

The Character of Crystalline Inclusions in Granulated Blast Furnace Slag

Motivation

- Granulated blast furnace slag (gbs) is increasingly being used as a mineral addition in cement
- Some of the gbs properties controlling its reactivity are still not well understood - in particular crystalline inclusions in gbs and their surrounding glass matrix
- Goal of the study is to characterize these crystalline devitrification products and the surrounding glass matrix

Methods

- Starting materials were gbs from two different blast furnaces
- Gbs samples were embedded in epoxy resin and polished cross sections were prepared
- The polished sample cross sections were subjected to Scanning Electron Microscopy (SEM) analysis where gbs grains with a high number of crystallites were selected
- Regions of interests were further prepared by producing TEM lamella with the Focussed Ion Beam (FIB) technique (Fig. 1)
- The lamella were analyzed by analytical Transmission Electron Microscopy (TEM) and by SEM-EDX with the focus on elemental composition, micro structure and phase identification by electron diffraction

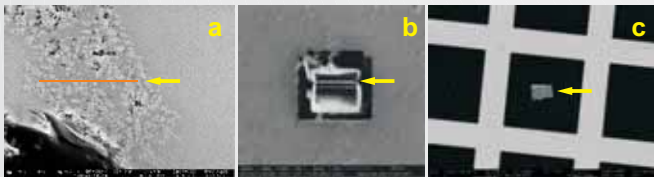


Fig. 1: Steps for the preparation of a TEM lamella by means of FIB: a. A region for a FIB section has to be defined on the sample surface (arrow); b. The lamella is milled out perpendicular to the polished surface by a Gallium ion beam (arrow indicates the lamella); after milling by FIB the lamella is lifted out from the sample by a micro manipulator and placed on a TEM grid (arrow indicates the lamella, SEM BSI).

Results

- The gbs samples from two different blast furnaces are variable in the amount of crystalline phases
- Within one sample gbs grains with a high number of gas bubbles exhibit a high amount of crystallites compared to grains with a lesser number of bubbles (Fig. 2a)
- The appearance of the crystallites within gbs grains is predominantly skeletal (Fig. 2b) but they can also be compact
- Crystallites can rather be found at grain boundaries or nearby gas bubbles than in the center of a grain (Fig. 2b)
- The majority of the investigated crystallites consisted of

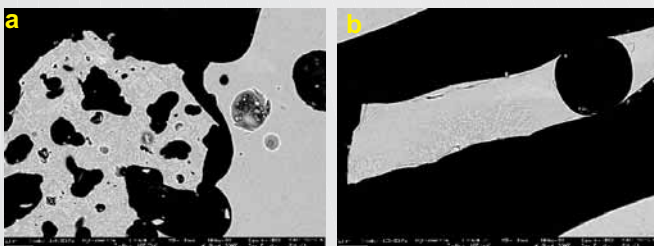


Fig. 2: SEM backscatter images of gbs grains. a. Grain with a high number of crystals and gas bubbles (left) next to a grain with no crystals (right). b. Skeletal crystals at the grain boundary.

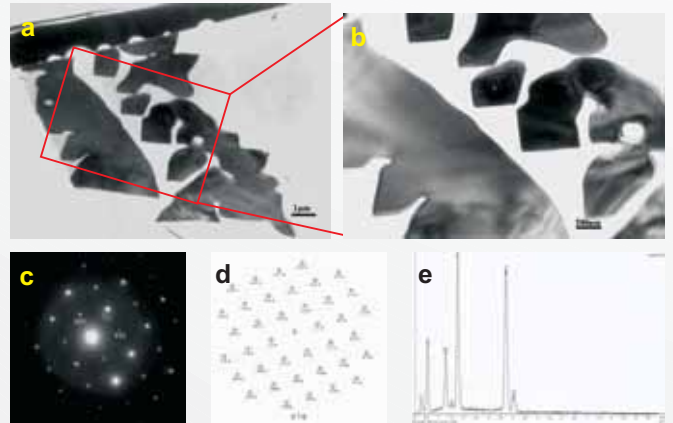


Fig. 3: a., b. TEM images of crystallites in gbs. c., d. Electron diffraction pattern with the simulated pattern of merwinite. e. Typical EDS spectra of merwinite.

merwinite $\text{Ca}_3\text{Mg}(\text{SiO}_4)_2$, which was confirmed by the results of electron diffraction and micro chemical analysis (Fig. 3)

- Micro chemical analysis on the TEM lamella indicates that merwinite crystals deviate significantly from the ideal merwinite composition: crystallites in gbs show a significant lower Mg/Ca atom ratio compared to the ideal formula (Fig. 4a)
- The glass between the crystallites exhibits a significant different chemical composition than the bulk glass (Fig. 4a, b); glass between crystallites shows considerably lower Mg/Ca atom

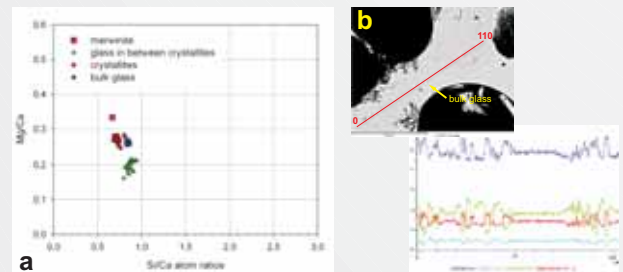


Fig. 4: a. Atom ratios of Si/Ca vs. Mg/Ca. from EDS data. Compared to the bulk glass, the glass in between crystallites is depleted in Mg. The Mg/Ca ratios of the crystallites exhibit a significant lower value as given by the ideal merwinite formula. b. SEM-EDX line scan over an area with crystallites and bulk glass. The glass between the crystallites shows lower Ca and Mg and higher Al intensities.

ratios and slightly higher Al/Ca atom ratios than the bulk glass

- The results from EDS and TEM analysis with high spatial resolution indicate the existence of inhomogeneities in the crystallites

Summary and Outlook

- SEM and FIB/TEM techniques are suitable tools for the analysis and characterization of the crystalline phases in gbs with a high spatial resolution
- The main crystalline phase of the analyzed gbs consisted of merwinite
- The merwinite in the gbs showed a significant lower Mg/Ca atom ratio, i.e. a higher Ca content, as suggested by the merwinite formula
- The glass in between the crystallites is depleted in Ca, Mg and