Competing redox reactions in Fe-containing AlO(OH) and Al₂O₃ matrices: A combined investigation by Mössbauer, ESR spectroscopy and thermal analysis

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Abstract. The investigation of iron-doped AlO(OH)/Al₂O₃ systems revealed that the combined employment of Mössbauer and ESR spectroscopies together with thermal analysis yields meaningful data with complementary information. This mutual complementarity is based on the coexistence of Fe point defects with the corresponding aggregated FeOₓ species which has been observed even for very low Fe concentrations. Competing redox processes between the dopant, the AlOₓ matrix, and the gas atmosphere during the thermal treatment enable the generation of solid phases exhibiting specific chemical properties. The entire reaction process is influenced by a specific mechanical and thermal pre-treatment that affects predominantly oxydative processes in the matrix. A protecting influence of the matrix preventing further reductive attack of the Fe³⁺ and Fe²⁺ ions by hydrogen has been established.

1. Introduction
Crystalline and amorphous hydroxylic (AlOOH) and oxidic (Al₂O₃) precursors of α-Al₂O₃ have been doped with iron species for various reasons: (i) to reduce the temperature of the phase transition yielding α-Al₂O₃ when forming corundum protective layers, and (ii) to yield particular mechanical properties of the polycrystalline product phases via an enhanced grain boundary concentration of FeOₓ or (FeₓAl₁₋ₓ)O₃. These processes are strongly influenced by mechanical activation both of the educts and the precursors for the Fe doping.

Both the mechanical activation and the thermal transformation to give α-Al₂O₃ have been investigated by employing the title methods. The activation depends on the kind of Fe compounds used for the doping and the gas atmosphere during the thermal analysis (TA) heating run. The competing redox processes occurring during the TA runs deliver unique information about the active role of the AlOₓ matrix for the solid state reactions. Furthermore, they allow directly to influence certain properties of the resulting materials.
2. Results and Discussion

For the present study, the Fe concentration given as Fe2O3 was limited by the range c ≤ 0.1 mol-%. Under these conditions, the combination of Mössbauer, ESR, and TA measurements yields complementary information. As an example, a sample of α-Al2O3 calcined at 1500 °C can be regarded (Figure 1g). It contains only very few iron impurities and exhibits the typical ESR spectrum for the system {α-Al2O3:Fe3+}. The position of the fine-structure transitions is undoubtedly governed by the symmetry of the matrix [1] (Figure 2a). Shape and intensity of the transitions depend on the mode of the Fe3+ insertion into the matrix and, therefore, on the given structural perfection of the α-Al2O3 lattice. Under these conditions, the concentration of the Fe3+ species placed on Al3+ positions is sufficient to yield a meaningful ESR spectrum such as displayed in Figure 2a. The integral of the spectrum, however, shows that these Fe3+ point defects affect only a comparably small part of the total ESR intensity (Figure 2b). The latter is predominantly located at g′~2 and originates from phase precursors of the approximative formula (FexAl1-x)2O3 [2] which yields the Mössbauer spectrum according to Figure 1g. Taking into account the above mentioned aspect of the present study to obtain complementary information from different analytical methods, this result can be regarded as a first approach: the Mössbauer data primarily correspond to the aggregated species being in coexistence or even in equilibrium with the point defects.

Comparable effects could be observed for the common educt of the α-Al2O3 formation, i.e. the crystalline AlO(OH) which already contains iron impurities. Here, we are dealing with the weakly aggregated and rhombohedrally distorted Fe-O species which cause ESR signals at g′~4.3 whereas the aggregated species are indicated by broad lines at g′~2. In this case as well, the Mössbauer data correspond to aggregated species and yield the parameters δ = 0.27 mm/s, Δ = 0.23 mm/s and Γ = 0.39 mm/s (Figure 1a). After strong mechanical activation by 50 hours milling (cf. Figure 3) the Mössbauer parameters change as follows: δ = 0.22 mm/s, Δ = 0.38 mm/s and Γ = 0.47 mm/s. This means that the mechanochemical reaction which is accompanied by a water release [3], shifts the value of δ down to a 4 to 5 coordination of the Fe3+ ions, whereas the values of Δ and Γ increase due to the mechanically induced broader statistical distribution of the bond angles in the {FeOx} polyhedra. These findings can be related to the properties of a nominally undoped sample being prepared via a sol-gel route and showing a low Fe concentration [c(Fe2O3) ~ 0.01 mol%] (Figure 1d). The corresponding Mössbauer parameter at 293 K are as follows: δ = 0.24 mm/s, Δ = 0.29 mm/s and Γ = 0.37 mm/s and, respectively, at 78 K: δ = 0.34 mm/s, Δ = 0.36 mm/s and Γ = 0.44 mm/s. The increasing values for Δ and Γ can be explained by the stronger distortion of the matrix at the low temperature. In general, the values represent the typical ones for Fe3+ ions in {FeOx} polyhedra with x = 4…6.

