Solidification of single droplets under combined cooling conditions

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Abstract. In this study, a pneumatic high-temperature droplet generator was used to generate individual droplets (diameter range: 350 – 1200 µm) which were cooled under combined cooling conditions. The individual droplets were cooled in a nitrogen atmosphere after ejection and during subsequent free fall. After a defined falling distance, the particles were quenched in either oil or water to further increase their cooling rate. Two alloys in different temperature ranges were used to study the effect of different cooling conditions quantitatively by the analysis of different microstructural features. To show the working range of the droplet generator, a metallic glass FeCo35.1Nb7.7B4.3Si2.8 (liquidus: 1210 °C) was used as a high-temperature alloy, and its resulting amorphous fraction was quantified as an indicator for different cooling conditions. Furthermore, the aluminium alloy AlCu4.5 (liquidus: 650 °C) was solidified under different conditions and the subsequent secondary dendrite arm spacing (SDAS) measurements were analyzed.

1. Introduction
Droplet generators can generate single droplets of a defined size [1-3] and are common tools to study phenomena such as droplet impact [4, 5] or droplet collisions [6, 7] under defined conditions. While droplet generation is simple to achieve with cold fluids, specific requirements for the droplet generators provide more challenges for the droplet generation of liquid metals with increasing melt temperature. Major requirements include the implementation of a suitable heating system, adequate refractory materials for the crucible, the orifice production in this material, and the necessity of an inert gas atmosphere. After ejection, the droplets cool down in a defined way in the inert atmosphere [8] which depends mainly on the particle size. However, if this cooling step is combined with subsequent quenching, the microstructure of one certain particle size can be adjusted by changing either the falling distance before quenching or the type of quenchant. The aim of the present work is to show how a high-temperature drop-on-demand droplet generator can be used to adjust the microstructure of generated particles exemplified with an Fe-based metallic glass and the conventional aluminium alloy AlCu4.5.

2. Experiments
The droplet generator consists of a crucible with a melt volume of 30 ml in a small pressure vessel (figure 1). A solenoid valve, which is connected to an overpressure reservoir, is opened for a short time (2 - 6 ms, depending on droplet size) allowing the pressure wave to travel through tubing (figure 2), the vessel, and subsequently through the melt. This introduces an overpressure and pushes the melt out. After the wave is reflected from the bottom of the crucible, the pressure drops and starts
to retract the melt. If the pressure drop is fast enough, the melt volume that was pushed out of the nozzle can separate and form a single droplet. The pressure wave is relieved through a vent hole at the top of the vessel. After the pressure wave has completely vanished, a new droplet can be generated. A high speed camera was used to ensure the parameters were correctly adjusted to achieve a drop-on-demand mode, generating exactly one droplet for each pressure pulse.

Figure 1. Schematic of experimental setup.

The entire system is placed in a chamber which is purged with nitrogen to avoid oxidation. The oxygen level under the droplet generator was measured to be below 50 ppm. However, the oxygen content in the vicinity of the nozzle is assumed to be much lower due to hot graphite parts. Induction heating is used to either heat a graphite crucible or a graphite susceptor that heats a boron nitride crucible by conduction. Temperatures of up to 1600 °C can be reached, allowing the use of a variety of technical alloys in the system. Particles can be collected in a quenchant in separate beakers after adjustable falling distances from the nozzle.

2.1 Experiments with FeCo35.1Nb7.7B4.3Si2.8 (metallic glass)
To show the effect of different combined cooling conditions, particles of the iron-based metallic glass FeCo35.1Nb7.7B4.3Si2.8 were collected after four different falling distances for a droplet diameter of 360 µm. If cooled in nitrogen only during free-fall, the particles crystallized fully [9]. Figure 3 shows schematically the cooling of a single droplet of a glass former alloy in a CCT diagram during free-fall in a gas atmosphere and subsequently quenched in a liquid after different falling times. If the particle is not quenched (condition a), it crosses the crystallization area slowly and crystallizes. If it is quenched early enough (condition b), crystallization is suppressed and a fully amorphous particle can be generated. In condition c, the particle is quenched shortly after it has entered the crystallization zone, causing partial crystallization. In condition d, the particle is quenched too late where crystallization was already complete. In the experiments, the falling distance was varied between 0.22 and 0.82 m for one particle size (table 1). The critical cooling rate of the alloy is approx. 5000 K/s [9].

Figure 2. Pressure curve in the droplet generator and ejection of a droplet.
Different quenching conditions in the CCT diagram, (a) gas cooling to achieve fully crystalline material, (b-d) with subsequent liquid quenching to achieve fully amorphous, partially amorphous and fully crystalline material, respectively.

2.2 Experiments with AlCu4.5

Figure 4 shows possible quenching conditions for droplets of different diameters from AlCu4.5 with regard to its phase diagram. For the largest droplet (condition a) the droplet is quenched in a fully liquid condition, so that its entire volume will cool down rapidly resulting in a very fine microstructure. However, if it is quenched below liquidus during dendrite growth (condition b), the remaining dendrite growth will yield smaller dendrites compared to the dendrite growth during gas cooling. Finally, if the particle is quenched below solidus (condition c), microstructural growth in the solid can still be avoided. In this study, the droplet diameter was changed for a constant quenching distance of 0.22 m (table 1).

