Thermodynamic Properties of Ln-O (Ln = La, Pr, Nd) Solid Solutions and Their Deoxidation by Molten Salt Electrolysis

by Toru H. OKABE¹, Koichi HIROTÀ², Yoshio WASEDA³ and K. T. JACOB⁴

The lanthanide metals lanthanum, praseodymium and neodymium containing 2200, 2600, 1850 mass ppm oxygen, respectively, were deoxidized to 20-30 ppm level at 1073 K by an electrochemical method. The metal to be deoxidized was used as the cathode in an electrolysis cell which consisted of a graphite anode and molten CaCl₂ electrolyte. The calcium metal produced at the cathode by electrolysis effectively deoxidized the lanthanide metal. Calcium oxide produced by deoxidation, dissolved in the melt. The liberation of carbon monoxide /dioxide at the anode was found to prevent accumulation of oxygen in the melt. For a quantitative discussion of the limits of deoxidation achievable by this technique, a thermodynamic investigation of the lanthanide-oxygen (Ln-O; Ln = La, Pr, Nd) solid solutions was conducted. The lanthanide metal, yttrium and titanium samples were immersed in calcium-saturated CaCl₂ melt, containing a small quantity of dissolved CaO, at 1063 K. The oxygen potential of the melt and the Ln-O solid solutions were obtained from the oxygen content of yttrium samples in equilibrium, and the known thermodynamic properties of yttrium-oxygen solid solution. The results were confirmed by using Y/Y₂O₃ equilibrium to control the oxygen potential of the molten salt reservoir. The oxygen affinity of the metals was found to decrease in the order: Y > Ti > Nd > Pr > La. The deoxidation results are consistent with the thermodynamic properties of the RE-O solid solutions.

KEY WORDS: Rare earth metals, Lanthanum, Praseodymium, Neodymium, Oxygen, Thermodynamics, Deoxidation, Purification, Electrochemistry

1. Introduction

Lanthanide (Ln) metals of high purity are required in several advanced applications (Gschneider, 1983; Gupta and Krishnamurthy, 1992). Although metallic impurities are reduced to 10 mass ppm level using available methods (Shindo and Miyazaki, 1992), removal of nonmetallic elements such as oxygen pose difficult problems. Depending on the source of the lanthanide metal, oxygen is usually present in amounts varying from 0.01 to 0.1% (100 to 1000 mass ppm). The strong affinity (Barin, 1989) and high solubility (Massalski, 1990; Carlson et al., 1974; Kuromoto et al., 1996) of oxygen renders the process of removal of the element from lanthanide metals extremely difficult. Reactive metals like calcium are required to deoxidize lanthanide metals. Unfortunately, the reactive metals often contain a substantial amount of impurities that contaminate the lanthanide metal. Thermodynamic properties of Ln-O solid solutions and the oxygen chemical potential that can be established in a deoxidation process set the ultimate limits of high-temperature purification of lanthanide metals.

Electrolysis of a pure fused salt such as CaCl₂ can be used to generate the reductant in situ at the surface of the lanthanide metal containing dissolved oxygen. Calcium oxide, which is formed as the deoxidation product, dissolves in molten CaCl₂, thus avoiding the build-up of a separate product phase at the reaction interface. By using a graphite anode, oxygen ions from the melt can be discharged as carbon monoxide or dioxide. Thus, the accumulation of oxygen in the melt is prevented and the activity of CaO in the fused salt is maintained at a low value. The usefulness of the electrochemical polarization method was demonstrated by melting titanium (Ti) containing less than 10 mass ppm oxygen, below the detection limit of the conventional gas analysis (Okabe et al., 1993). This method was also used for the removal of oxygen directly from yttrium-oxygen (Y-O) (Okabe et al., 1996 a), and heavy lanthanide-oxygen (Ln-O, Ln = Gd, Tb, Dy, Er) (Hirota et al., 1998) solid solutions. By utilizing the electrochemical method, these metals containing several thousand mass ppm oxygen were deoxidized below the 100 ppm level (Okabe et al., 1996 a; Hirota et al., 1998). The present article describes a study of deoxidation of lanthanide (Ln = La, Pr, Nd) metals by the electrochemical method. For a quantitative discussion of the deoxidation limit, the deoxidation experiments were preceded by thermodynamic investigation of the Ln-O solid solutions.