After co-milling of the originally crystalline AlO(OH) with 1 wt-% Fe(NO3)3 · 9H2O and a subsequent TA heating run under N2/10%H2 (Pt) (Figure 3) one obtains a doublet (δ = 1.10 mm/s, Δ = 1.82 mm/s, Γ = 0.64 mm/s) in coexistence with a sextet (δ = 0.01 mm/s, Δ = 0.01 mm/s, Γ = 0.27 mm/s, hf = -33.34 T) with ~8.2 % and 91.8 % relative intensity, respectively (Figure 1c). These parameters unambiguously represent Fe0 being formed by reduction. Interestingly enough, the doublet of ~8% represents Fe2+ ions, which were not reducible due to a stabilization via reactive implementation into the matrix.

This idea is supported regarding a further sample doped by adding Fe(NO3)3 · 9H2O in a sol-gel process. The sample contains 0.13 mol-% Fe2O3 and, after TA under N2, yields a part of the total intensity of ~60% indicating Fe3+ ions (δ = 0.26 mm/s and Δ = -0.02 mm/s), and ~39% of a second phase with δ = 0.14 mm/s, Δ = -0.66 mm/s, hf = -33.35 T. It may represent Fe0 or Fe3N [4]. Preferably, however, the second phase is assigned to be Fe3N due to an isomer shift larger than zero. Fe3N should be not only a product of a reduction (e.g. by organic residues), but also of an internal nitridation of Fe3+ via intermediarily formed NH3. This would explain that the Tp decrease ends up at ~1110 °C, i.e. the number of appropriate FeOx seeds [5] is not sufficient.
Figure 1. Mössbauer spectra of differently treated compounds:
(a) AlO(OH) crystalline (commercial, Nabaltec);
(b) as (a), 50 h milled, after TA under N₂/10%H₂ (1200 °C);
(c) as (a), 8h co-milled with 1 wt-% Fe(NO₃)₃·9H₂O,
after TA under N₂/10%H₂ (1200 °C);
(d) AlO(OH) xerogel, undoped, measured at 78 K;
(e) AlO(OH) xerogel, Fe(NO₃)₃·9H₂O (0.52 mol-% Fe₂O₃) added to the sol;
(f) as (e) after TA under N₂/10%H₂ (1200 °C);
(g) α-Al₂O₃ (commercial, VEB Laborchemie Apolda), calcined at 1500 °C;
(h) Fe(NO₃)₃·9H₂O after TA under N₂/10%H₂ (1200 °C);
Figure 2. ESR spectra of \( \{\alpha\text{-Al}_2\text{O}_3:Fe^{3+}\} \) powder measured at 78 K (a) and its first integral (b).

If the external reductive force is enhanced (e.g. by heating under \( N_2/10\%H_2 \)) an unexpected result is obtained. The sample yields a Mössbauer spectrum with a \( Fe^{3+} \) doublet (\( \delta = 0.21 \) and \( \Delta = -0.002 \text{ mm/s} \)). Quite surprisingly, it amounts to ~50% of the total intensity, whereas the remaining 50% are caused by \( Fe^{0} \). Despite of the reductive conditions, a large part of \( Fe^{3+} \) is formed by chemical reaction with the matrix being under formation and structural reorganization. As a consequence, further reductive attack is prevented.

