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PROCEEDINGS

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ASSESSING THE CRYSTALLISATION AND SEGREGATION OF Ta-RICH MINERAL PHASES IN WEEE PYROMETALLURGICAL RECYCLING

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Introduction

Most Critical Raw Materials such as In, Ga, Se, rare earths, and Ta are typically found in pyrometallurgical recycling slags of Waste Electrical and Electronic Equipment (WEEE). However, they are not recovered due to the low concentration in this material stream, which makes its extraction processing economically unsuitable [1]. Different directives demand to reduce waste disposal while promoting finding solutions for extracting these critical raw materials more holistically within the circular economy of metals [2,3]. Such slags, mainly composed of fayalite (Fe_2SiO_4), are associated with magnetite since it is constrained under oxidising conditions by breaking into quartz and magnetite at the phase boundary. The magnetite content in fayalitic slag will depend on oxygen diffusion and solid mixture precipitation[4]. In principle, under proper handling in terms of cooling rates, oxygen partial pressure, and liquidus temperature, the engineered artificial slag can promote ideal crystallisation. In this study, the crystallisation and formation of Fe inversed spinel structure has been investigated to determine if Ta could be sequestered into amorphous phases, forming a solid Ta solution. In addition, this study aims to engineer the slag mineralogy and crystallisation strategy to promote and enhance Ta-rich mineral phases that may potentially be separated later through mechanical processing techniques.

Materials and methods

An industrial copper and an artificial fayalitic slag were used as the medium to process Ta-containing scraps at large and laboratory scale, respectively. In the large-scale trial, approximately 300 kg of fayalite slag generated from Cu recycling were charged in a Top Blown Rotating Converter (TBRC) and melted at 1475°C for 4 h. Subsequently, 18 kg of

HDDs, which contain Ta capacitors, were added to the melt and homogenised during 2 h at the same temperature. Finally, the slag was cast in a mould, where phases were crystallised at room temperature. The cooling temperature over time was measured through a thermocouple and recorded in a data logger. Three samples were analysed in a Malvern-Panalytical Axio X-ray fluorescence (XRF) at different stages throughout the experiment. In addition, a lab-scale trial was conducted to understand the crystallisation behaviour and the Ta distribution among the solidified phases. Here, a synthetic slag sample was produced in alumina crucible in an electric resistance heating furnace with the chemical composition of 55 wt% FeO, 25 wt% SiO_2, 15 wt% CaO, and 5 wt% Al_2O_3. For this trial, 4.2 g of commercial Ta capacitors were used. The maximum temperature was 1300°C. Afterwards, the sample was cooled down to 20 h. Throughout the heating operation, the furnace was under an inert atmosphere, and for the cooling operation, the gas addition ceased to facilitate the oxidation and diffusion mechanisms. FactSage 8.2 ® was utilised to simulate the potential precipitating phases. The produced lab-scale samples were analysed using micro X-ray fluorescence (µXRF), X-ray computed tomography (CT). At first, the complete scan of the whole sample was performed by CT scan and then the sample was broken into smaller pieces to obtain the targeted regions for a higher resolution scan with CoreTOM Tescan XRE instrument at the X-ray voltage of 180 kV, 1 mm copper filter and the remaining parameters were adjusted to the resolution.

Results and discussion

The large-scale samples cooled down under air atmosphere, showed an average cooling rate of 145°C/h. Through the sample, it was possible to observe a few small regions of crystallised phases among several amorphous areas, mainly related to the inhomogeneous crystallisation in the pyrometallurgical treatment of industrial fayalitic slag. Regarding Ta, thermodynamics indicates that Ta_2O_5 (with a density of 8.2 g/cm^3) is one of the oxides that should form. If this is true in a system, which also contains Cu in molten state (density 8.02 g/cm^3), Ta should gradually finish below the metal phase and thus, part of this element should finish in the lining or in the bottom of the ladle used for the casting. Table 1 shows the results of XRF analysis in which Ta concentration decreases throughout the experiment.

Table 1: Chemical composition of the samples in wt%

Description	Al_2O_3	CaO	SiO_2	FeO	Cu	Ta
TBRC-charging & smelting	5.1%	3.9%	23.3%	47.3%	15.4%	349 ppm
TBRC- 2 h treatment	7.7%	4.6%	24.8%	52.2%	5.7%	122 ppm
TBRC-casting	8.3%	4.6%	27.5%	48.8%	5.9%	43 ppm
Lab-scale artificial fayalite (Crucible diameter 5 cm)	6.1%	6.2%	27.3%	55.4%	0.1%	7300 ppm

The performed simulations indicate spinel and olivine as the first potential precipitating phases at the equilibrium between 1150-1050°C with an oxygen partial pressure of 10^{-11} bar (Figure 1). At these conditions, spinel crystals should form and represent around 50 wt% of the formed crystals. Nevertheless, their sizes are mainly dependent on the oxygen absorption within the system. In relation to the lab-scale sample, Ta appears concentrated in Si-Al-Ca microstructures, possibly amorphous, formed between the dendritic Fe-rich phases around the larger spinel crystals as shown in Figure 2. In this context, CT measurements reveal large rounded spinel crystals in the sample (Figure 2), which tend to precipitate during cooling. Other minor elements such as Cr, Mn, and Ti, present in added capacitors [5], also appear associated with this mineral phase.

Moreover, in Figure 2, globular Fe structures contain a higher amount of Cr than the dendritic ones associated with the phases with higher Ta content. Furthermore, Ni and Ag appear as small metallic droplets. Cu also appears associated with the same phases as Ta, although the Ta/Cu ratio seems to increase towards the bottom. These preliminary results indicate that at least part of Ta remains dissolved in the last liquid phases, which can be found in the amorphous phases.

