

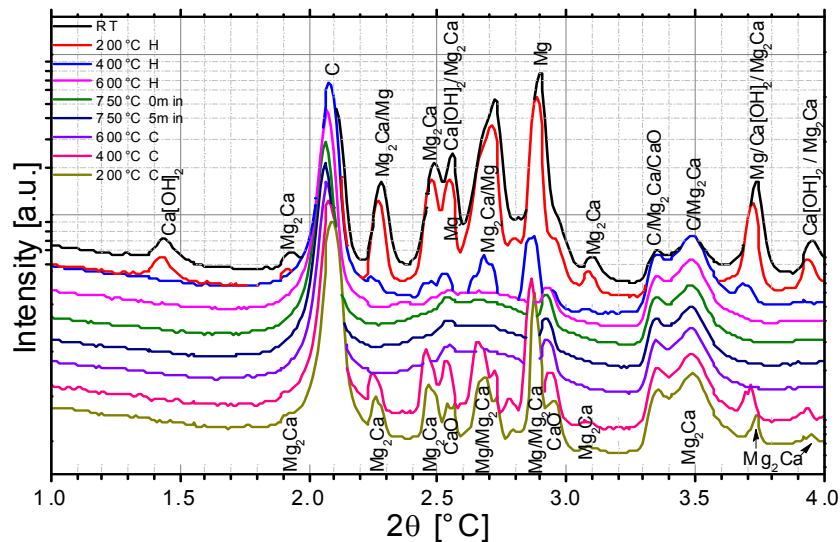
# ***In situ* diffraction of the melting and the solidification of magnesium alloys containing CaO**

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The interaction between Mg and CaO is critical for evolution of the microstructure and the resulting mechanical- and corrosion properties of the newly developed ECO magnesium (Environment CONscious magnesium) alloys [1]. The previous investigations considered the effect of CaO additions on the microstructure and mechanical properties of commercial Mg alloys. Investigation of CaO in pure Mg [2] and Mg alloys [1,4-6] show that CaO dissolves in the molten and solid Mg and no evidence of CaO was observed after casting. In the case of as-cast alloys containing CaO in pure Mg [2] and Mg alloys [3] it was found that Ca disperses and there is no evidence of CaO. According to the Ellingham diagram, CaO should be more stable than MgO [4]. Kondol et al. [3] calculated the standard Gibbs free energy for the reaction in Eq. 1 for the case of pure Mg with CaO. This system showed a decrease of the standard Gibbs free energy for the disassociation of CaO and the formation of Mg<sub>2</sub>Ca laves phase [3].

In order to understand the thermodynamics associated with the reaction it is necessary to understand the reactions between Mg and CaO in the solid and liquid state as well. Therefore, it is important to determine which phases are present during solidification and to follow the dissolution of CaO in pure Mg. In collaboration with the Metallurgy Institute of the Technical University Clausthal the ternary Mg-Ca-O phase diagram was calculated in order to understand the dissolution of CaO and the formation of Mg<sub>2</sub>Ca. The understanding of the reaction kinetics and phase transformations associated with the investigation proposed will allow a better gas protection of the Mg-Ca-O and Mg-Al-Ca-O systems. This investigation coupled with other casting experiments are used to optimize the use of CaO. In the present stated the thermodynamic calculations are not agree with the experimental data. For example the Figure 1 show the melting and the solidification of the Mg16Ca+6 wt% CaO sample this experiment showing that the MgO are forming already in the presence of liquid metal and the thermodynamic calculations predict the reaction CaO to MgO formation in a solid state reaction at 105°C. This primary calculation for equilibrium solidification of the Mg-Ca-O system needs further investigations.

