

INFLUENCE OF PARAMETERS ON THE CRYSTALLISATION BEHAVIOUR OF OXIDIC SLAG SYSTEMS DETERMINED BY CLSM INVESTIGATIONS

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Introduction

The energy transition is one of the major tasks for mankind in modern days, as the transition from fossil fuels to renewable energies needs tremendous effort. Therefore, the demand for bridging technologies is high and the usage of gasification technology, with its various sorts of fuel and its load flexible operation, has the potential to fill this gap.¹

During entrained flow gasification, slag is produced constantly under reducing conditions. The slag adheres on the refractory walls, flows down and prevents slag blocking.² However, changes of the slags state, such as crystallisation, influence its viscosity and fluid behaviour.¹ Furthermore, gasifier slags are used in the construction industry as a concrete additive to enhance mechanical strength. Accordingly, a fully glassy slag with an isotropic structure is preferably used, while crystallisation hinders its usage due to its anisotropic structural character.

This contribution examines the impact of process parameters such as sample homogeneity, atmosphere and interactions of the crucible material on the crystallisation behaviour of artificial oxidic slags. Investigations were conducted with a confocal laser scanning microscope (CLSM). The experiments proved that the usage of sample powder entails a heterogeneous crystallisation even at high temperatures of above 1500°C. The crystallised phases remained during the cooling process, hence results are not representative. The partial pressure of oxygen also affects the crystallisation tendency. Higher oxygen partial pressures lead to higher melting points and to faster crystallisation kinetics. Commonly as crucible material for experimental investigations used Pt interacts with Fe-containing slags under reducing conditions. An alloy is formed that causes the crucible to disintegrate subsequently. The usage of Mo instead is more reasonable due to its high melting point and only minor interactions with oxidic slags.

Artificial slag samples and previous investigations

Based on previous coal ash analysis,⁴ three different coal ash systems were chosen to be analysed (Table 1). The number of compounds was reduced to four and five, respectively. Alkali elements were excluded to ensure sample stability during the experiments and to prevent compound volatility.

First, equilibrium calculations of the slag systems were performed using FactSage. Calculations revealed several phases that should crystallise in the slag. In ST-D-2 and HKT slag, the dominant crystalline phases are Anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and Cristobalite (SiO_2). In HKR slag, crystallisation is more diverse. The main crystalline phases are: Olivine ($(\text{Fe,Mg})_2\text{SiO}_4$), Spinel (MgAl_2O_4) and Melilite ($\text{Ca}_2(\text{Al,Mg})(\text{Si,Al})_2\text{O}_7$).

The crystallisation characteristics were investigated by a quenching experiment further on. By choosing several isothermal steps, slag samples were quenched time dependently to examine crystal evolution and to gather kinetic information. Afterwards, the samples were analysed by SEM and XRD. The identified phases showed good agreement with the previous results from equilibrium calculations. Though, the crystallisation temperature and the crystal content varied. Equilibrium calculations predicted first crystallisation at approx. 1300°C, which is consistent with the quenching results. However, HKR slag showed crystallisation at approx. 1250°C, though FactSage predicted initial crystallisation at 1400°C. To increase the temporal resolution, the artificial slags were also observed *via* CLSM.

Table 1: Composition of the analysed artificial slag systems in wt%

	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO
ST-D-2	60%	20%	11%	9%	-
HKR	33%	10%	30%	15%	12%
HKT	55%	21%	15%	3%	6%

CLSM

CLSM provides an in-situ view on the slag and therefore documents the crystallisation processes in detail. A small amount of sample (approx. 10 mm³) is placed on a sample holder in the upper area of an Au-coated, oval furnace. The furnace is heated by a halogen lamp and hence, provides high heating and cooling rates (up to 300 K/min). The furnace is flushed with Ar-gas, whose O₂-impurities were partially removed by the usage of a Mg-containing furnace.⁵ The sample is observed *via* a laser microscope through a sapphire glass window from the top. The laser microscope is connected with a computer in order to control the furnace parameters and capture the images. The results shown in this study refer to the HKR slag, which was chosen due to its

lower viscosity and thus higher atom mobility. Hence, crystallisation processes are expected to be clear observable.

State of sample – Necessity of Annealing

CLSM in-situ observations were performed by using artificial HKR slag in form of oxidic powder and pre-annealed particles. Investigations were conducted in Pt-crucibles. As can be seen in Figure 1a, the slag powder melts heterogeneously during heating. In consideration of the individual melting points of oxidic compounds, this behaviour is reasonable. In the following, at peak temperatures of 1500°C (corrected according to temperature calibration), the liquid slag droplets showed some inner structures, which should not be present in a pure liquid (Figure 1b). The CLSM image indicates the presence of some particles with a maximum diameter of approximately 20 nm. By comparing that image with c), the same particles can still be identified. However, their polygonal morphologies are visible more clearly. Image c) was captured during cooling at 1160°C, indicating that the particles have grown in between. The SEM image d) shows the morphology in more detail. BSE analysis identified these crystals as Mg-Fe-Al spinels.