2. Experimental

2.1 Materials

The grade, amount and nature of the metal samples used in this study are listed in Table 1, along with the initial concentrations of oxygen and nitrogen. Two sets of metal
Table 1 Analytical values of oxygen and nitrogen initially present in lanthanide metal, yttrium and titanium samples used in the present study.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Grade</th>
<th>Oxygen concentration, (mass ppm)</th>
<th>Nitrogen concentration, (mass ppm)</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lanthium</td>
<td>99.9%</td>
<td>800</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Praseodymium</td>
<td>99.9%</td>
<td>100</td>
<td>&lt; 10</td>
<td>0.5 to 1.5 g / small pieces</td>
</tr>
<tr>
<td>Neodymium</td>
<td>99.9%</td>
<td>100</td>
<td>&lt; 10</td>
<td>0.5 to 1.5 g / small pieces</td>
</tr>
<tr>
<td>Yttrium</td>
<td>99.9%</td>
<td>9700</td>
<td>250</td>
<td>0.5 to 1.0 g / small pieces</td>
</tr>
<tr>
<td>Titanium-1</td>
<td>99.99%</td>
<td>210</td>
<td>10</td>
<td>0.1 to 0.2 g / small pieces</td>
</tr>
<tr>
<td>Titanium-2</td>
<td>99.9%</td>
<td>550</td>
<td>20</td>
<td>1.1 mm diameter wire</td>
</tr>
<tr>
<td>Titanium-3</td>
<td>99.9%</td>
<td>670</td>
<td>30</td>
<td>1.9 mm diameter wire</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>99.9%</td>
<td>2230</td>
<td>100</td>
<td>1.0 to 2.0 g / small pieces</td>
</tr>
<tr>
<td>Praseodymium</td>
<td>99.9%</td>
<td>2600</td>
<td>&lt; 10</td>
<td>1.0 to 2.0 g / small pieces</td>
</tr>
<tr>
<td>Neodymium</td>
<td>99.9%</td>
<td>1850</td>
<td>140</td>
<td>1.0 to 2.0 g / small pieces</td>
</tr>
<tr>
<td>Gadolinium</td>
<td>99.9%</td>
<td>2100</td>
<td>130</td>
<td>1.0 to 2.0 g / small pieces</td>
</tr>
<tr>
<td>Yttrium</td>
<td>99.9%</td>
<td>9700</td>
<td>260</td>
<td>1.0 to 2.0 g / small pieces</td>
</tr>
</tbody>
</table>

* a: Excluding gasous elements.
  b: Commercial grade.
  c: Electro-deposited metal.
  d: Used for comparison with lanthanide metals.

Table 2 Conditions for equilibration experiments at 1,093 K.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Samples*</th>
<th>Holding time</th>
<th>Mass of chemicals</th>
<th>Equilibrium forming oxygen potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>Pr, Nd, Y, Ti</td>
<td>690</td>
<td>350</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>CaO, Ca, Y, Y₂O₅</td>
<td>350</td>
<td>345</td>
<td>1.69</td>
</tr>
<tr>
<td>S</td>
<td>La, Pr, Nd, Y, Ti</td>
<td>1210</td>
<td>350</td>
<td>3.45</td>
</tr>
</tbody>
</table>

* 3-4 pieces each (see Table 1 for details)

Fig. 1 Reaction vessel used for equilibration at ultra low oxygen potentials.

samples were used: samples with high concentration of oxygen for deoxidation studies, and samples with lower oxygen content for thermodynamic measurements. The electrolyte CaCl₂ was prepared from reagent grade anhydrous powder of 99.9% purity by drying under vacuum at 600 K for more than 600 ks (7 days) prior to use. A high-purity (99.9%) graphite rod (120 mm-length, 60 mm-dia.) was used as the anode.