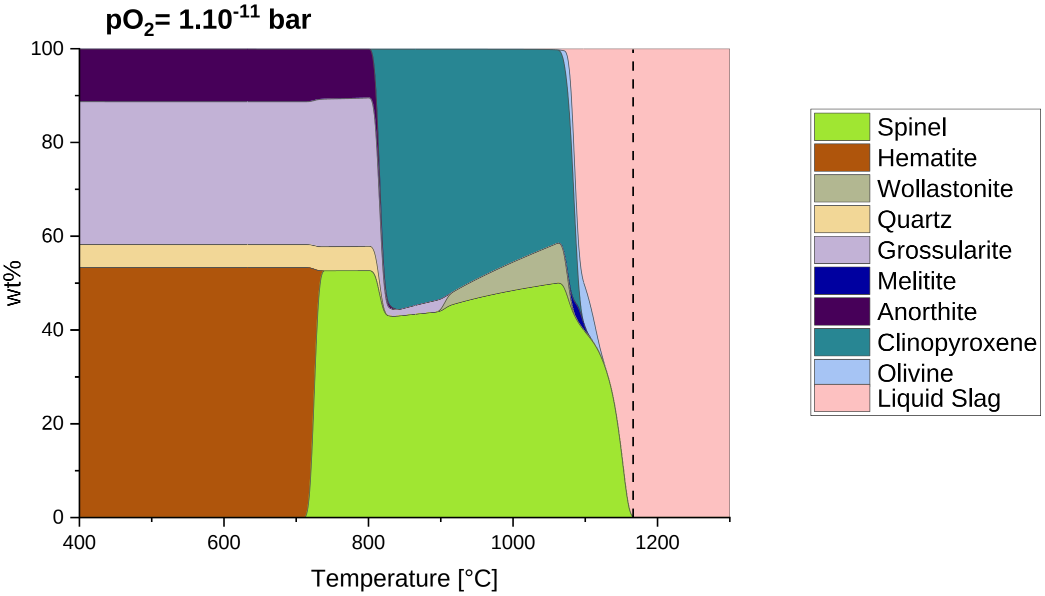

Figure 1: Phase formation as a function of temperature using a fixed oxygen partial pressure of $1x10^{-11}$ bar

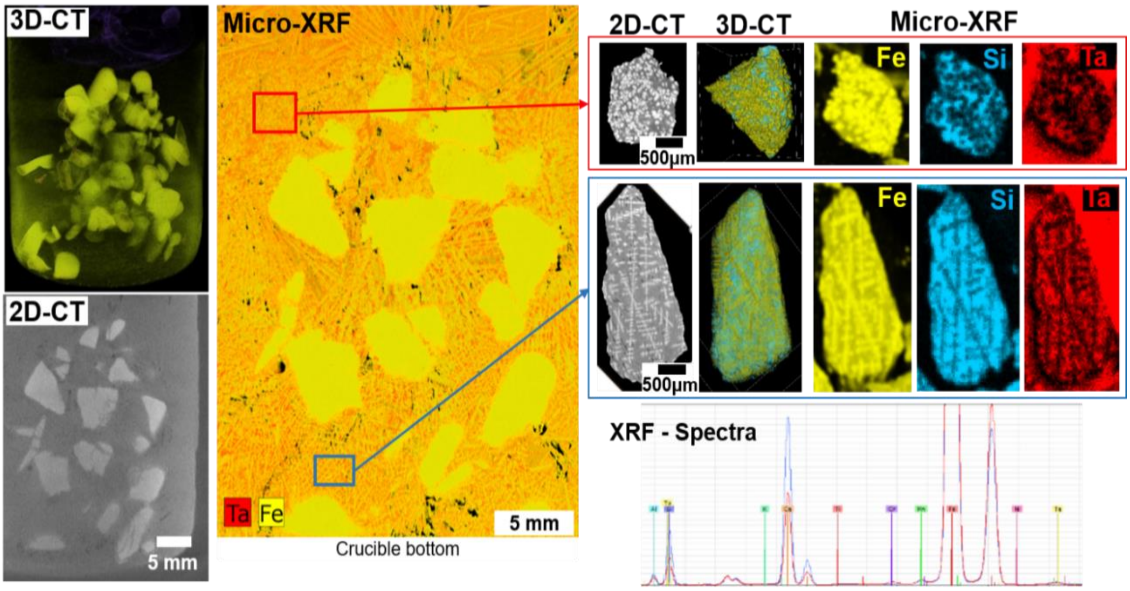

Figure 2: CT image of the entire sample (spinel crystals in yellow) and the µ-XRF of a vertical cross-section (only Fe-yellow and Ta-red are shown) both with 100 µm resolution. The slag particles were also analysed with correlative CT/µ-XRF after crushing to achieve higher resolution. Two examples of microstructures are shown with 20 µm resolution to illustrate that higher concentration of Ta (red) overlaps with the Si-rich (blue) microstructures and not with the Fe-rich (yellow)

Conclusions

Preliminary results show that Ta, a critical element present in capacitors, is not dissolved in spinel phases. Instead, due to its high density, part of Ta precipitates out of the slag phase. In contrast, the rest is dissolved in amorphous or other Si-Al-Ca-containing phases. Therefore, a controlled cooling rate strategy, such as lower cooling rates, should promote targeted crystallisation and control Ta mobility into specific mineral (artificial) phases, which can be later processed by mechanical processing techniques and recovered as a concentrate. Furthermore, future work should involve slag design by fluxing strategy since Ta was also found dissolved in Si-Al-Ca-phases.

Acknowledgements

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