A4: Exploration of the compositional phase space of metallurgical slag models for rational design of processes of refractory metal recovery through smelting and recrystallization

Contacts: Manuel Vollbrecht, m.vollbrecht@iwt.uni-bremen.de
Dr. Krishnanjan Pramanik, krishna1@hmi.uni-bremen.de
Dr. Wilke Dononelli, wido@uni-bremen.de
Prof. Dr.-Ing. habil. Lutz Mädler, lmaedler@iwt.uni-bremen.de
Prof. Dr.-Ing. Lucio Colombi Ciacchi, colombi@hmi.uni-bremen.de

Overview

The SPP 2315 aims to establish a novel recovery technology for critical raw elements through engineerable recrystallization of metallurgical slags. In particular, project A4 addresses the chemistry and subsequent pyrometallurgical treatments of **Cu and Sn model slags** in a combined experimental and simulative approach to enrich refractory metal elements in yet unknown Engineered Artificial Mineral (EnAM) phases.

The multicomponent, complex nature of slag systems offers great advantages with respect to a wide portfolio of crystal phases that can form after smelting and controlled cooling. These crystal phases can be recovered by selective separation from the slag matrix. However, the same complexity poses great challenges to a rational design of processes which guarantee (i) sufficient loading of the crystals with the essential elements that are worth being recovered and (ii) viability in terms of recovery rate (process speed) and turnover (process efficiency). In this project we will implement a rational methodology for the identification and characterization of Engineered Artificial Mineral (EnAM) phases rich in **refractory metal elements (especially Ta, Nb, Mo)** from metallurgical Sn and Cu slags.

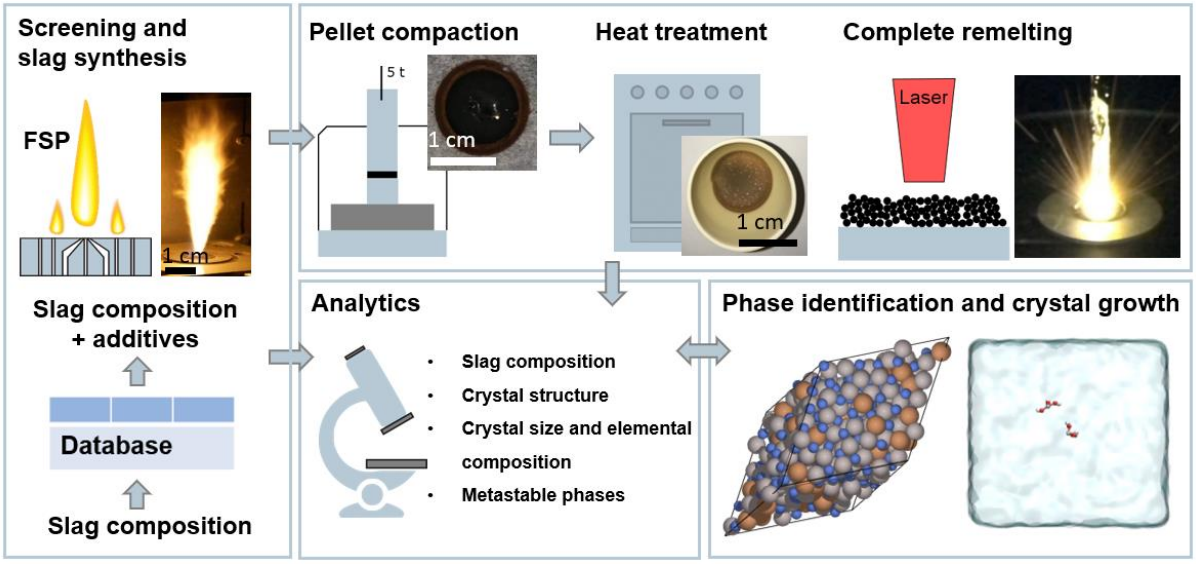

Figure 1: Methodological approach for an efficient recovery process design of refractory elements from Cu and Sn slags

