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Investigation of the Demixing Process in the System Fe_3O_4(Magnetite)-$FeAl_2O_4$(Hercynite)

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Silver-alkali halides show two clearly distinguishable stages during their demixing process. The chemical demixing in the spinodal regime occurs on a shorter time scale than the subsequent relaxation of the lattice. The present work is embedded in the major question whether these findings can be transferred to completely different systems such as the spinels.

The system magnetite (Fe_3O_4) - hercynite ($FeAl_2O_4$) exhibits a well defined miscibility gap at temperatures below 867 °C. According to Putnis and coworkers [1], the early stages of chemical demixing are characterized by the mechanism of spinodal decomposition. Results from transmission electron microscopy and susceptibility measurements suggest a characteristic timescale of several hours.

The present work aims at a further investigation of the demixing kinetics of this system by X-ray powder diffraction.

$Mag_{50}Hec_{50}$ samples were synthesized from hematite, corundum, iron and magnetite. The purity of magnetite was tested by refinement from X-ray powder diffraction data as well as Raman spectroscopy. There was no indication for any impurity phase like maghemite, *e.g.*, the preparation followed a modified route for synthesis of pure hercynite [2]. The sample was investigated by X-ray powder diffraction from a MoK_α source. After quenching from the homogeneous phase at about 1000 °C to room temperature, the diffractogram remains almost unchanged. No significant broadening or line splitting is observed compared with a diffractogram obtained well above the critical temperature. This indicates that the mixture is still homogeneous. The lattice constant was determined by Rietveld refinement as 8.31 Å which is between the values of magnetite (8.39 Å) and hercynite (8.17 Å). The deviation from Vegard's Law is probably due to the change of spinel site occupation. While Fe_3O_4 exhibits basically an inverse spinel structure, the cation distribution in Fe_3O_4 corresponds to the normal spinel type.

In order to obtain information about the kinetic of phase separation, *in situ* X-ray diffraction experiments were performed in a temperature interval from 300 °C to 800 °C. The measuring time ranged from 5 to 9 days. During this time-interval, no significant changes in the diffractograms could be observed at any temperature.

In order to investigate the long-time behaviour another sample was synthesized by the same route and annealed *ex situ* at 600 °C for 25 days before it was cooled to room temperature within one day. The sample exhibits significant changes in the diffractogram compared to the homogenous phase: The peaks are shifted to smaller angles and the lines are considerably broadened. As an example, Fig.1

shows the variation of the (440)-reflection. In the homogeneous phase, the $K_{\alpha1}$-$K_{\alpha2}$-splitting is clearly seen. After ageing for 25 days at 600 °C, however, the intensity distribution becomes broad and a second broad component can be distinguished due to the phase separation. The angular splitting of the peak is about 0.4° which is still considerably smaller than expected for a completely demixed system.

The results indicate that the demixing needs at least more than one week to be observed by Bragg reflections and is definitely not finished after more than three weeks. In view of the results of Putnis and coworkers [1] who observed compositional fluctuations within several hours by transmission electron microscopy, the present findings indicate that chemical demixing occurs much faster than the lattice relaxation. Such a two-stage mechanism was previously also observed in silver-alkali halide systems [3-6]. Further investigations with small angle scattering or inelastic neutron scattering are planned to verify this assumption and to provide more detailed insight into the basic mechanism of demixing in the magnetite-hercynite system.

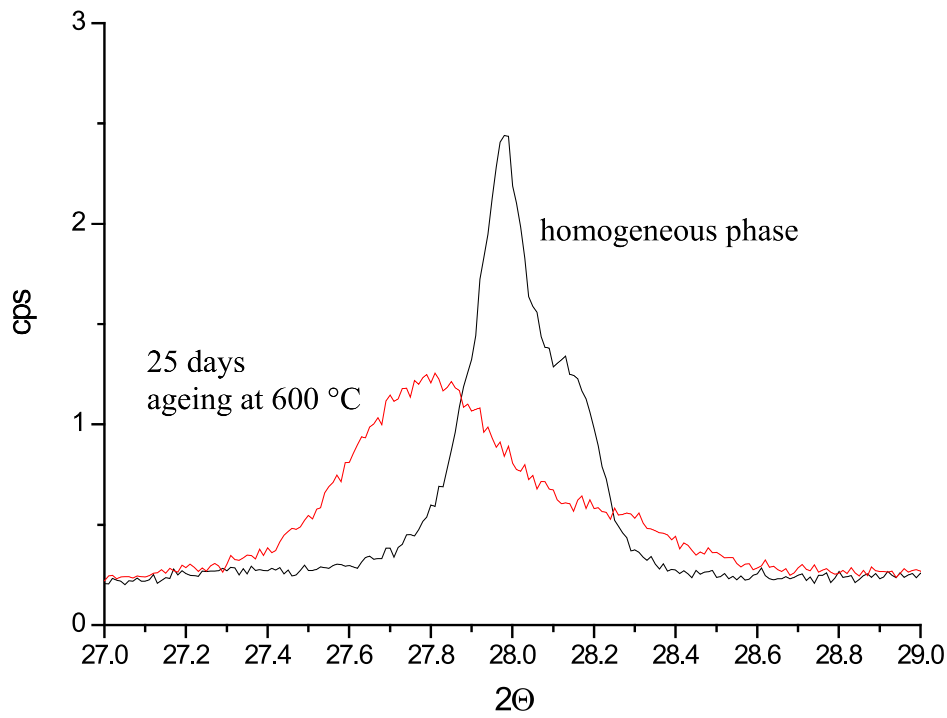

Fig. 1 Profiles of the (440)-reflection in the homogeneous phase and after ageing at 600 °C for 25 days.

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