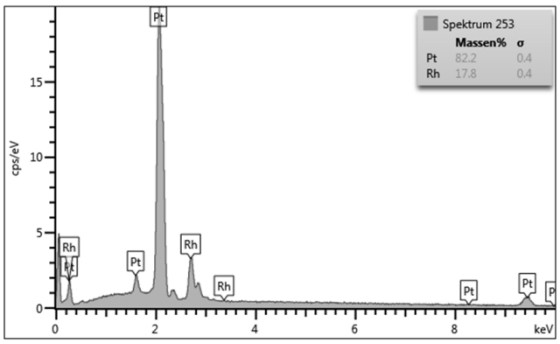

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Figure 10: Results of the EDS analysis of platinum rhodium powder after the ALM process a) SEM micrograph overview with the measurement points, b) EDS spectrum 251, c) EDS spectrum 253

The analytical investigations by EDS show that the powder could achieve the desired chemical composition without any significant contamination. Furthermore, it can be seen that there is no difference of the chemical composition between the powder before and after the ALM process. The chemical compositions of the powders correspond to the chemical requirement.
Additional, to analyse the distribution of platinum and rhodium at a powder particle surface mappings were performed. The results of the mappings are given in Figure 11.

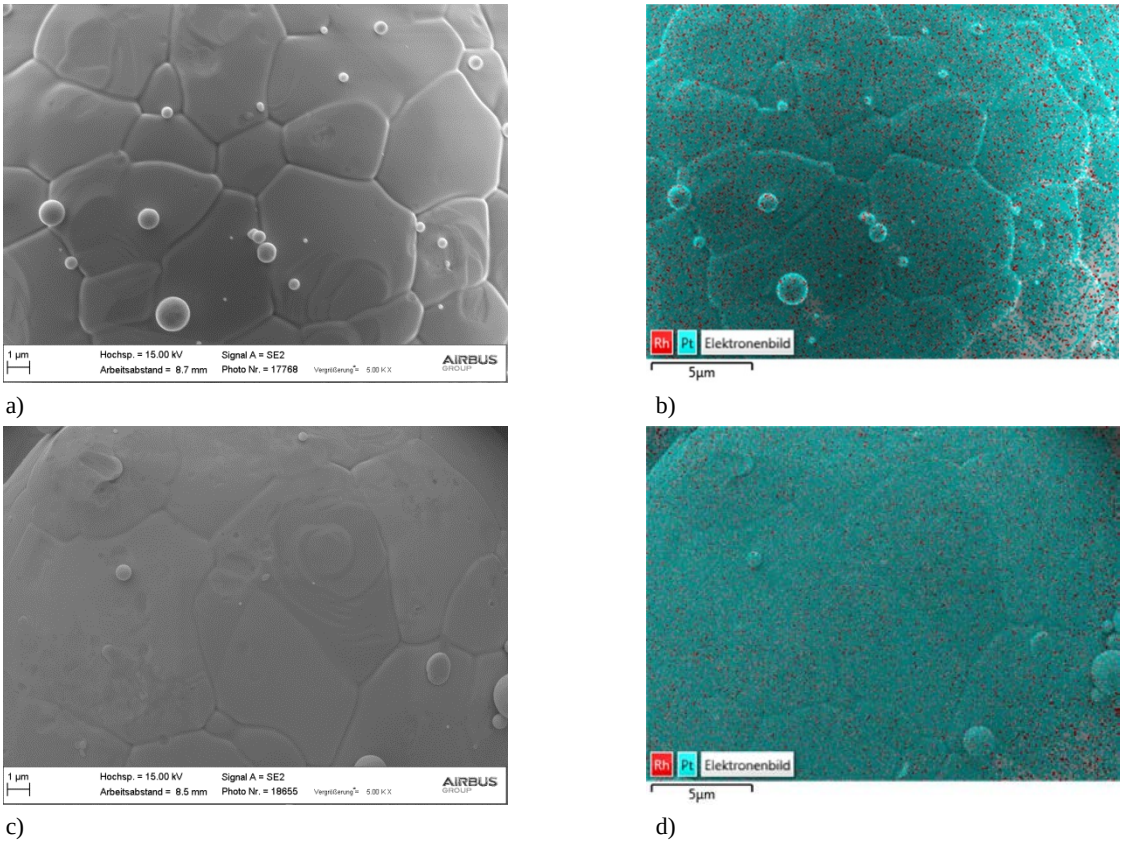

Figure 11: Mappings of powder particles a) before the ALM process (SEM micrograph), b) before the ALM process (mapping), c) after the ALM process (SEM micrograph), d) after the ALM process (mapping); turquoise: platinum, red: rhodium

