Crystalization in High Iron Containing Silicate Glasses – Electron Microscopy Investigation

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Introduction

Many glass ceramic materials show very interesting characteristics in comparison with traditional glasses and ceramics. These materials with their good forming ability and appropriate high performance of crystalline materials combining the properties of micro(nano) crystals with those of the glassy matrix are widely used in different technical applications. Glass ceramics from the systems Na_2O-CaO-Fe_2O_3-SiO_2 and Na_2O-Al_2O_3-B_2O_3-Fe_2O_3-SiO_2 with up to 30 mol-% of ironoxid were investigated because of their special electric (specific conductivity: 10^{-6}-10^{-3} S/m) and magnetic properties.

Preparation of the glass

Two different glass systems have been investigated:

16 Na_2O -10 CaO - x Fe_2O_3 - (74-x) SiO_2 ; $5 \leq x \leq 30$

(24-y) Na_2O - y Al_2O_3 - 14 B_2O_3 - 25 Fe_2O_3- 37 SiO_2 ; y = 8, 10, 14, 16

The glasses were melted from a mixture of reagent grade raw materials Na_2CO_3, $CaCO_3$, SiO_2, H_3BO_3, Fe_2O_3 and $Al(OH)_3$ in a Pt crucible at 1400 °C for 2.5 to 5 h. Different cooling procedures were used (pouring on Cu block, press quenching, casting in a graphite mould). Some of the as prepared glasses were further heat treated (annealing at 480 °C for 10 - 20 min). The glass investigated by electron backscatter diffraction (EBSD) was additionally tempered at 580 °C for 1 h.

Methods

In a first step, all samples were characterized by differential thermal analysis (DTA), dilatometry, and X-ray diffraction (XRD).

Scanning (SEM) and transmission electron microscopy (TEM) were used for imaging. SEM combined with energydispersive X-ray microanalysis (EDX) and electron backscatter diffraction (EBSD) were used for phase identification.

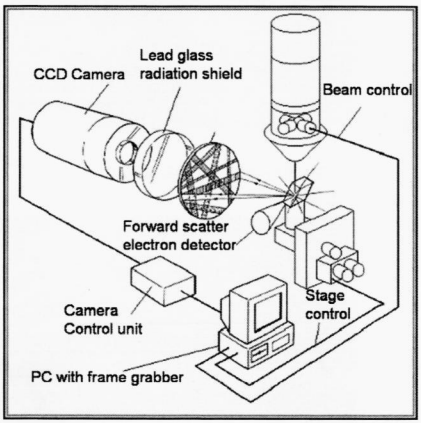

Fig. 1:
Schematic of an EBSD system in a scanning electron microscope

To remove the surface deformation layers resulting from mechanical polishing and to get a strain-free surface, the specimens for the EBSD-measurements were additionally polished with colloidal silica. For TEM imaging, replica were prepared by coating with a C-Pt-Ir mixed layer and dissolving the sample; thin samples by grinding, dimpling, and ion milling with Ar^+ ions (3 kV, 1.5 mA, incidence angle ≈ 6°).

Results

In all glasses containing Al_2O_3 and B_2O_3, phase separation was observed (fig. 2). After heat treatment, crystallization started in the spherical phase (fig 3). In some samples, such as the glass 16 Na_2O - 10 CaO - 20 Fe_2O_3 - 54 SiO_2, Pt particles dissolved from the crucible act as nuclei for the iron oxide crystallization (fig 4).

In the SEM micrograph of the glass 16 Na_2O - 10 CaO - 25 Fe_2O_3 - 49 SiO_2, which was heat treated in 2 steps, different crystals (fig. 5) were found. Only haematite (Fe_2O_3) and magnetite (Fe_3O_4) could be identified in the XRD pattern (fig. 6). The needle like crystals (fig. 7) were then selected for further investigations by EBSD. EBSD enables the elucidation of the relationships between neighbouring grains (misorientation) and the orientation of individual grains in comparison to a reference plane. Figure 8 demonstrates for a representative needle, that these crystals are

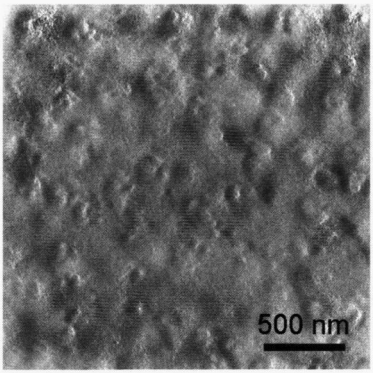

Fig 3:
TEM replica of a phase separated Na_2O-Al_2O_3-B_2O_3-Fe_2O_3-SiO_2 glass

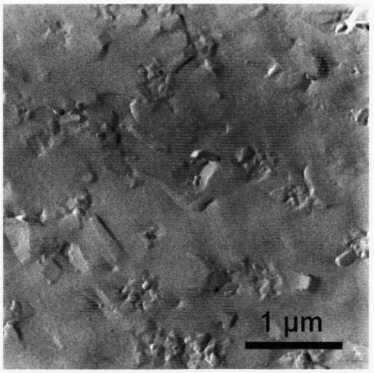

Fig 2:
Crystallization of the glass from fig. 2 (SEM)