2.2 Measurement of the oxygen potential of RE-O solid solutions

A schematic diagram of the apparatus used for equilibration experiments is shown in Fig. 1. Five to ten pieces of lanthanide metals, yttrium and titanium were placed in a titanium cup filled with CaCl₂. The different metals were separated from each other by titanium foil. The titanium cup containing the metallic samples and CaCl₂ was sealed in an outer stainless steel vessel with an excess of calcium metal. To avoid contamination of the samples by impurities—mainly oxygen and nitrogen—in metallic calcium, calcium metal was physically isolated from the fused salt. Calcium was supplied to the CaCl₂ melt at unit activity via the vapor phase. The solubility of calcium metal in fused CaCl₂ is ~ 19 mol % (Eastman et al., 1960). The CaCl₂ acts as an oxygen reservoir in which oxygen potential is maintained at a constant value. The oxygen potential is established by the Ca/CaO equilibrium, with CaO present in the fused salt at reduced activity. The maximum solubility of CaO in CaCl₂ at 1,093 K is 18 mol % (Threadgill, 1965). In another experimental setup, a mixture of yttrium metal turnings and yttria (Y₂O₃) powder were placed in the titanium cup along with CaCl₂ but without calcium metal, to set the oxygen potential at a value corresponding to Y/Y₂O₃ equilibrium.

The sealed stainless steel vessel was heated in an electric furnace at 1,093 K. Experimental conditions are given in Table 2. The holding time was between 690 ks (8 days) and 1,210 ks (14 days), after which the vessel was quenched into water. The equilibration time was selected based on previous studies on the Ti-O (Okabe et al., 1991, 1992) and Y-O (Okabe et al., 1996) systems. Values of the diffusion coefficient of oxygen in praseodymium (Pr) and neodymium (Nd) are not available in the literature. However, the values for oxygen in Y, lanthanum (La) and gadolinium (Gd) are larger than the value in Ti (Madelung, 1982). It is anticipated that the diffusivity of oxygen in Pr and Nd metals used in this study is close to that in La and Gd.

After quenching the reaction vessel to room temperature, calcium-saturated fused salt in the titanium cup was mechanically removed, and the lanthanide and titanium samples were collected. The lanthanide samples were cleaned in water, and mechanically polished. The titanium samples were cleaned in water, alcohol and acetone, and then allowed to dry.

2.3 Electrochemical removal of oxygen from RE-O solutions

Since the principle of the electrochemical deoxidation technique has been discussed earlier (Okabe et al., 1993, 1996 a), only a brief outline of the experimental procedure is presented here. A schematic illustration of the apparatus used for electrochemical deoxidation is shown in Fig. 2. Dehydrated CaCl₂ flux was contained in a steel crucible (90 mm-dia., 200 mm-height) and set in a vertical stainless steel reaction tube, closed at one end. A cathode basket, made from strands of Ti wire, about 50 mm long, contained lanthanide samples (about 1-2 g each), yttrium and titanium (about 0.1 g). The anode, the cathode and the thermocouple tubing were inserted into the reaction tube through a gas-tight water-cooled stainless steel head.

After assembling the cell, the reaction tube was evacuated and checked for gas-tightness. The cell was then heated to about 600 K in vacuum to remove residual moisture. High-purity argon gas was subsequently introduced into the reaction tube, and the temperature was increased to a preset value between 1,073 and 1,173 K. The temperature of the molten salt was measured using a chromel-alumel thermocouple protected by a nickel sheath. After melting of CaCl₂, the high-purity graphite anode was lowered into the molten salt, and pre-electrolysis was conducted for eliminating residual metallic and gaseous impurities in the molten salt. A d.c. voltage of about 3.2 V was applied between the crucible and the graphite.
anode for about 4 ks, producing a current of about 2 A through the molten salt. About 50 g of silver was placed at the bottom of the crucible to absorb the calcium metal produced during pre-electrolysis.

After pre-electrolysis, the Ti cathode basket containing the lanthanide samples was lowered into the molten salt and positioned about 30 mm from the anode. Controlled current electrolysis was performed. The experimental parameters are summarized in Table 3.

After reaction, the electrodes were removed from the melt, and the cell was allowed to cool in a stream of argon gas. In some cases, it was possible to use the same salt and anode to deoxidize additional metal samples (Exp. E 01 and E 03 in Table 3). The fused salt adhering to the surface of metal samples was removed mechanically. The samples were carefully polished and analyzed for dissolved gases, oxygen and nitrogen, and metallic trace elements.