The aforementioned results conflict with previous results from quenching experiments. Heterogeneous melting of slag powder may also occur during the pre-annealing of the quenching samples. Though, these spinels were never found individually, or with a comparable chemistry in the quenching sample. The main difference from the pre-annealing to the CLSM experiment is its long holding time at maximum temperature of at least five hours. That is long enough to re-melt possible crystallised phases again. After these observations, some pre-annealed slag particles were used in the CLSM instead of the powder. In the end, such crystal forming during the heating procedure was never observed again. After these results were revealed, Pt crucibles were rejected and replaced by Molybdenum crucibles.



Figure 1: Synthetic HKR slag powder on Pt crucible; a) Heterogeneous melting at 1260°C; b) crystals at $T_{\max} = 1500^{\circ}\text{C}$; c) crystals at 1160°C; d) SEM image of crystalline phase

Crystallisation behaviour – reducing atmosphere

CLSM investigations also exposed an impact on the crystallisation characteristics by the partial pressure of oxygen applied to the sample. Firstly, an Ar-atmosphere was set for the experiments. By taking gas impurities into account, an O₂ partial pressure of about 10⁻⁷ atm was applied and the furnace chamber was sealed afterwards. Molybdenum, the crucible material, reduced the atmosphere further to 10⁻¹⁴ atm as measured by an O₂-sensor. Alternatively, an Mg-furnace was added to the Ar-atmosphere that reduced the Ar-gas constantly to an O₂ partial pressure range of 10⁻²⁰ atm to 10⁻²⁶ atm. Due to the intensive oxidation behaviour of Mo crucibles, strong reducing conditions were the most achievable for the experimental studies.

The distinctions in the crystallisation tendency of the two different reducing regimes are major. As displayed in Figure 2a), HKR slag shows several small (< 50 mm), polygonal crystals at temperatures of 1380°C, while more reducing conditions did not lead to a crystallisation at that point. Figure 2b) (~ 1160°C) indicates that crystal contents increased in the less reduced sample, while crystallisation was observed firstly in the highly reduced sample. In the highly reduced sample, a huge (diameter > 150 mm) pyramidal crystal grew quickly. In contrast, crystallisation proceeded slowly in the less reduced one. At lower temperatures of approx. 990°C the slag is fully crystallised and the crystallisation characteristics are quite dissimilar (Figure 2c)). The highly reduced sample experienced a low temperature but high-speed crystallisation. As it was possible to quench fully amorphous slag samples in the quenching experiment at 1250°C, CLSM and quenching results show great accordance. Therefore, it is likely that high oxygen partial pressure leads to an overestimation of initial crystallisation.

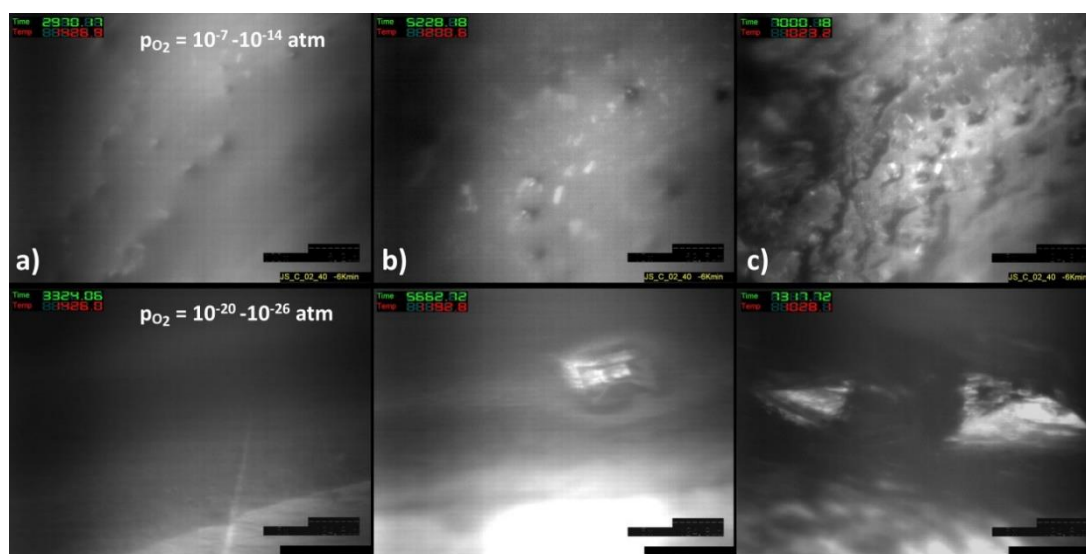


Figure 2: Comparison of two experimental runs containing pre-annealed HKR slag in Mo crucibles; Figure a) = 1380°C, b) = 1160/1153°C, c) = 988/993°C