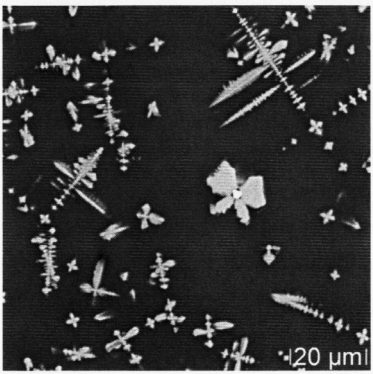

Fig 5:
Iron oxide crystal, grown on a Pt nucleus (SEM micrograph)

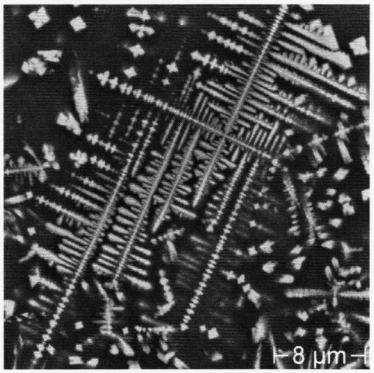

Fig. 4:
SEM micrograph of the sample, investigated by EBSD

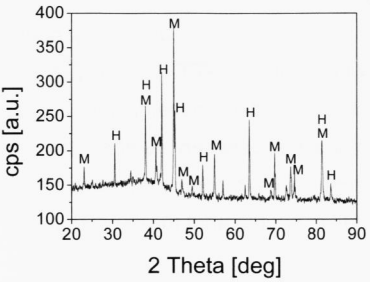

Fig. 6;
XRD pattern of the sample, investigated by EBSD
H: Haematite (Fe_2O_3)
M: Magnetite (Fe_3O_4)

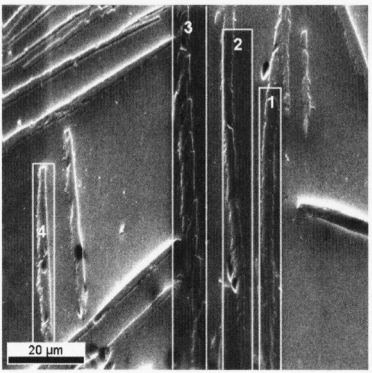

Fig. 7: EBSD sample

often polycrystalline, and that they additionally can consist of both Fe_2O_3 and Fe_3O_4. As the inverse pole figures show, a texture is present: The [101] crystal axis of the cubic grains lies in the direction of the needle axis. The individual grains may be rotated against each other around this axis. The image quality map is a measure for the quality of the diffraction patterns (higher brightness corresponds to better electron diffraction patterns). Grain boundaries are defined by a misorientation angle greater 5°. In case of insufficient quality of the patterns across a grain this grain could be interpreted to be composed of several grains. Most surprising is, that both cubic and trigonal phases appear as immediate neighbours in the same needle.

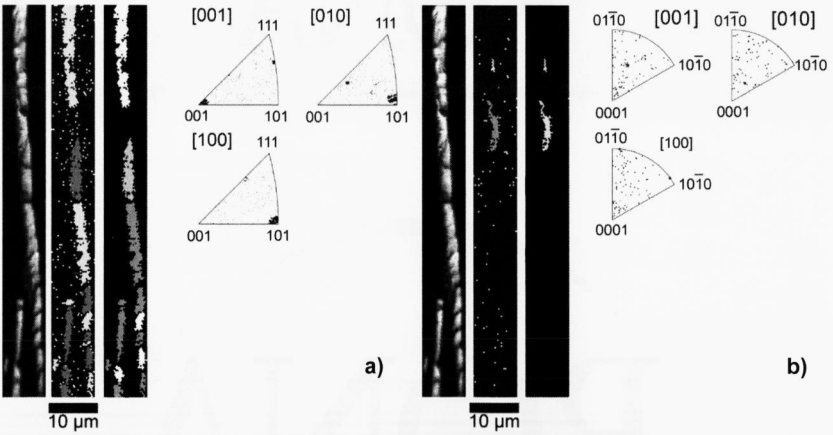

Fig. 8: a): map of Fe_3O_4; b): map of Fe_2O_3 (marked region - 2 - of fig. 7) from left: pattern quality map, grain map, inverse pole figure map (surface normal of fig. 7 as sample direction; equivalent grey levels describe equivalent orientations of the grains). Originally, the grain map is colour coded.