2.4 Chemical analyses

The concentrations of oxygen and nitrogen in the metal samples were determined by an inert gas fusion-infrared absorption method (LECO TC-436 analyzer). Prior to the oxygen and nitrogen analyses, the samples were again mechanically polished, and the titanium samples were chemically etched with a 1:4:10 mixture of HF: HNO₃: H₂O. For oxygen and nitrogen extraction, 0.1 g of the sample enclosed in 1 g of platinum or nickel foil was dropped into a graphite crucible and heated to a temperature above 2,000 K. The average blank values of oxygen and nitrogen during analysis were 50 (± 1.0) µg and 0.5 (± 0.2) µg, respectively. The concentrations of calcium and other metal impurities in the samples were determined by X-ray fluorescence analysis (XRF, Rigaku 2270) and by inductively coupled plasma-atomic emission spectrometry (ICP-AES, SEIKO SPS-1200 A).

3. Results and Discussion

3.1 Thermodynamic properties of oxygen in RE-O solid solutions

The results of the equilibration experiments at 1,093 K are summarized in Table 4. In Exp. F, the metal samples were equilibrated with calcium-saturated CaCl₂ melt. The oxygen concentration of yttrium and titanium samples was found to decrease during equilibration. The metal samples were equilibrated with Y/Y₂O₃ via the molten salt in Exp. S. In this case, the oxygen content of yttrium was close to the solubility limit reported in the literature (Carlson et al., 1974), and oxygen concentration in the lanthanide metals (La, Pr, and Nd) ranged between 50 and 350 ppm.

Although oxygen concentrations of yttrium and lanthanide samples were found to reach constant values during the experiments, oxygen content of titanium samples did not attain equilibrium. The oxygen content of titanium samples after the experiment depended on their initial concentration. This is probably due to slow diffusion of oxygen in solid titanium compared to that in the other metals at this temperature (Okabe et al., 1998). Several experiments were performed at temperatures above 1,093 K to obtain the temperature dependence of the Gibbs energy of solution of oxygen in the lanthanide metals. However, it was difficult to recover the metallic samples suitable for the oxygen analysis. The samples were found to be deformed in many cases, probably because of the relatively low melting point of the light rare-earth metals.

The nitrogen concentration of the equilibrated samples was found to be independent of the experimental conditions. During the high temperature experiment, the nitrogen content increased from the initial value by about 10 ~ 100 parts per million for lanthanide metals, and 10 ~ 1,000 parts per million for titanium. Calcium concentration in La metal was unchanged from its initial value (~ 150 ppm.), but for Pr and Nd the concentration increased to 1 and 0.26 mass %, respectively, during the experiment. These results indicate that Pr and Nd have relatively larger solubility of calcium than La at 1,093 K.

The relationship between the square root of oxygen partial pressure, pO₂, and equilibrium oxygen concentration, C₀ (mass ppm) for the Ln-O solid solutions at 1,093 K is shown in Fig. 3. The values of pO₂ were calculated from the equilibrium oxygen concentration in the yttrium samples and known thermodynamic properties of the Y-O solid solution (Okabe et al., 1998 b). The data, especially for the La-O system, are associated with large relative uncertainties in oxygen analysis (~ ±10 ppm). The solid lines represent Sieverts' law for Ln-O systems investigated in the present study. Dashed
lines in the figure show the corresponding relationship for oxygen in Gd, Tb, Dy, Er, and Y, which were determined in previous studies (Okabe et al., 1996b, 1998). The slope of each line gives the value of the Sieverts’ law constant.

The affinity between oxygen and lanthanide metals increase with atomic number of the lanthanide metal. For all the systems investigated, the affinity between oxygen and the lanthanide metals is weaker compared to that of yttrium metal.

The standard Gibbs energy change for the solution of diatomic oxygen gas in lanthanide metal, ΔG°_1, can be evaluated from the results of this study. For the reaction,

\[ \frac{1}{2} \text{O}_2(g) = \text{O} \text{(Ln)} \quad \text{(1)} \]

\[ \Delta G°_1 = -R \ln \left( \frac{\text{O}_2}{\text{O}} \right) \left[ \text{mass } \% \text{O}_2 \right] \quad \text{(2)} \]

where \[ \left[ \text{mass } \% \text{O}_2 \right] \] is the equilibrium concentration in mass \% of oxygen in Ln-O solid solution at temperature \[ T \text{, } \frac{\text{O}_2}{\text{O}} \text{(Ln)} \] is the Sievert's constant (in atm), and \[ \rho_o \] is the oxygen partial pressure in atm. The standard state for dissolved oxygen is an infinitely dilute solution in which the activity of the solution is equal to its concentration in mass \%. When Sievert’s law is obeyed by oxygen dissolved in the metal, the value of the Sievert’s constant is unity.