Competing redox processes without the participation of a matrix can be observed in the case of pure \( Fe(NO_3)_3 \cdot 9H_2O \) being subjected to a TA heating run under \( N_2/10\%H_2 \). The characterization of the residue of the TA treatment by Mössbauer spectroscopy (Figure 1h) led to the following composition:

- 13.0% \( Fe^{2+} \) (\( \delta = 1.08 \text{ mm/s}, \Delta = 0.31 \text{ mm/s} \) and \( \Gamma = 0.49 \text{ mm/s} \));
- 15.6% \( Fe^{0} \) (\( \delta = 0.006 \text{ mm/s}, \Delta = -0.02 \text{ mm/s} \) and \( h_f = 33.27 \text{ T} \));
- 27.5% Magnetite A-sites \( \delta = 0.27 \text{ mm/s}, \Delta = -0.03 \text{ mm/s} \) and \( h_f = 49.10 \text{ T} \);
- 43.7% Magnetite B-sites \( \delta = 0.65 \text{ mm/s}, \Delta = -0.02 \text{ mm/s} \) and \( h_f = 46.09 \text{ T} \).

Figure 3. DTA curves of \( AlO(OH) \) in \( N_2/10\%H_2 \) (Pt crucibles) for different sample pre-treatments.
It is noteworthy that only 15.6% Fe(0) and a considerable amount of magnetite are formed. The oxydative atmosphere, formed during the thermal decomposition of Fe(NO₃)₃·9H₂O, effectively competes with the hydrogen of the carrier gas in the TA run. However, at higher temperatures (TA up to 1200 °C) the fraction of reduced Fe species in the product mixture increases.

Finally, another interesting way to obtain Fe-doped α-Al₂O₃ should be mentioned here. It concerns the formation of alumina in an O₂/H₂ flame starting from a Fe-doped AlN precursor yielding a strongly distorted system (g′~ 4.3 in the ESR [6], not shown here). There is a coexistence of weakly aggregated point defects with precursors of (FeₓAl₁₋ₓ)₂O₃. This system is characterized by two doublets in the Mössbauer spectrum: δ₁ = 0.23 mm/s, Δ₁ = 0.82 mm/s and Γ₁ = 0.78 mm/s (Fe³⁺ ions representing ~80 % of the spectral intensity);

δ₂ = 0.84 mm/s, Δ₂ = 1.77 mm/s and Γ₂ = 0.78 mm (Fe²⁺ ions in the aggregated part, ~20 %).

Obviously, this kind of a “pulse-like” pyrolysis of AlN, which yields hollow balls of α-Al₂O₃, creates a partly reductive atmosphere thus explaining the formation of Fe²⁺ species. A further reduction, however, which would lead to Fe(0), or even to a nitridation of iron could not be observed here. The applied temperature-time regime, obviously, prevents the reductive action.

3. Conclusions
For concentrations of c(Fe₂O₃) ≤ 0.01 mol-% already, a distribution of Fe species could be established both in polycrystalline and amorphized systems: (i) as point defects in the matrix lattice which can be followed by ESR spectroscopy, and (ii) as aggregated species acting as precursors of phases like (FeₓAl₁₋ₓ)₂O₃, Fe₂O₃, Fe₃O₄, and Fe(0) which can be successfully studied by Mössbauer spectroscopy. The actual phase composition together with the possible formation of further species such as FeAlO₄ precursors can be directed by redox processes of internal (residual carbon from the sol-gel process, NO₃⁻ etc.) or external (H₂; O₂) reaction partners during or prior (!) to the thermal matrix transformation. A comprehensive inspection of the spectroscopical and thermoanalytical findings shows that

(i) the FeOₓ phases can significantly decrease the phase transformation temperature to yield α-Al₂O₃ provided the FeOₓ phases exhibit both a suitable grain formation kinetics and particle size;

(ii) the transforming matrix does not exhibit only oxydative properties due to the in situ water release and the related formation of reactive surface sites, but is able as well to prevent the reduction of the matrix-incorporated Fe³⁺ ions up to ~50 % of the total amount by the external hydrogen gas flow covering the temperature range up to 1200 °C.

4. References
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