The methodology of this work is based on the supervised exploration of the compositional phase space of the slags, in order to screen for, identify and synthesize EnAM phases after addition of additives to promote crystallization of desired phases and hinder the formation of unwanted ones. The leading hypothesis is that the rational and unbiased knowledge of the

slag compositional phase space and EnAM formation mechanisms will enable us to design processes for the elemental recovery through smelting and recrystallization with high recovery rates and efficiency. The work towards this hypothesis will be structured in three steps, namely: (1) the fast theoretical screening of a very large number of potential EnAM candidates for the recovery of a set of target elements via database searches and density functional theory (DFT) calculations, followed by the synthesis of selected candidates via flame-spray pyrolysis; (2) the design and mechanistic understanding of a laser-induced smelting and recrystallization process for model slags, including the addition of additives promoting the formation of large and separable EnAM crystals rich in target elements; (3) the precise identification of the EnAM phases at the atomic scale combining several material characterization methods with a theoretical global-optimization method for the unbiased determination of crystal structures.

This study is expected to provide **profound knowledge of the thermodynamics and kinetics of the formation of crystal phases** rich in refractory elements from multicomponent systems.

Slag systems

Within the scope of this project, mainly two different model slag systems are of particular interest from which refractory metals are to be recovered by controlled recrystallization. The first material system comprises the Fe-Si-Ca-Mg-Al-O system (Cu slags) from which Mo, Co and Cu are to be recovered. The Sn model slag is given by the Fe-Si-Ca-Ti-Al-O system which contains significant amounts of Ta and Nb to be recovered. Both slag systems will be enriched with additives which may trigger EnAM formation, namely S and P in the first step. Based on the database screening also other elements are considered as promising additives.

Methods

Experimental

Slag samples are synthesized by flame spray pyrolysis (FSP) to enable a versatile adjustment of the slag compositions. The nanopowder is compacted to pellets for better handling in subsequent investigations. Heat treatments are performed to grow crystal seeds in the as-prepared slags and to examine the phase evolution at or near the thermodynamic equilibrium with slow cooling rates. Additionally, the slags are smelted selectively using a laser and recrystallized under high, process-owned cooling rates. All three slag states (as-prepared, heat treated, smelted) are examined with a variety of analytical experiments. Identification of both stable and metastable phases including their crystal structure is performed with XRD. SEM, EDX and TEM measurements are carried out to analyze the slag composition, elemental distribution as well as crystal sizes. The application of a two-color pyrometer and a high-speed CCD camera during laser treatment aims at correlating the slag remelting and solidification conditions with the crystal nucleation and growth of wanted EnAM phases.

Simulative

The DFT calculations, with self-consistent Hubbard scheme taken into account for accurate description of transition metal oxides, are being carried out using the open source program Quantum Espresso (Giannozzi, 2017) (Ricca, 2019). For high-throughput calculations, it is also advantageous to use the AiiDA plug-in (Pizzi, 2016) for automatizing the work-flow, as well as for scanning provenance for existing calculation to reduce our computational workload. For precise determination of the newly identified EnAM phases, the Genetic Algorithm Based Global Optimization (Bisbo, 2020) scheme is to be used. The atomic-scale insight of the crystal growth process is to be investigated by molecular dynamics simulations within the scheme developed by Kawska and Zahn (Kawska, 2008).

Works Cited

Giannozzi, P. A. (2017). Advanced capabilities for materials modelling with Quantum ESPRESSO. *Journal of physics: Condensed matter*, 29(46), 465901.

Ricca, C. T. (2019). Self-consistent site-dependent DFT+ U study of stoichiometric and defective SrMnO 3. *Physical Review B*, 2(2), 094102.

Pizzi, G. C. (2016). AiiDA: automated interactive infrastructure and database for computational science. *Computational Materials*, 111, 218-230.

Bisbo, M. K. (2020). Efficient global structure optimization with a machine-learned surrogate model. *Physical review letters*, 124(8), 086102.

Kawska, A. D. (2008). Atomistic mechanisms of ZnO aggregation from ethanolic solution: ion association, proton transfer, and self-organization. *Nano Lett*, 8(8), 2336-2340.