Figure 11 a) and b) show the SEM micrograph and the corresponding mapping of the powder, which was investigated before the ALM process. The SEM micrograph and the corresponding mapping of the powder, which was analysed after the ALM process is illustrated in Figure 11 c) and d). Both mappings show a homogeneous distribution of platinum and rhodium at a powder particle. There is no significant influence of the distribution, which depends on the ALM process.

4. Conclusion

Within this study the investigation and characterization of platinum alloy powder used for additive layer manufacturing (ALM) is presented. Platinum rhodium powder (PtRh 80-20) is investigated by chemical and physical analytics. Beside the investigation and characterization of the platinum rhodium powder this study gives an overview of the powder manufacturing process. Hereby, the process chain is composed of four essential process steps: Starting with the supply of raw material, followed by the powder atomization process, then a sieving process would be performed and finally when the sieving process results in a grain size distribution, which meets the requirement of the ALM provider, the powder will be procured.
The platinum rhodium powder was analysed before and after an ALM process to identify any potential influence or alteration of the powder quality induced by the ALM process itself. The powder morphology has been analysed by means of scanning electron microscope (SEM). The platinum powder shows a homogeneous spherical structure. The powder diameter varies strongly between 3 and 40 µm. Additional, metallographic investigations were accomplished. The results show that the powder is homogeneous and features no pores. Furthermore, energy-dispersive X-ray spectroscopy (EDS) was performed. This analytical method shows that the powder could achieve the desired chemical composition without any significant contamination. The investigations show that no significant

differences of the structure and chemical composition between platinum rhodium powder before and after the ALM process can be detected.
The comparison shows that the ALM process has no significant influence on the powder structure itself. In terms of quality, the morphology and chemical composition of the platinum rhodium powder can be maintained through successive ALM loops. The performed investigations could demonstrate the maturity of the platinum alloy powder production, for use in ALM manufacturing processes.

5. References

[1] Rdzawski, Z., M. and J., P. Stobrawa. Microstructure and properties of the new Pt–Rh based alloys for high-temperature applications. *Journal of Materials Processing Technology*. vol. 153-154, pp. 681–687. 2004.

[2] Soriano, C., M. Platinum. Potentials, IEEE. vol. 16, pp. 29-32. 1998.

[3] Astrium Propulsion and Equipment. 10N Bi-Propellant Thruster. 2012.

[4] Antonysamy, A., A. Microstructure, Texture and Mechanical Property Evolution during Additive Manufacturing of Ti6Al4V Alloy for Aerospace Applications. PhD Thesis. University of Manchester, Faculty of Engineering and Physical Sciences. 2012.

[5] Brandl, E. Microstructural and mechanical properties of additive manufactured titanium (Ti-6Al-4V) using wire. PhD Thesis. Brandenburg University of Technology Cottbus–Senftenberg, Faculty of Mechanical, Electrical and Industrial Engineering, Chair in Metal Science and Material Engineering. 2010.

[6] Greitemeier, D., Schmidtke, K., Holzinger, V. and C. Dalle Donne. Additive Layer Manufacturing of Ti-6Al-4V and ScalmalloyRP®: Fatigue and Fracture. In: 27th ICAF Symposium. 2013.

[7] Nelis, T. and R. Payling. Glow Discharge Optical Emission Spectroscopy: A Practical Guide. The Royal Society of Chemistry. 2003.

[8] NANOVAL GmbH & Co. KG. Production of fine and ultra fine metal powder. http://www.nanoval.de/verfahren_eng.htm (last accessed on 4th of June)

[9] Malvern Instruments GmbH. Laser Diffraction - Particle size distributions from nanometers to millimeters. http://www.malvern.com/de/products/technology/laser-diffraction/ (last accessed on 4th of June)