Z1: Central project – Slag synthesis, design and characterization

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Overview

The SPP 2315 deals with the production, processing and characterization of engineered artificial minerals (EnAM) from a metallurgical slag with the aim of enriching dissipated chemical elements. Subproject Z1, or central project, will focus on slag generation and characterization Li-EnAM. This central project is a collaboration of IME RWTH Aachen for the slag generation and MVTAT TU Freiberg for the slag characterization.

There are two main parts of the central project. The first one is the central support for the other project in the SPP 2315, which will provide defined formulated and characterized slag samples for other projects, especially the concentration and size distribution of the EnAM-grains. The service will contribute to provide sufficient slag material to the other project in the SPP 2315. Central project will also provide service with the analysis methods to the slag generating projects of the PP. The second part is the research part for the EnAM development. This part will focus on two areas: (1) metallurgical-engineering investigations and quantification of the Li-EnAM system complementary to the service synthesis of the material and (2) the ongoing development of 3D geometallurgical characterization methods and their application to create a deep insight in the structure and the composition of the heterogeneous material structure of the Li-EnAM system.

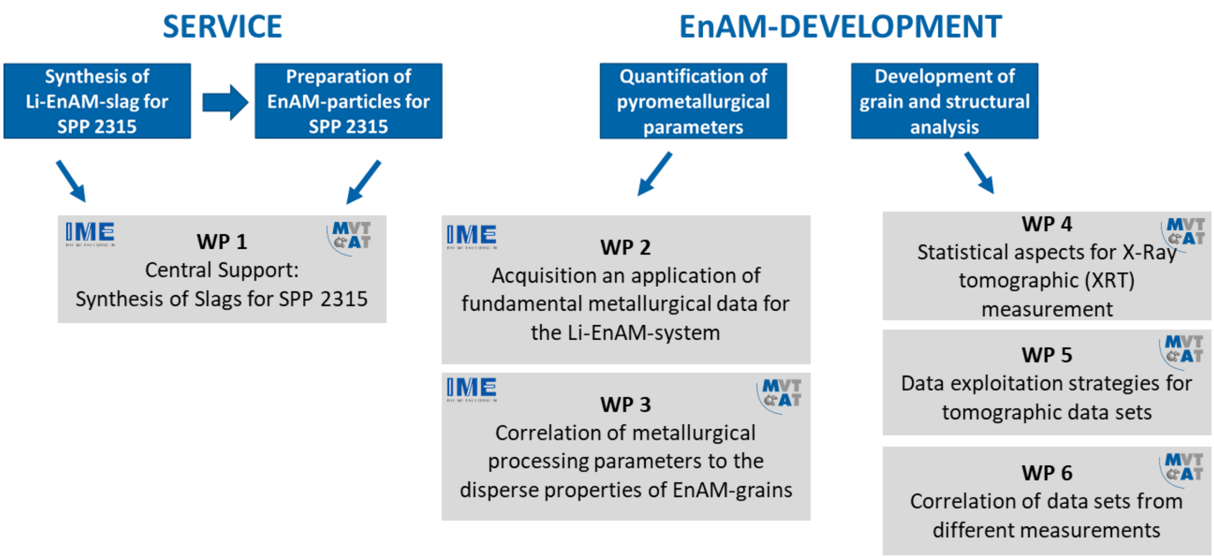

Figure 1 Schematic overview of the central project work package

Slag System and Design

The slag system to be provided is based on a previously metallurgically investigated Li-Co-system, which originally derives from the pyrometallurgical processing of LiCo-batteries. Co had mainly been transferred to the reduced metallic phase and within the slag the Li bearing mineral (Li-EnAM = $LiAlO_2$*nSiO_2) grows in an oxide (Al, Ca, Mg) matrix. The central project will use pure ingredients to be able to provide a synthetic (model) material with $LiAlO_2$-cystals multiple batches with defined EnAM-properties to subprojects in SPP 2315.

The goals of EnAM are to studying crystallization and segregation by controlling cooling conditions and working atmosphere; designing an accurate EnAM model close to the real LIB system; determining decomposition mechanisms of LIBs at high temperature; and optimizing physical properties by accurate modelling and fluxing strategy.