Table 1. Experimental parameters

|                  | FeCo35.1Nb7.7B4.3Si2.8 | AlCu4.5 |
|------------------|------------------------|---------|
| Melt temperature / °C | 1250                   | 750     |
| Inert gas        | nitrogen               | nitrogen|
| Nozzle diameter / µm | 350                    | 250, 350|
| Falling distance / m | 0.22, 0.35, 0.48, 0.82 | 0.22, 0.48, 0.82 |
| quenchant        | oil                    | distilled water |

3. Analyses

3.1. Particle size

Image analyses of the size of the spherical particles were performed using the Malvern Morphologi G3. For the metallic glass, a tight particle size distribution with a number median diameter $d_{50,0} = 360\mu m$ geometric standard deviation of $d_{94,0} / d_{50,0} = 1.08$ was achieved (figure 5).
Since semisolid particles can deform as they strike the quenchant, image analysis is not possible and a sphere-equivalent average particle diameter was determined from the mass of 20 particles. Due to the lower surface tension and viscosity of AlCu4.5, a tighter particle size distribution was achieved with a geometric standard deviation <1.05 for all particles.

3.2. Microstructure
Micrographs of particles were prepared from both alloys for different process conditions to show the effect of cooling conditions on the microstructure. While the metallic glass was etched in aqua regia for 3 s, the aluminium alloy was etched in NaOH 5% for 30 s. Light microscopy was used for evaluation. The amorphous fractions of the metallic glass samples were measured using differential scanning calorimetry (Perkin Elmer Pyris 1) as proposed by Ciftci et al. [9]. The AlCu4.5 alloy was evaluated using secondary dendrite arm spacing (SDAS). The average dendrite arm spacing and its standard deviation were measured by image analysis of micrographs.

4. Results and discussion

4.1. Metallic glass
Figure 6a shows micrographs of the metallic glass for a falling distance of 0.22 m, 0.48 m and 0.82 m (corresponding to a falling time of 190, 300 and 410 ms). While the particles appear featureless for the shortest falling distance of 0.22 m, crystalline fractions increase as the falling distance increases. This shows that the cooling rate resulting from gas cooling is insufficient for glass formation. It is so low that the shortest falling time is still too long to avoid the crystallization area as denoted in figure 3.

Figure 5. Unsieved particle size distribution for the Fe-based metallic glass
To achieve a fully amorphous sample, either the quenching distance could be reduced or the melt temperature could be raised, so that the particles are quenched at a higher temperature. However, both options might result in deformed particles due to the hotter impingement condition. Figure 6b shows the amorphous fraction as determined from DSC analysis. An amorphous fraction of 90% was achieved for the shortest falling distance and decreases to 4 % with increasing falling distance. The standard deviation of less than ± 3 % indicates a high reproducibility for each measured sample.

4.2. AlCu4.5

Figure 7 shows micrographs of AlCu4.5 droplets with different droplet diameters for different cooling conditions. For the smallest droplet diameter, 350 µm, two different sizes of dendrites were observed where the majority of the dendrites were larger. This reflects cooling condition (c) from figure 4 where the larger dendrites form during gas cooling, while the remaining dendrites are formed during quenching. If the droplet diameter is increased to 820 µm, the dendrites size greatly decreases. This could be due to cooling condition (b), where the particle cooling is so slow that it is quenched fully or almost liquid. If the droplet diameter is increased further to a diameter of 1065 µm, the droplet still impinges in a state that refers to condition (b). A possible reason for the increased dendrite size is the occurrence of the Leidenfrost effect. A maximum cooling rate of the droplet is achieved if the heat released by instantaneous evaporation of the quenchant during the impingement is high enough for full solidification; if there is liquid left when an insulating vapour film builds up, this will greatly reduce the cooling rate. This effect heightened as the droplet diameter is increased to 1600 µm.
Figure 7 also shows the results of the quantitative secondary dendrite arm spacing. The qualitative trend discussed previously can also be found here. A minimum dendrite size is achieved with a droplet diameter of approx. 820 µm. At this size, the droplet has not cooled below liquidus and has a small enough mass that the dendrites can be formed during impingement. The liquid fraction of the impinging droplets was calculated by the method proposed by Whiskel et al. [8]. Droplets with a diameter smaller than 300 µm are predicted to impinge fully solid, while droplets above 850 µm are predicted to impinge fully liquid. This fits well with experimental results described previously.

5. Conclusion
Through of the experimentation of an iron based metallic glass and the alloy AlCu4.5, it is evident that drop-on-demand droplet generation with subsequent quenching is a proper technique to alter the microstructure of the resulting particles. The amorphous fraction of the metallic glass could be adjusted between 4 and 90 % for an average particle diameter of 360 µm and falling distances between 22 and 82 mm. For the aluminium alloy, the droplet diameter was changed to evaluate the influence of the quenchant. It was found that the effect on the SDAS is limited to a range of droplet diameters: small droplets are almost solidified when they are quenched while large droplets contain too much mass to allow a quenching without the Leidenfrost effect. The droplet diameter with the strongest quenching effect was found to be in the range of 820 µm for a falling distance of 0.22 m.

Figure 7. Micrographs of AlCu4.5 droplets of different diameter (falling distance: 0.22 m) and measured secondary dendrite arm spacing (SDAS)
6. References

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