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PRODUCTION OF RARE-EARTH ELEMENT OXIDES BY THERMAL DECOMPOSITION OF DISPERSED SALTS AND THEIR AQUEOUS SOLUTIONS IN A PLASMA REACTOR

A.L. MOSSE, L.I. KRASOVSKAYA, I.A. DVINDENKO and A.V. GORBUNOV

Luikov Heat and Mass Transfer Institute, BSSR Academy of Sciences, Minsk, U.S.S.R.

Abstract - Production of oxides of rare-earth elements from dispersed aqueous salt solutions in an electric arc plasma reactor has been studied numerically and experimentally. Experimental studies have also been made for oxalates and carbonates.

1 - INTRODUCTION

Plasmachemical treatment of salts and their aqueous solution is one of the new methods to produce various-purpose metal oxides. Such an approach is especially promising when used in the industry of rare-earth element (REE). The latter is characterized by the processes including both separation of raw material by extraction and ion exchange, treatment of the resultant solutions of REE nitrates, sulfates and chlorides, that is their transformation into carbonates or oxalates, drying, roasting and thermal decomposition in muffle furnaces. This paper is aimed at studying direct production of oxides from REE carbonates, oxalates and nitrate solutions in arc plasma reactors.

2 - PLASMACHEMICAL PRODUCTION OF REE OXIDES FROM NITRATE SOLUTIONS

2.1 - Numerical Calculations of Interaction of Dispersed Nitrate REE solutions and an Air Plasma Flow

The basic equations of the mathematical model of the process are the equations of particle number conservation (1), of gas (2) and of condensed phase (3) continuity, of particle movement (4), of energy balance for dispersed material (5) and for plasma-forming gas (6):

\[ \frac{d}{dx} \left( \omega_p n_p \right) = 0 ; \]  
\[ \frac{d}{dx} \left( \omega g \rho g \right) = - n_p \omega_p \frac{dn_p}{dx} ; \]
where \( C_D \) is the coefficient of the aerodynamic drag of the droplet (particle), \( d \) is the particle diameter, \( g \) is the acceleration due to gravity, \( h \) is the specific enthalpy, \( m \) is the mass, \( n \) is the number of particles per unit volume, \( Q \) is the heat flux, \( S \) is the surface area, \( T \) is the temperature, \( \omega \) is the velocity, \( x \) is the distance along the axis of a reactor channel, \( \rho_p \) is the density of the condensed phase. The subscripts are: \( g \), gas; \( p \), totality of the particles, which form condensed phase; \( pr \), products of evaporation and reactions, \( W \), reactor wall.

Equations (1) - (6) are completed with expressions for determining the coefficients of intercomponent heat transfer, aerodynamic drag of the droplet, heat flux to the reactor wall and the density of the gas flow from the droplet surface, with approximate expressions of temperature dependencies of thermophysical characteristics of plasma, raw material and products as well as by equations, which describe the kinetics of chemical reactions and some other relations required to close the system of equations. Mathematically, the study of the heating and phase changes of particles by the described model is reduced to computer solution of the Cauchy problem for the system of ordinary differential equations. The computation algorithm is given in /1/.

The attempt to use such a mathematical model for studying thermal decomposition of REE nitrates was not a success. First, it was due to the lack of required kinetic data. Second, as in the lanthanum nitrate case, the available data /2/ gave contradictory results: for example, with the heat fluxes to a particle sufficient for its heating up to the temperatures exceeding that of thermal stability of lanthanum nitrate, the calculation degree of dissociation remains to be close to zero. Probably, the use of the kinetic relations obtained at heating rate of 5 K/min /2/ for plasma temperatures requires their correction. So, the assumption was made that the reaction of lanthanum nitrate dissociation proceeds only upon the nitrate achieves 1053 K /3/ and the dissociation degree (\( \alpha \)) is determined by the amount of heat got into a particle (droplet) (\( Q_p \)) and by the thermal effect of the reaction at this temperature (\( \Delta H_r \)); \( \alpha = Q_p / \Delta H_r \).