$LiAlO_2$ formed defined crystals and both the size and the occurrence of the crystals could be engineered, e.g. by variation on the temperature regime, temperature gradient during cooling. The composition of the melt is an influencing parameter on the crystallization as well. The presence of Mn (Ni-Co-Mn battery materials) significantly reduced the LiAlO formation whereas additional Al supported the growth and occurrence of the $LiAlO_2$ crystals. Si from SiO_2 is also able to interact with crystallization of $LiAlO_2$ eg $LiAlSiO_4$ eucryptite or $LiAlSi_2O_6$ spodumene. Therefore, studying of the influence of Mn and Li in the formation of Li_2AlO_2 and the influence of fluxes would be important (Figure 2).

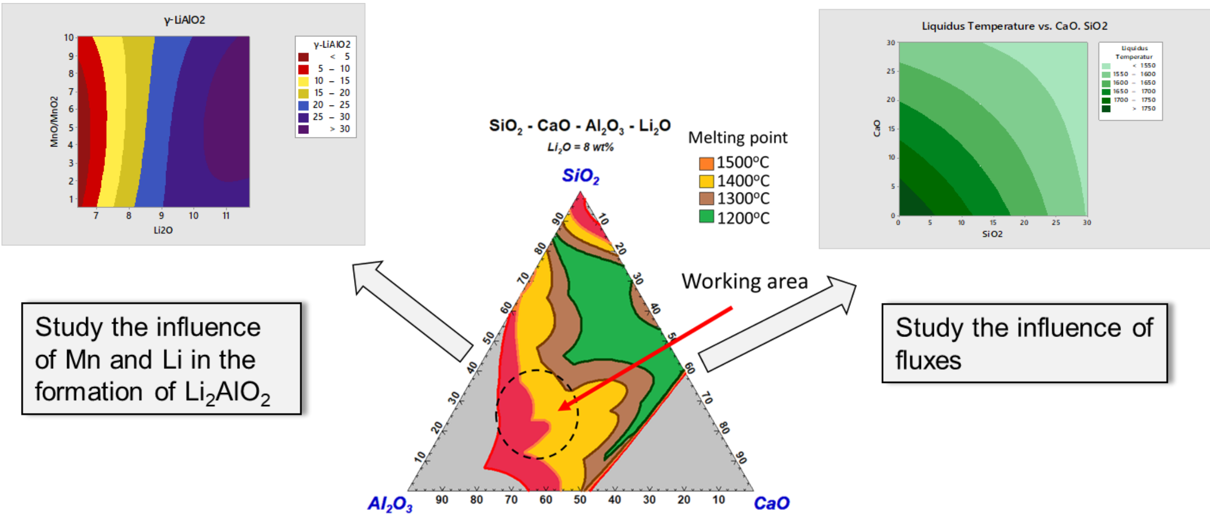

Figure 2 Modelling LIBs base EnAM

The fundamental engineering-metallurgical challenge aims understanding the influence of the process, cooling parameters and properties of the Li-EnAM like grain-size, grain-shape. The elemental complexity of each melt challenges concerning the prediction of the thermodynamic equilibrium. (Li-EnAM = $LiAlO_2$ * n SiO_2). Due to the heat transfer, the cooling rate is a function of the radial position of an individual volume element. In the center of the sample, the cooling rate is the lowest. These investigations will also allow satisfying the material requests of some projects, which are interested in samples with different grain sizes of EnAM.

In addition, information about the thermophysical properties of the studied slag systems will be generated such as viscocity, electroconductivity, density and superficial tension, which will be linked to a digital modelling of the thermodynamic properties using specialized software (Factsage) with extended generated data. Differential Scanning Calorimetry (DSC) and differential thermal analysis (DTA) measurements will support partner projects for modelling structural change and stability analysis.

Some focuses on this slag generation would be as follows: influence of chemistry and chosen fluxes in the EnAM properties; studying cooling and crystallization conditions for enhancing

$LiAlO_2$; acquisition of fundamental metallurgical data; and definition of the process parameters of up-scaling.

Slag Characterization

The characterizing part of the central project applies image based correlated methods on the slag structure and supports the metallurgical research on the LiAlO2*SiO2-system. It aims at the development of a holistic characterization method for the EnAM, to quantify the 3D-structure, elemental and mineralogical composition of the solidified slag using 3D X-ray tomography or computed tomography (CT). This will help to understand the distributed nature of volumetric crystallization und segregation effects, which is the key for process developments of the slag generating and processing projects.

