



The non-magnetic surface of magnetic particles in nanostructured glass ceramics studied by SANS

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Abstract

Nanosized crystallites of ferrimagnetic magnetite, Fe_3O_4 , were prepared by heat treatment of a rapidly quenched silicate glass melt of composition 27.4CaO–42.8SiO₂–6.1B₂O₃–23.7Fe₂O₃ (mol%). SANS experiments of samples annealed at different heat treatment conditions were performed to determine the evolution and nature of the non-magnetic surface layer of the nanocrystals. It is suggested that this layer is formed by the distorted crystalline structure and thermally induced effects at the surface region and by the formation of a segregation shell enriched with Fe₂O₃ and subsequent surface oxidation of the Fe_3O_4 nanocrystals as well. © 2000 Elsevier Science B.V. All rights reserved.

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Previous SANS investigations [1] of the glass ceramic sample with the maximum volume fraction of magnetite, Fe_3O_4 , revealed a bimodal size distribution of the nanocrystalline phase. Furthermore, they provided the result that the magnetically active core is surrounded by a non-magnetic surface layer.

In the present study we report on SANS experiments of a sample set annealed isothermally at 700°C for 0.5, 2, 4, and 16 h in order to clarify the nature of the nanocrystal surface regions. The SANS experiments were performed at the instrument V4 at the neutron reactor BER II of the Hahn-Meitner-Institute in Berlin. In order to separate the magnetic scattering contribution from the nuclear scattering the samples were placed in a homogeneous magnetic field perpendicular to the direction of the primary beam. From the two-dimensional SANS patterns the isotropic scattering part, $A(q)$, and the anisotropic part, $B(q)$, were extracted according to $I(q) = A(q) + B(q)\sin^2\alpha$, where α is the angle between the

external magnetic field, \mathbf{H} , and the scattering vector, q . $A(q)$ is the nuclear scattering term and $B(q)$ is the magnetic scattering contribution in case of complete alignment of the magnetization vector of the nanocrystals parallel to \mathbf{H} . The latter condition is fulfilled by the given experiment for all crystals with diameters $D > 7$ nm [1]. The incomplete alignment of the magnetization vector of smaller crystals leads to a contribution to the magnetic scattering, which is weighted by $\{1 - 3L(x)/x\}$, where $L(x)$ is the Langevin function [1], but it has a neglecting influence on the strong isotropic scattering term.

The volume size distributions, dw/dD , of all samples are shown in Figs. 1a–d. The initially bimodal volume size distributions for 0.5 h (Fig. 1a) change to unimodal size distributions at the longest heat treatment time of 16 h (Fig. 1d). The shapes of dw/dD obtained from the nuclear as well as from the magnetic scattering at the same heat treatment stage are very similar. This result is really essential, since it evidently shows that both particle population consist of magnetite. The function $\{1 - 3L(x)/x\}(dw/dD)_{\text{mag}}$, corresponding to the volume size distribution of the magnetizable part of the particles, reflects apparently smaller crystallite sizes than $(dw/dD)_{\text{nuc}}$. This effect observed for all treatment stages