The following values were taken to be basic in calculations: the initial temperature of particles (droplets) was 298K, the initial particle velocity 4 m/s, temperature of the reactor walls was 500K, the pressure in the system of \( 10^5 \) Pa and the solution concentration was 50 mass.%. The initial temperature of plasma was varied between 3500 and 6000K.
Fig. 1 The length of complete lanthanum nitrate dissociation (a) and gas temperature corresponding to the moment of maximum lanthanum nitrate dissociation (b) vs initial droplet diameter. Plasma temperature: 1, 6000; 2, 5500; 3, 5000; 4, 4500; 5, 4000; 6, 3500 K.

Calculations were performed for the droplets with the initial sizes of 50, 100, 150, 200, 250 μm for the 0.1 m diameter reactor. As shown, for raw material and gas flow rates of 10 g/s each, the gas temperature corresponding to the moment of complete nitrate decomposition essentially exceeds particle temperature of 1053 K under different plasma temperatures.

Table 1 Calculated parameters of plasma treatment of 50% lanthanum nitrate solution for raw material and gas flow rates of 20 g/s and 10 g/s, respectively

<table>
<thead>
<tr>
<th>Parameters</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum degree of decomposition, %</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>70.6</td>
<td>53.4</td>
</tr>
<tr>
<td>Distance, cm</td>
<td>9</td>
<td>9.9</td>
<td>9.9</td>
<td>9.9</td>
<td>25.1</td>
<td>216</td>
<td>365</td>
<td>496</td>
</tr>
<tr>
<td>Time, ms</td>
<td>4.57</td>
<td>21.5</td>
<td>56.3</td>
<td>135</td>
<td>17.7</td>
<td>172</td>
<td>300</td>
<td>415</td>
</tr>
<tr>
<td>Gas temperature, K</td>
<td>2076</td>
<td>1812</td>
<td>1637</td>
<td>1421</td>
<td>1246</td>
<td>1058</td>
<td>1058</td>
<td>1058</td>
</tr>
<tr>
<td>Maximum degree of decomposition, %</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>97.6</td>
<td>108</td>
<td>108</td>
<td>108</td>
<td>108</td>
</tr>
<tr>
<td>Distance, cm</td>
<td>15</td>
<td>71.2</td>
<td>278</td>
<td>682</td>
<td>67</td>
<td>163</td>
<td>256</td>
<td>350</td>
</tr>
<tr>
<td>Time, ms</td>
<td>9.46</td>
<td>48.7</td>
<td>202</td>
<td>524</td>
<td>54.3</td>
<td>139</td>
<td>228</td>
<td>318</td>
</tr>
<tr>
<td>Gas temperature, K</td>
<td>1524</td>
<td>1313</td>
<td>1126</td>
<td>1058</td>
<td>1058</td>
<td>1058</td>
<td>1058</td>
<td>1058</td>
</tr>
</tbody>
</table>
conditions. This can hardly be considered rational as far as complete use of thermal energy of a plasma flow is considered. If the admissible final gas temperature is taken as 1500 K, then the initial plasma temperature should be 5000 K and below depending on droplet sizes (Fig. 1b, area between dashed lines). However, it is not always possible to use minimum permissible plasma temperatures because of extreme increase of the reactor length (Fig. 1a). On this view, the region of optimum parameters is the one hatched in Fig. 1a. It means that at raw material and gas flow rates of 10 g/s each, the initial droplet sizes may be varied from 50 to 100 μm, while the plasma temperature may range from 3500 to 5000 K.

Fig. 3 gives the nitrate lanthanum dissociation degree vs specific energy consumption for the process realized in 0.1m dia reactor at gas and solution flow rates of 10 and 20 g/s, respectively. In addition to specific energy consumption, to determine optimum process conditions requires regarding for the time of particle residence in the reactor necessary for complete nitrate dissociation and determining the reactor length, heat losses to reactor walls with a leaving gas and its temperature (Table 1). For example, at 6000 K complete dissociation of 50, 100, 150 and 200 μm particles can be achieved. However, taking into account the reactor length and final gas temperature, the regimes marked in Table 1 with asterisks should be considered most efficient. Fig. 3 gives the distribution of the most important parameters of plasma treatment of the lanthanum nitrate solution along the reactor channel for one of the above optimum conditions: particle size of 50 μm, initial plasma temperature of 5000 K and raw material consumption of 20 g/s. Under this regime, water is evaporated at a distance of 0.61 cm for 0.99 ms, the gas temperature reducing to 2106 K. Nitrate dissociation starts 1 cm apart, which corresponds to the time, 2.2 ms, of particle residence in the reactor.

