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BEHAVIOR OF Al₂O₃ AND SiO₂ WITH HEATING IN A
Cl₂ + CO STREAM

L. K. Shchetinin

Translation of "O poved Al₂O₃ i SiO₂ pri nagrevanii v toke Cl₂ + CO", Izvestiya vysshhikh uchebnikh zavedeniy. Tsvetnaya metallurgiya, No. 1, 1982, pp. 43-46.
**Behavior of Al₂O₃ and SiO₂ with Heating in a Cl₂ + CO Stream**

**Abstract**

Differential thermal analysis (DTA) and Thermogravimetric analysis (TGA) were used to study the chlorination of α-Al₂O₃, γ-Al₂O₃, and amorphous SiO₂ in a Cl₂ + CO stream, for the preparation of AlCl₃ and SiCl₄. The chlorination starting temperatures were 235°C for Al₂O₃ and 680°C for SiO₂. The chlorination of α- and γ-Al₂O₃ takes place via the formation of AlOCl as an intermediate product, and its subsequent dissociation at 480-560°C, according to 3AlOCl → AlCl₃ + Al₂O₃. The chlorination activation energies are given for the three oxides.
BEHAVIOR OF Al₂O₃ AND SiO₂ WITH HEATING IN A Cl₂ + CO STREAM

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The available data in the literature on the reaction of Al₂O₃ and SiO₂ with a mixture of Cl₂ + CO [1-3] show their greater resistance to chlorination than for many other oxides. However, taking into account the increasing interest in aluminum and silicon chlorides, produced by chlorination of a natural raw material [4], the indicated processes are studied in more detail in the present study, with the utilization of modern physical and chemical methods.

For this purpose, γ-Al₂O₃ and amorphous SiO₂ were prepared by calcination of grade 18-1A especially pure Al(OH)₃, and chemically pure silicic acid at 700° C, as well as α-Al₂O₃ at 1100° C. The individuality of the oxides was corroborated by X-ray diffraction analysis. Chlorine and carbon monoxide were produced by well-known methods. Temperature recording was carried out on the FPK-59. The kinetics of the processes were studied utilizing McBain balances and a KM-6 cathetometer: in all cases, the weighed portion of the sample was 50 mg, the size of the oxide particles was 0.040-0.045 μm, and the rate of heating during chlorination was ~15 degrees/minute.

According to differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the heating of α-Al₂O₃ in a stream of Cl₂ + CO (Fig. 1a) and chemical analysis of the exhaust gases, the exo-effect of 80-180° C corresponds to the formation of phosgene. With subsequent heating, its amount decreases, which is evidently brought about by a reduction in the catalytic activity of the α-Al₂O₃, and dissociation of the COCl₂.

*Numbers in the margin indicate pagination in the foreign text.*
From the TGA curve and chemical analysis, it is evident that chlorination of the α-Al₂O₃ begins \( \left( T_H \right) \) at 235°C, with its interaction with phosgene, and is accompanied by the formation of AlOCl

\[
\text{Al}_2\text{O}_3 + \text{COCl}_2 = 2 \text{AlOCl} + \text{CO}_2. \tag{1}
\]

This reaction is thermodynamically possible. At 370-770°C, an endo-effect occurs on the thermogram, which is evidently brought about by the superimposed processes: additional chlorination of the AlOCl, its dissociation, and distillation of the AlCl₃:

\[
\text{AlOCl} + \text{COCl}_2 = \text{AlCl}_3 + \text{CO}_2. \tag{2}
\]

\[
3 \text{AlOCl} = 2 \text{AlCl}_3 + \text{Al}_2\text{O}_3. \tag{3}
\]

This is indicated by the diminishing of the weight of the sample being chlorinated above 480°C, and the liberation of AlCl₃ vapors, beginning at 520°C. The obtained data agree with [5], where it is indicated that, up to 500°C, AlOCl is thermally stable, while at 560-570°C, it dissociates completely. With subsequent heating of the α-Al₂O₃ in a Cl₂ + CO stream, the rate of interaction increases, and the exothermal nature of the summary process becomes preferable, as a result of the reaction

\[
\text{Al}_2\text{O}_3 + 3 \text{Cl}_2 + 3 \text{CO} = 2 \text{AlCl}_3 + 3 \text{CO}_2. \tag{4}
\]

however, the degree of conversion of the oxide and chloride remains comparatively low.

The DTA curve of heating of γ-Al₂O₃ in a Cl₂ + CO stream has almost the same appearance as that for α-Al₂O₃ (Fig. 1b). The drop in the weight of the sample, beginning at 165°C, evidently corresponds to the removal of the moisture contained in the oxide (about 0.6%). A similar process, proceeding from the analysis of the DTA curves of heating of γ-Al₂O₃ in a chloride stream and with its absence, is proposed in [6].
An appreciable interaction of $\gamma$-$\text{Al}_2\text{O}_3$ with $\text{Cl}_2 + \text{CC}$ ($\Delta m \geq 1\%$) begins, like in the case of $\alpha$-$\text{Al}_2\text{O}_3$, at $235^\circ C$ (Fig. 1b), and, with an increase in temperature, takes place according to the scheme (1-4). Above $560^\circ C$ (dissociation of $\text{AlOCI}$), the degree of conversion of the oxide into chloride increases sharply, which is evident from the course of the TGA curve. It was established through X-ray diffraction analysis that the oxide, which forms with dissociation of the $\text{AlOCI}$, undergoes conversion into $\alpha$-$\text{Al}_2\text{O}_3$. The appearance of $\alpha$-$\text{Al}_2\text{O}_3$ lines on the X-ray diffraction pattern of the radicals from the chlorination of aluminum oxide with a $\text{Cl}_2 + \text{CO}$ mixture above $600^\circ C$ is also noted in study [1]. By analyzing the data in [1], the authors of [4], in the interval $550-600^\circ C$, assume a transition of the $\gamma$-modification into $\alpha$-$\text{Al}_2\text{O}_3$, with a simultaneous increase in the rate of the process of chlorination (so-called Hedvall effect [7]).