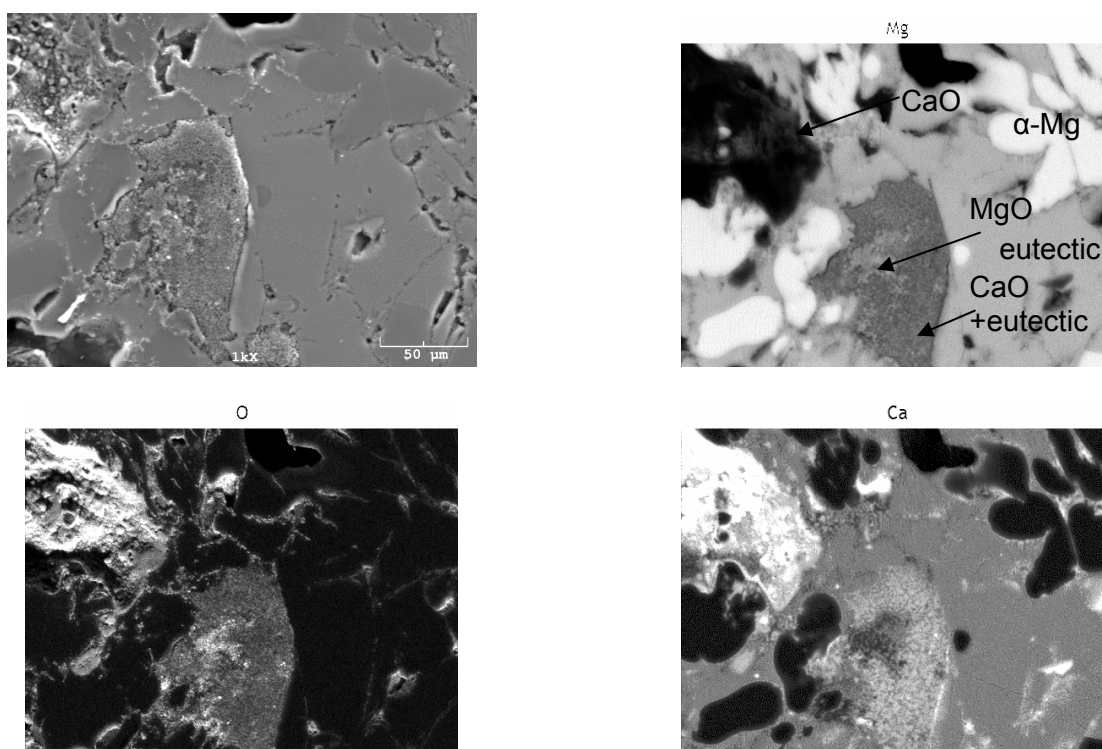


**Figure 2:** Diffraction patterns of the melting and the solidification of the Mg16Ca+6 wt.% CaO sample some diffraction.

The initial samples contain Mg or Mg-Al alloy chips with different CaO powder concentrations, pressed to pellets with sample compositions. The experiment was conducted using the induction coil of a furnace build for *in situ* synchrotron measurements. The samples were heated up to 750°C

at a heating rate of  $10 \text{ Kmin}^{-1}$ . The samples were held at  $750^\circ\text{C}$  for 5 min, and cooled at a rate of  $10 \text{ Kmin}^{-1}$  to  $200^\circ\text{C}$ . The time-temperature program was controlled by a type S thermocouple welded on a steel cub of the graphite crucible applied to contain the molten sample. The measurement was performed at the P07 (HEMS) beamline of PETRA III, with a beam energy of 100 keV corresponding to a wavelength of  $\lambda = 0.0124 \text{ nm}$ . The two dimensional (2D) diffraction patterns were recorded at every 10 s with an acquisition time of 0.5 s using a PerkinElmer XRD 1622 Flatpanel with a sample-to-detector-distance of 1162.7 mm. Conventional X-ray line profiles were obtained by the azimuthal integration of the 2D diffraction patterns.

The patterns show the dissolution of the CaO in Mg and the formation of  $\text{Mg}_2\text{Ca}$  phase, Figure 1. In the pre molten state peaks from  $\text{Mg}_2\text{Ca}$ , CaO and Mg was observed. In the molten state, the intensity of the CaO peaks decreases. The SEM investigation of the solidification of Mg16Ca-6 wt.% CaO sample showed the formation of the  $\text{Mg}_2\text{Ca}$  laves phase (eutectic), MgO and CaO in the Mg matrix, shown in Figure 2. This formation of  $\text{Mg}_2\text{Ca}$  occurs at the eutectic composition ( $\sim 16.3 \text{ wt.}\%$ ) and MgO in the solidification process. In the experiment the intensity of the CaO peaks decrease and the MgO appear.



**Figure 2:** Mg16Ca+6 wt% CaO alloy showing SEM EDX-mapping of Mg, O and Ca.

The investigation shows that the CaO dissolves in the molten Mg and Mg alloys and the Laves phase forms in the solidification process.

## References

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