The adequacy between the thermodynamical properties and temperature ranges of thermal stability of REE nitrates /3/ enables one to consider the reported data typical not only for lanthanum nitrate but also for nitrates of other rare-earth elements.
Pig. 3. Distribution along the reactor of: 1, lanthanum nitrate dissociation; 2, particle temperature; 3, gas temperature; 4, particle velocity; 5, gas velocity; 6, heat losses with gas; 7, heat losses to reactor walls; 8, amount of heat for raw material heating and constitutional and chemical changes. The initial plasma temperature is equal to 5000 K, particle size, to 50 μm.

2.2 - Experimental

Plasma treatment of REE nitrates was studied on an experimental setup having as a main unit a vertical water-cooled cylindrical reactor with a three-jet mixing chamber. A plasma flow was formed due to mixing of the jets of three electric-arc d.c. plasma generators spaced 120° apart and normal to the side surface of the mixing chamber. The reactor input power did not exceed 170 kW. The raw material supply unit was a pneumatic sprayer with liquid and air mixed inside it. The material flow rate through the sprayer was regulated by the pressure in the buffer solution tank and by the air flow rate. As follows from the calculation of sprayer dispersion at the solution and gas flow rates of 15 g/s and 0.75 g/s, respectively, the mean droplet diameter constituted 50 μm. The diameter of the main fraction droplets between 60 and 80 μm was found experimentally using the technique of droplet capture in an immersion medium [41].

The solution included 300 g/l mixture of three-valent REE nitrates. As referred to oxides, it included 55% of Ce₂O₃; 25% of La₂O₃; 12% of Nd₂O₃; 6% of Pr₂O₃ and 2% of Sm, Eu, Gd oxides, in total. Besides the solution contained 30g/l nitric acid, which corresponds to the acid content in liquid semiproducts of REE oxide production used, for example, for synthesizing the polyoxide abrasive material POLYRITE. The reaction flow was supplied from the reactor to a bunker to be removed then to a steel grid filter. The product output on the filter accounted for 60% of the
theoretically possible amount, that is the one in case of complete REE oxide capture on the filter regarding for Ce(+3)→Ce(+4) transition.

Table 2 gives the operating regimes of the setup and the results to estimate the efficiency of the process. A good agreement was observed between experimental data and theoretical results.

Table 2. Main characteristics of experimental plasma treatment of the dispersed REE nitrate solution

<table>
<thead>
<tr>
<th>Run</th>
<th>Flow rate, g/s</th>
<th>Reactor input, kW</th>
<th>Plasma temperature, K</th>
<th>G_p/G_s</th>
<th>Nitrato dissociation degree (a), %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Plasma gas G_g</td>
<td>Solution G_s</td>
<td>Disperser gas G_p</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>7.14</td>
<td>22</td>
<td>0.1</td>
<td>58.9</td>
<td>4210</td>
</tr>
<tr>
<td>2</td>
<td>10.8</td>
<td>8.8</td>
<td>0.4</td>
<td>79.5</td>
<td>4210</td>
</tr>
<tr>
<td>3</td>
<td>7.4</td>
<td>6.5</td>
<td>0.75</td>
<td>92.8</td>
<td>5400</td>
</tr>
<tr>
<td>4</td>
<td>6.8</td>
<td>6.5</td>
<td>0.55</td>
<td>92.7</td>
<td>5580</td>
</tr>
<tr>
<td>5</td>
<td>8.4</td>
<td>7.0</td>
<td>0.9</td>
<td>109.3</td>
<td>5430</td>
</tr>
<tr>
<td>6</td>
<td>8.1</td>
<td>6.9</td>
<td>0.8</td>
<td>103.8</td>
<td>5320</td>
</tr>
<tr>
<td>7</td>
<td>8.1</td>
<td>16</td>
<td>0.3</td>
<td>110.4</td>
<td>5540</td>
</tr>
<tr>
<td>8</td>
<td>8.1</td>
<td>13</td>
<td>0.8</td>
<td>106.1</td>
<td>5400</td>
</tr>
<tr>
<td>9</td>
<td>8.1</td>
<td>13</td>
<td>0.8</td>
<td>94</td>
<td>4910</td>
</tr>
</tbody>
</table>