The standard Gibbs energy change associated with the solution of oxygen gas in yttrium is available in the literature (Okabe et al., 1996b). For the reaction,

\[ \frac{1}{2} \text{O}_2(g) = \text{O} \text{(Y)} \quad \text{(3)} \]

\[ \Delta G°_3 = -R \ln \left( \frac{\text{O}_2}{\text{O}} \right) \left[ \text{mass } \% \text{O}_2 \right] \quad \text{(4)} \]

Combining Eq. (2) and Eq (4) yields,

\[ \Delta G°_1 = \Delta G°_3 - R \ln \left( \frac{\text{O}_2}{\text{O}} \right) \left[ \text{mass } \% \text{O}_2 \right] \quad \text{(5)} \]

The standard Gibbs energy change for reaction (1), \[ \Delta G°_1 \], can be determined from the value of \[ \Delta G°_3 \] (~531 kJ at 1,093 K) available in the literature (Okabe et al., 1996b) and the measured distribution coefficient of oxygen between the lanthanide metal and yttrium, \[ K_{\text{Ln/(Y)}} \left[ \text{mass } \% \text{O}_2 \right] \], assuming Sieverts’ law to be valid:

\[ \Delta G°_1 = \Delta G°_3 - R \ln \left( K_{\text{Ln/(Y)}} \right) \quad \text{(6)} \]

The values for standard Gibbs energy of dissolution of oxygen gas are: −494 kJ/molO for La, −490 kJ/molO for Pr, and −494 kJ/molO for Nd at 1,093 K.

In Fig. 4, the values of \[ \Delta G°_1 \] at 1,093 K for the three lanthanide metals are compared with the standard Gibbs energies of formation of their respective sesquioxides, \[ Y_2O_3 \text{ and } CaO \], per mole of O (Barin, 1989). The figure shows that lanthanide metals (Ln = La, Pr, Nd) containing 1 mass \% oxygen can be deoxidized either by calcium or yttrium metal. Furthermore, it is seen that oxygen potentials for the Ln mass \% O solid solutions (\[ \Delta G°_1 \]) is slightly higher than that for their respective metal/oxide equilibrium. This indicates that oxygen solubility in these metals (La, Pr, Nd) is less than 1 mass \%.

The solid lines in Fig. 4 represent \[ \Delta G°_1 \] for Gd, Tb, Dy, Er, determined separately in the temperature range 1,093 to 1,223 K (Okabe et al., 1998). These lines locate lower than those for the three metals covered in this study. By utilizing the electrochemical deoxidation technique, ultra low oxygen potentials (0.5 RT ln \[ \rho_o = -560 \pm 10 \text{ kJ} \], \[ T = 1,200 \text{ K} \]) can be attained (Okabe et al., 1998). The theoretical deoxidation limit of the process for the Ln-O solid solutions at 1,093 K is below the detection limit of the gas analyzer (10 mass ppm O for 0.1 g sample) at the same oxygen potential.

3.2 Deoxidation by molten salt electrolysis

Some representative analytical results for oxygen concentration in lanthanide, yttrium and titanium samples before and after electrochemical deoxidation are given in Table 5. As indicated by the results of experiments E 01 and E 03, lanthanum, praseodymium and neodymium were deoxidized to 30 ~ 30 mass ppm level. Yttrium and titanium were used as a reference materials in order to facilitate the determination of the value of the partial pressure of oxygen at the cathode. From the value of the residual oxygen concentration in yttrium, the effective oxygen partial pressure of the cathode metal is estimated as approximately 10^-2 atm at 1,073 K. During electrochemical deoxidation, equilibrium may not be fully established. Considering slow diffusion of oxygen in solid Y-O at this temperature, the oxygen potential at the cathode surface might be up to one order of magnitude lower than the value calculated from its average bulk composition.

Nitrogen concentration of the metal samples either remained unchanged or decreased by about 10 ~ 100 mass ppm during electrolysis. As there is no thermodynamic data on nitrogen solubility in the metal or the molten salt for the systems investigated, a quantitative discussion of the behavior of nitrogen cannot be attempted at this stage.