The slag is characterized using CT to get 3D measurement of the Li-EnAM. This 3D measurement will be supported with 2D mineral and chemical analysis, such as XRD and MLA. The data sets of both measurement methods will be combined to get the more defined information for the EnAM.

Statistical aspects for CT measurement will help with sample selection and preparation; CT measurement condition, and virtual sampling, e.g. bootstrap resampling (Figure 3). Workflow will be made on this characterization process. A general overview scan of the slag block (depending on the slag block size) will be necessary before a smaller sample is taken from the whole slag. The sampling method will depend on the slag characteristic, whether it can be drilled to a small cylinder or cut to a cube shape sample. This smaller slag sample will be used to get more detailed scan with better resolution. Apart from this small sample scan, part of the slag block will also be crushed and milled into fine size fractions to see the EnAM grains characteristic. Particle sample scan will give homogenous structure distribution of the grains.

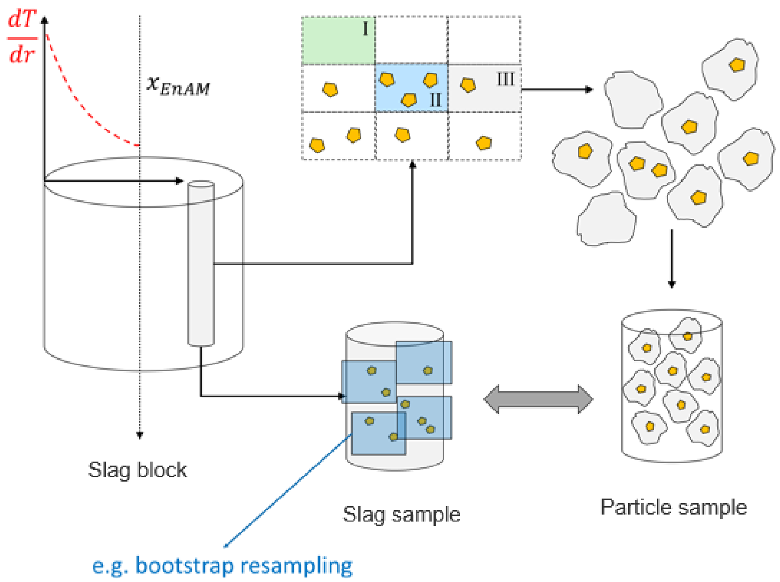

Figure 3 Sample selection and preparation for CT measurement

In case of wide grain size distributions, which do not fit into the specification of voxel size and field of view, correlative methods combining two different resolutions will be used. Images with larger voxel size will be used to identify and quantify the upper part of the PSD and a second measuring campaign delivers a representative section with smaller voxel size to detect the lower part of the PSD.

Challenge in the analysis is the identification of the individual species in the sample. The grey scale of the X-ray images only allows distinguishing between the present phases, but does not identify them. Phantom method can be used for material identification. The phantom has a defined material composition, having a characteristic X-ray attenuation and corresponding to the original sample. Both samples, the original sample and the phantom are measured consecutively with the CT. The grey scales from the phantom are used to identify the different materials. Correlative image analysis integrated with 2D-SEM-EDX will also be done to support the characterization.

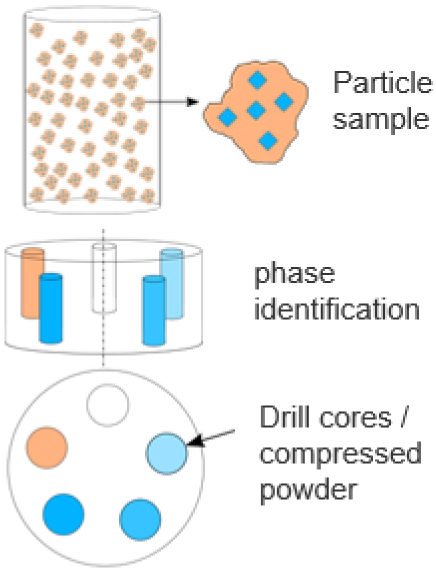

Figure 4 Phantom for material identification