2.3- REE Nitrato Thermal Decomposition Products

Fig. 4 shows the IR-spectra of the products obtained on the plasma-chemical setup as well as when the initial REE nitrate solution was evaporated and the dry residue was roasted within an hour in a laboratory furnace. Curve 4 stands for the plasma treatment product with 0.07% roasting losses. It is identical to the spectrum of product formed when a dry residue was roasted in the furnace at 500°C (curve 3). For the product obtained in run 1 (Table 2) with the solution flow rate increased up to 22 g/s and dispersed-gas pressure several times decreased, i.e. under less essential dispersion, the roasting losses accounted for 15.3%. The spectrum (curve 5) corresponding to such a product is intermediate between Spectra 1 and 2. For optimum conditions, roasting losses of the products on the filter and in the bunker constitute < 1%. This points both to complete nitrate dissociation and to the absence of recombinations interactions of REE oxides with nitrate oxides contained in a gas phase. The results of the X-ray phase analysis agree with the IR-spectroscopy data and indicate that the produced oxides have a cubic structure.

Statistical interpretation of the REE sample observations using the scanning electron microscope Nanolab-7 has shown that the oxide particle produced due to plasmachemical treatment are close to spherical ones. For one of the typical samples the shape factor $S=4*3.14*P_p/P_{St}$, where $S_p$ is the particle area and $P_p$ is the particle perimeter, ranged from the minimum 0.005 to the maximum 1.099 and costituted 0.859, on the average.

At $W > 180$, that is typical of the conditions under study, secondary aerodynamic atomization of solution droplets should be realized without essential changing of their temperature /5,6/. Estimations show that 60-80 μm droplets are atomised into secondary 2.5-4.5 μm droplets which is equivalent to oxide particles of 0.5-2.5 μm. This agrees with electron-microscope observations, which give the following length-wise particle distribution (chosen from 487 particles). Particles less than 2 μm
Fig. 4. IR-spectra of 1, dry residue due to evaporation of REE nitrate solution at 120°C; 2,3, products of dry residue roasting within an hour at 300 and 500°C; 4,5 products of plasma treatment of the nitrate solution with 0.07 and 15.3% roasting losses.

in size account for 24.3%, those from 2 to 4 μm, for 36.9%, particles from 4 to 6 μm make up 15.1% and large particles run 23.7%. No fused articles were observed, thus indicating such an essential decrease of the plasma flow temperature for the time of water evaporation and nitrate dissociation that even the finest oxide particles do not reach the melting point.

3 - PLASMACHEMICAL PRODUCTION OF REE OXIDES FROM OXALATES AND CARBONATES

Experimental studies were performed on the setup different from the one used for treating the solutions by the raw material supply unit. The greater bulk of studies was made for neodymium, cerium and yttrium oxalates. In a number of experiments carbonates of the cerium group were studied. The plasma temperature was varied from 4000 to 6000 K, the flow rate ratio ranged between 0.7 and 5. The power supplied to the plasma jet reactor per 1 kg raw material, i.e. the power spent to treat the raw material, was between 0.4 and 4.2 kWh/kg. As found, the degree of dissociation of oxalates and carbonates essentially depends on specific energy consumption which may be considered as a complex characteristic of a production process (Fig. 5). Studies of the composition and properties of products have shown that the products obtained at high dissociation degrees of salts comply with industrial requirements. In experimental production of cerium oxide, the content of Fe, Cu, Cr, Ni, Mn and Ca in products was controlled. Iron did not exceed 0.02%, the copper content was no more than 0.005%, the
Fig. 5. Degree of REE oxalates and carbonates dissociation vs specific energy consumption; a, neodymium oxalate; b, cerium oxalate; c, yttrium oxalate; d, cerium group oxalates

contents of other elements were much below these values. It should be noted, when plasmatrons operated at 120-140 A, iron and copper amounts were lower than at 200-220 A which is due to less essential electrode erosion in the former case.

Thus, an electric arc plasma may be used not only to produce REE oxides from nitrate solutions, but also to enhance thermal decomposition of REE oxalates and carbonates. Traditional furnace roasting of these salts takes much time, is low-efficient, and not all of the end product meets the requirements to its composition due to nonuniform heating of raw material.

REFERENCES

/3/. Glushakova, V.B., Polimorfism of Rare-Earth Element Oxides, Leningrad, 1967.