Modeling of magnetization curves of iron oxide/ cerium dioxide reactive sorbents

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AIM: Structural and magnetic characterization and modeling of the hysteresis loops of iron oxide/cerium dioxide sorbents.

Materials preparation

- Magnetic core – required amount of ferrous sulphate dissolved in diluted sulphuric acid, addition of equivalent amount of PREFLOC and the concentrated NaOH for precipitation of magnetic iron oxides, the reaction mixture agitated for two additional hours in nitrogen atmosphere, the precipitated iron oxide (presumably magnetite) separated with the aid of permanent magnet and washed several times in deionized water
- Iron oxide/cerium dioxide sorbent – precipitated iron oxide re-dispersed in the solution of cerium nitrate, cerium carbonate precipitated with the solution of NH4HCO3, composite precursor with 20% of CeO2 separated with the aid of permanent magnet, washed with deionised water and dried at 110°C
- Calcination – the temperature treatments of the powder precursor was done in an open porcelain crucible at temperatures ranging between 473 K and 1173 K in a muffine furnace

Experimental techniques

- XRDP (X-Ray Powder Diffraction) – X’Pert PRO diffractometer by PANALYTICAL, CoKα irradiation (λ = 0.17902 nm), Bragg-Brentano geometry, 28 range 20° + 110°, evaluation – Rietveld structure refinement method by semi-automatic mode using the High Score Plus program
- PPMS (Physical Property Measurement System) – Quantum Design Inc., magnetization curves measured at room (300 K) and low (2 K) temperatures with maximal applied magnetic field ± 4000 kA/m (5 T)

Theoretical models

- Jiles – Atherton model (isotropic) – J-A model for simulations of major hysteresis loops of ferro-/ferrimagnetic materials is described by differential equation

\[
dM = \frac{dM}{dt} = M(1-(\sinh(\frac{H}{kM})^2 + (\frac{H}{kM})^2)^{1/2}(1-(\frac{H}{kM})^2)^{1/2}) = \frac{M_{max}}{M} - M
\]

where \(M_{max}\) is anhysteretic magnetization, \(H\) is effective magnetic field, \(M\) is saturation magnetization of material. \(a\) is constant, 1 for increasing field, -1 for decreasing field. Four parameters are fitted by the least squares method:
- \(a\) – characterizes domain walls density in the magnetic material, 
- \(k\) – determines the hysteresis losses, 
- \(\alpha\) – the mean field parameter representing inter-domain coupling, 
- \(c\) – represents reversible domain wall motion.

- Langevin model – used for paramagnetic or superparamagnetic materials, hysteresis loop is simulated by modified Langevin function \(L(x) = \cos x - \frac{x}{\pi}\). We assume spherical shape of particles with diameter \(d\), which can be found by fitting method. Magnetization of hysteresis curve is described by

\[
M = M_0 L(\frac{H}{kM})
\]

The values of J-A and Langevin coefficients are optimized to obtain the root square deviation \(R^2\) (Pearson coefficient) close to 1 showing minimum difference between the experimental and simulated magnetization curves.

Experimental

Sorbent calcined at 673 K

Jiles-Atherton (J-A) model

<table>
<thead>
<tr>
<th>(T_{\text{meas}}) (K)</th>
<th>2</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H_{c}) (kA/m)</td>
<td>27.51</td>
<td>1.71</td>
</tr>
<tr>
<td>(M_r) (Am^2/kg)</td>
<td>18.75</td>
<td>1.78</td>
</tr>
<tr>
<td>(M_s) (Am^3/kg)</td>
<td>56.42</td>
<td>50.69</td>
</tr>
<tr>
<td>(\sigma) (kA/m)</td>
<td>33.74</td>
<td>30.11</td>
</tr>
<tr>
<td>(k) (kA/m)</td>
<td>28.12</td>
<td>2.96</td>
</tr>
<tr>
<td>(a)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>(\epsilon)</td>
<td>0.004</td>
<td>0.004</td>
</tr>
<tr>
<td>(r^2)</td>
<td>0.999</td>
<td>0.999</td>
</tr>
</tbody>
</table>

- high degradation efficiency against parathion and paraaxon methyl (40% and 72%)
- 20.1% of CeO2, 15.3% of Fe3O4 and 64.6% of \(\gamma\)-Fe2O3 with the crystallite sizes 6.63 nm, 7.89 nm, and 15.54 nm
- simulated loops sensitive to parameters \(a\) and \(k\)

Sorbent calcined at 1073 K

Jiles-Atherton (J-A) model

<table>
<thead>
<tr>
<th>(T_{\text{meas}}) (K)</th>
<th>2</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H_{c}) (kA/m)</td>
<td>39.12</td>
<td>78.15</td>
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<tr>
<td>(M_r) (Am^2/kg)</td>
<td>0.06</td>
<td>0.16</td>
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<tr>
<td>(M_s) (Am^3/kg)</td>
<td>0.17</td>
<td>0.41</td>
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<tr>
<td>(\sigma) (kA/m)</td>
<td>24.47</td>
<td>53.67</td>
</tr>
<tr>
<td>(k) (kA/m)</td>
<td>51.65</td>
<td>106.04</td>
</tr>
<tr>
<td>(a)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>(\epsilon)</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>(r^2)</td>
<td>0.997</td>
<td>0.996</td>
</tr>
</tbody>
</table>

- lower degradation efficiency against parathion and paraaxon methyl (5% and 36%)
- crystallite size and amount of CeO2 obtained from XRD: 28.94 nm and 20.7%
- iron oxides completely transformed to hematite (93.36 nm, 79.3%)
- at higher magnetic fields, linear dependence of magnetization indicates anti-ferromagnetic behaviour of hematite, while at lower fields typical ferromagnetic reversal with high \(H_c\) and low \(M_r\) (see Table) is observed
- increase of \(a\), \(k\), and \(\epsilon\) parameters in comparison to 637 K calcined sorbent refers to growth of energetic losses and reversible component of magnetization
- cooling below 263 K (Morin transition) should lead to suppression of spin canting, nevertheless measured loop at 2 K still exhibits ferromagnetic contribution with lower \(H_c\) and \(M_s\) at than 300 K (decrease of parameters \(a\) and \(k\))

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