It is evident from Figure 1a, b that, under equal conditions, the degree of conversion of $\gamma$-$\text{Al}_2\text{O}_3$ into chloride is considerably greater than for $\alpha$-$\text{Al}_2\text{O}_3$. The higher activity of the $\gamma$-$\text{Al}_2\text{O}_3$ to chlorine is evidently brought about by the electron-donor nature of the surface of the oxide, on which, according to the data in [8], active centers ($\text{Al}^{2+}$) form during the process of its dehydration, which have surplus electrons, which do not take part in...
the valent bonds.

It is evident from analysis of the DTA and TGA curves of heating of the prepared SiO₂ in a Cl₂ + CO stream (Fig. 1c) that the T₁₁ of the interaction corresponds to ~680 °C, which is evidently accompanied by a simultaneous removal of the moisture, contained in the oxide (about 0.7%). The conversion of SiO₂ into SiCl₄ takes place most intensively above 900 °C.

![Kinetic curves of the process of chlorination of oxides.](image)

Fig. 2. Kinetic curves of the process of chlorination of α-Al₂O₃ (a), γ-Al₂O₃ (b) and SiO₂ (c) in a Cl₂ + CO stream at 500 (1), 600 (2), 700 (3), 850 (4), 1000 (5) and 1150 (6) °C.

The rate of interaction with Cl₂ + CO was studied for all of these oxides. From the obtained kinetic curves of the chlorination process (Fig. 1), it is evident that the degree of conversion of α-Al₂O₃ and γ-Al₂O₃ into chloride reaches 100% at 1150 °C within 116 and 55 minutes, respectively, i.e., all other conditions being equal, the weighed portion of the α-modification is chlorinated nearly two times more slowly than the γ-Al₂O₃. As far as SiO₂ is concerned, at the given temperature, it is 85% chlorinated within 2 hours. A considerable increase in the rate of interaction of the oxides with the Cl₂ + CO takes place, beginning at 600 °C, for γ-Al₂O₃, 700 °C for α-Al₂O₃, and 850 °C for SiO₂.

The experimental data are satisfactorily described, up to the 60% degree of conversion of oxides into chlorides, by the Kolmogorov-Yerofeev equation [9]. The results of the analysis
Results of Kinetic Analysis of Experimental Data

<table>
<thead>
<tr>
<th>Chlorinated Matter</th>
<th>t. °C</th>
<th>n</th>
<th>K</th>
<th>E. (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al₂O₃</td>
<td>600</td>
<td>2.25</td>
<td>0.0046</td>
<td>40.6</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>2.60</td>
<td>0.0075</td>
<td>40.6</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>2.73</td>
<td>0.0090</td>
<td>40.6</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>2.81</td>
<td>0.0107</td>
<td>40.6</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>2.88</td>
<td>0.0116</td>
<td>40.6</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>600</td>
<td>1.91</td>
<td>0.0028</td>
<td>33.9</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>2.02</td>
<td>0.0061</td>
<td>33.9</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>2.13</td>
<td>0.0084</td>
<td>33.9</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>2.22</td>
<td>0.0105</td>
<td>33.9</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>2.31</td>
<td>0.0131</td>
<td>33.9</td>
</tr>
<tr>
<td>SiO₂</td>
<td>850</td>
<td>2.60</td>
<td>0.0025</td>
<td>30.5</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>2.65</td>
<td>0.0082</td>
<td>30.5</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>2.13</td>
<td>0.0118</td>
<td>30.5</td>
</tr>
</tbody>
</table>

show (table) that the processes of chlorination of α-Al₂O₃, γ-Al₂O₃, and SiO₂ have a comparatively complex nature; therefore, it is difficult to unequivocally draw a conclusion relative to the stage which limits them. The weak dependence of the rate constant on temperature, and the low values of the apparent energy of activation indicate that the interaction of the oxides with Cl₂ + CO evidently occurs in the diffusion region.

Conclusions. 1. Studied herein is the chlorination of α-Al₂O₃, γ-Al₂O₃, and amorphous SiO₂ with a mixture of Cl₂ + CO. It is established that the interaction of the modifications of oxides of aluminum begins at 235° C, and for SiO₂ — 680° C.

2. It is assumed that chlorination of α- and γ-Al₂O₃ occurs via the formation of an intermediate product (aluminum oxychloride AlOCl), with subsequent dissociation of this product at 480-560° C and polymorphous conversion of the liberated oxide into the α-form.

3. Kinetic analysis of the experimental data is carried out. The values of the apparent energy of activation for the processes of chlorination of the oxides are calculated.
REFERENCES