Chemical side effects – The influence of crucible material

The crucible material is a significant factor when it comes to experimental studies. Common crucible materials are: platinum, corundum and molybdenum. Corundum (Al_2O_3) is an inappropriate material for oxidic slag systems as it can be dissolved in the slag itself. In contrast, platinum is commonly used for these systems due to its general chemical inertness and its high melting point. Molybdenum instead, is hard to process and tends to oxidise, though its high melting point is an advantage as well. So, first CLSM experimental runs were performed in Pt-crucibles. By flushing the furnace with Ar-atmosphere no abnormalities were observed in the experiments, except the aforementioned unexpected crystallisation. However, as the atmosphere was reduced by using the Mg-furnace subsequently, HKR slag behaved differently. As slag droplets flowed over the Pt-crucible during heating and at peak temperature, its colour varied afterwards. In addition, the laser beam was reflected poorly on these areas as well, which indicates that Pt experienced an alteration. Furthermore, slag droplets suddenly disappeared from the Pt-crucible. Figure 3 displays frayed holes in the crucibles bottom.

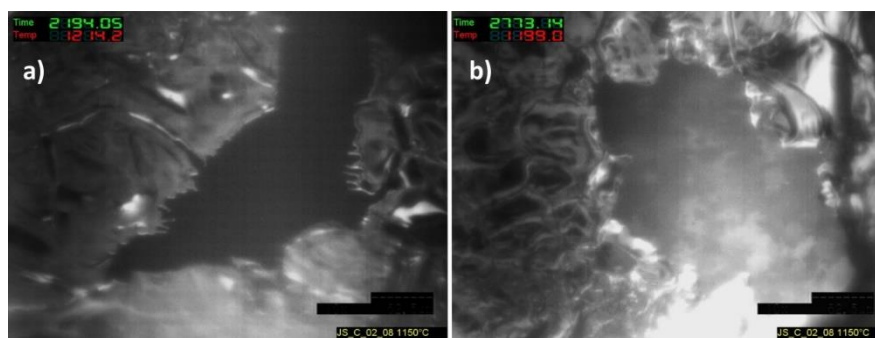


Figure 3: Damaged Pt-crucible due to Pt-Fe-alloy forming, observed in the CLSM

These frayed structures indicate an involvement of chemical processes and exclude the probability of a material failure due to bending and folding. In Figure 3 b) the underlying Al_2O_3 powder is visible through the crucible hole. After finishing this experimental run, the crucible was attached on the sample holder and slag was bound in the underlying Al_2O_3 powder layer displayed above. This phenomenon can be explained by the reduction of Fe_2O_3 to elemental Fe that subsequently formed a Pt-Fe-alloy with the crucible. The alloys melting point is lower than the peak temperature of 1500°C , so the alloy liquefied. Henceforth, Mo-crucibles were used to prevent this phenomenon. Though, the partial pressure was as low as in the abovementioned example with Pt, the forming of reduced Fe was almost never observed. Due to its catalytic properties, Pt enhanced the reduction of Fe_2O_3 in the slag and formed the alloy already after a few minutes of exposure. In contrast, Mo has no or less catalytic influence, so that Fe was not fully reduced (or at least only partially reduced, after several hours of exposure).

Conclusion

An experimental study on the crystallisation characteristics of oxidic slag systems was conducted by using thermochemical calculations, quenching experiments and especially the CLSM set-up³. The slag was heated beyond its melting point and subsequently cooled below the liquidus temperature. Crystallisation characteristics were permanently observed *via* CLSM and the influence of several parameters on the crystallisation processes were examined:

1. State of sample: Oxide powder led to heterogeneous melting, resulting in temporarily varied slag chemistry. Accordingly, crystalline phases precipitate in the partial liquid slag. Crystal precipitation prevents the forming of a homogeneous, liquid bulk slag.
2. Impact of oxygen partial pressure: Due to the grade of reducing atmosphere, different crystallisation behaviours were observed. Higher O₂ partial pressures lead to high-temperature-shifted crystallisation with low growth velocities, while intense reducing conditions allow higher grades of supercooling and, therefore, high crystallisation kinetics.
3. Influence of crucible material: It was documented that Pt crucibles in combination with Fe-containing slags form a Pt-Fe-alloy under reducing conditions. This alloy has a low melting point and is responsible for crucible failure.

Acknowledgements

This work was supported by the Federal Ministry for Economic Affairs and Energy on the basis of a decision by the German Bundestag within the project “HotVeGas” (FKZ 0327773K).

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