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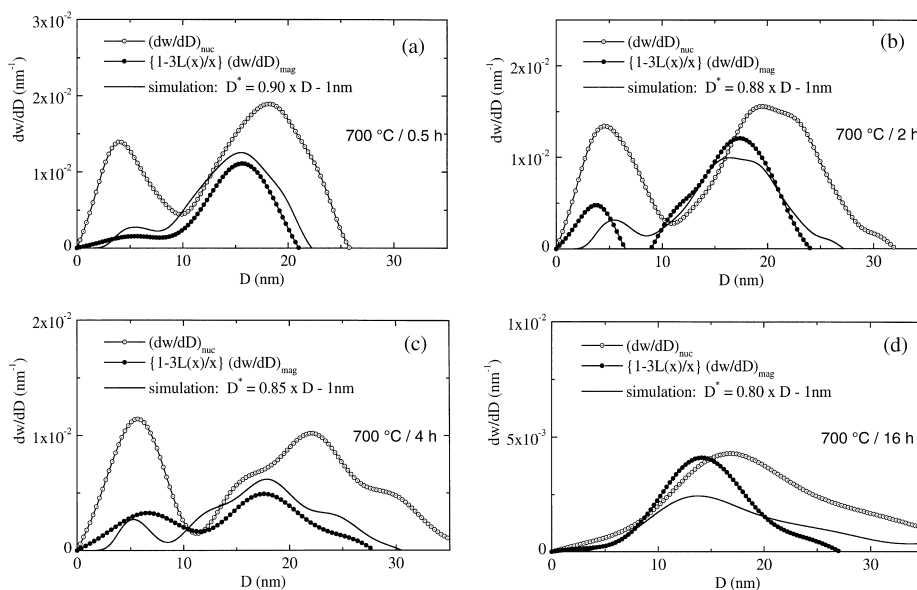


Fig. 1. Comparison of the volume size distributions obtained from the nuclear scattering part, $A(q)$, from the anisotropic scattering term, $B(q)$, and from a simulation of the magnetic core of the particles for different heat treatments (a–d).

can be explained in terms of a non-magnetic surface layer formed around the magnetite core. The diameter of the magnetically active core, D^* , can be related to the diameter, D , of the crystallites by $D^* = aD - b$ (Figs. 1a–d). This equation simulates the apparent crystallite shrinkage effect and even the loss of very small crystallites for the magnetic scattering term which should be caused by the non-magnetic surface layer.

The parameter b should correspond to the distorted magnetic structure of the particle at its surface. A very unexpected result is the nearly constant or even slightly decreasing parameter a with increasing treatment time. This finding implies a growth of the thickness of the non-magnetic particle shell with a rate which is at least proportional to the growth rate of the diameter of the magnetite core. This tendency observed for the time-dependence of the parameter a is consistent with a constant relation of the volume of the magnetic core to the volume of the non-magnetic shell of the nanocrystals.

Qualitatively, this result can be interpreted in terms of the formation of a segregation shell enriched with Fe_2O_3 , which should be structurally distorted, the volume of which is growing proportional to the magnetite core volume during annealing. This behavior can be well understood, because of the redox relation $\text{Fe}^{3+}/\text{Fe}^{2+} > 2$ in the as-prepared glass melt. Consequently, in case of formation and growth of magnetite clusters ($\text{Fe}_3\text{O}_4 = \text{Fe}_2\text{O}_3 \cdot \text{FeO}$; $\text{Fe}^{3+}/\text{Fe}^{2+} = 2$), which obviously have the highest probability for cluster formation in the present glass, locally their environment becomes

enriched with Fe^{3+} and O^{2-} ions. These species are able to form a shell surrounding the magnetite cluster which should be enriched with Fe_2O_3 and might consist of matrix components, too. We observe a definite volume relation cluster/shell for the whole growth stage of magnetite up to 4 h. In the late treatment stages (> 4 h), the shell thickness and, therefore, the shell volume grow faster than the magnetic core as indicated by the parameter a decreasing to 0.85. Therefore, it can be suggested that the non-magnetic shell is growing at the expense of the magnetite core by oxidizing the surface of the Fe_3O_4 nanocrystals.

This hypothesis presented for the origin of the non-magnetic surface layer is supported by experimental results which show that, for very long treatments at 700°C (72 h) or higher temperatures, iron metasilicate and hematite are the dominating nanocrystalline phases, whereas only very few large magnetite crystals survive. One possible reason for the suggested magnetite oxidation could be the diffusion of oxygen from the air into the glass ceramic flake. A quantitative description of the crystallization kinetics in the magnetic-glass-ceramic and the influence of the atmosphere will be the subject of further investigations.

References

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