The fate of $\text{Fe}^{3+}$ ions in the system \{AlO(OH)-xerogel/ Fe-compounds\} after mechanical activation and different thermal treatments studied by Mössbauer, ESR spectroscopy and thermal analysis

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Abstract Co-milling of AlO(OH) xerogels with various iron(III) compounds such as $\alpha$-$\text{Fe}_2\text{O}_3$ or $\text{K}_3[\text{Fe(CN)}_6]$ has been used for mechanochemical activation leading to Fe/Al oxide phases in coexistence with the activated main component. The results obtained allow a deeper insight into the chemical processes occurring during activation, doping, and thermal treatment in atmospheres of different chemical activity ($\text{H}_2\text{O} ; \text{N}_2; \text{O}_2/\text{N}_2; \text{H}_2/\text{N}_2$). Evidence will be given for $\text{Fe}^{3+}$ species being able to form suitable crystallization germs and to lower the crystallization temperature. One can distinguish between the incorporation of $\text{Fe}^{3+}$ ions into the alumina matrix at the crystallite growth (e.g. on $\text{Fe}_2\text{O}_3$-like seeds) and the incorporation of $\text{Fe}^{3+}$ ions during the last steps of crystallization. These last-mentioned $\text{Fe}^{3+}$ ions are provided by coexisting Fe/Al oxide phases. In contrast to alumina matrices equilibrated at high temperatures (e.g. at 1,200–1,500°C), the matrices formed \textit{in situ} are able to incorporate $\text{Fe}^{3+}$ ions by diffusion at temperatures of $\sim$900–1,100°C in a short time regime.

Keywords Mössbauer · ESR · Thermal analysis · High energy ball milling · Activation/deactivation processes · Local mechano-chemical reactions · Heterogeneous redox reactions

1 Introduction

The production of protecting $\alpha$-$\text{Al}_2\text{O}_3$ coatings, e.g. for turbine blades or other important engine components, is an important and rapidly developing field of the...
actual materials science. We started with the sol-gel process [1] and ended up at the phase transition to $\alpha$-Al$_2$O$_3$ [1–3] at temperatures below 1,000°C. The quality of the coatings and the transition temperatures can be influenced by doping (e.g. with Fe$^{3+}$ species) as well as by mechanical activation (“high energy ball milling”) of the corresponding xerogels. In this regard, some open questions remain, mainly concerning the solid state chemical reaction which proceeds (i) at the activation in the presence of dopants, and (ii) at the thermal treatment of the doped systems up to the transition to the main phase $\alpha$-Al$_2$O$_3$.

Therefore, our recent investigations were directed to the combined application of both Mössbauer and ESR spectroscopy, together with thermal analysis. The results show that the Fe species are not only monitors for the local structures and phases but also active components at the expected phase transitions. This paper primarily reports on the results of Mössbauer spectroscopy and thermal analysis and, secondarily, regards findings of ESR spectroscopy.

2 Experimental

2.1 Materials

The AlO(OH) xerogels have been synthesized as described previously [1] and mechanically activated by using a Pulverisette 7 (Fritsch, Germany). The “high energy ball milling” procedure has been applied to pure or mixed samples of 2 g per milling beaker utilizing 5 milling balls (beaker and balls made from silicon nitride). The milling time was between 2 and 8 h with 600 r.p.m. Hematite, $\alpha$-Fe$_2$O$_3$ (Merck), was used as commercially available; all other chemicals, e.g. K$_3[Fe(CN)$_6$]$, or the precursors for synthesizing the xerogels were chemically pure (p.A.) and taken from usual laboratory stocks.

2.2 Thermal analysis

The thermoanalytical (TA) curves (T, DTA, TG, DTG) have been recorded utilizing a Netzsch STA 409 C Skimmer® device in the conventional mode. Various gas atmospheres have been applied (Synthetic air, N$_2$, N$_2$/10%H$_2$). Further experimental details were as follows: DTA-TG sample carrier system with Pt/PtRh10 thermocouples, heating rate 10 K/min, platinum or corundum crucibles (0.8 ml), sample mass 40–80 mg, measured against empty reference crucible, carrier gas flow 70–100 ml/min, data evaluation utilizing the manufacturer’s software Proteus® (v. 4.1) without smoothing etc. For details of the temperature evaluation concerning the onset, $T_{on}$, extrapolated onset, $T_{on}^{ex}$, and peak temperatures, $T_p$, of the characteristic temperatures, as well as for discussing DTA curve shapes and base line variations see [4] and the literature cited there.

2.3 Mössbauer and ESR spectroscopy

The ESR spectra have been obtained with an X-band spectrometer ERS 300 manufactured by ZWG-Magnettech GmbH (Berlin-Adlershof, Germany).