Table 5

<table>
<thead>
<tr>
<th>Sample*</th>
<th>Initial</th>
<th>After deoxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>2200</td>
<td>30, 50, 80</td>
</tr>
<tr>
<td>Pr</td>
<td>2500</td>
<td>40, 50, 20, 40</td>
</tr>
<tr>
<td>Nd</td>
<td>1800</td>
<td>30, 50, 20, 40</td>
</tr>
<tr>
<td>Y</td>
<td>9700</td>
<td>3500, 4000, 6500</td>
</tr>
<tr>
<td>Ti</td>
<td>210</td>
<td>20, 100, 200</td>
</tr>
</tbody>
</table>

* See Table 1 for details

Table 5 Chemical analysis of lanthanide metal samples before and after electrochemical deoxidation.

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Table 6 Summary of deoxidation results for lanthanide elements obtained by various techniques.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method</th>
<th>Reference</th>
<th>Temperature (K)</th>
<th>Holding time (hr)</th>
<th>Oxygen concentration (mass ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>Oxide</td>
<td>Fort et al., 1981</td>
<td>1193</td>
<td>34</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Oxide</td>
<td>Corbett et al., 1986</td>
<td>1123</td>
<td>192</td>
<td>2095</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>Kamihara et al., 1993</td>
<td>1143</td>
<td>18</td>
<td>2100</td>
</tr>
<tr>
<td></td>
<td>N/2O</td>
<td>This Study</td>
<td>1093</td>
<td>336</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>Elec.</td>
<td>This Study</td>
<td>1073</td>
<td>8</td>
<td>2200</td>
</tr>
<tr>
<td>Pr</td>
<td>SSE*</td>
<td>Muirhead &amp; Jones, 1976</td>
<td>1103</td>
<td>520</td>
<td>516</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>Kamihara et al., 1993</td>
<td>1143</td>
<td>18</td>
<td>1300</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>Ogasawa et al., 1993</td>
<td>1153</td>
<td>12</td>
<td>2000</td>
</tr>
<tr>
<td></td>
<td>Elec.</td>
<td>This Study</td>
<td>1073</td>
<td>10</td>
<td>2600</td>
</tr>
<tr>
<td>Nd</td>
<td>SSE*</td>
<td>Mattocks et al., 1977</td>
<td>1113-1163</td>
<td>750</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>Oxide</td>
<td>Corbett et al., 1986</td>
<td>1063</td>
<td>257</td>
<td>155</td>
</tr>
<tr>
<td></td>
<td>SSE*</td>
<td>Fort et al., 1987</td>
<td>1093-1136</td>
<td>500</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>CaO</td>
<td>Kamihara et al., 1993</td>
<td>1143</td>
<td>18</td>
<td>830</td>
</tr>
<tr>
<td></td>
<td>Oxide</td>
<td>Sano et al., 1997</td>
<td>1723</td>
<td></td>
<td>3000</td>
</tr>
<tr>
<td></td>
<td>Elec.</td>
<td>This Study</td>
<td>1073</td>
<td>8</td>
<td>1850</td>
</tr>
</tbody>
</table>

*: Solid State Electrometallurgy
**: Chemical Deoxidation

Substantially smaller than that after the equilibration experiment. This might be indicative of smaller diffusivity of calcium in Pr and Nd compared to oxygen, and the possibility of kinetic control of calcium contamination in the lanthanide metals.

Compared in Table 6 are the results of electrochemical deoxidation obtained in this study with data obtained by other deoxidation treatments reported in the literature (Fort et al., 1981; Corbett et al., 1986; Kamihara et al., 1993; Muirhead et al., 1976; Ogasawa et al., 1993; Mattocks et al., 1977; Fort et al., 1987; Sano et al., 1997). The electrochemical method outlined here is seen to be very effective for removing oxygen directly from the Ln-O solid solutions.

Kamihara et al. (1993) have investigated deoxidation of lanthanides by calcium metal at 1143 K resulting in the formation of essentially pure CaO. They obtained metals containing between 30 and 570 ppm oxygen. From the thermodynamic information obtained in this study and the standard Gibbs energy of formation of CaO (ΔG^°_{CaO} = -528 kJ/mol) (Barin, 1989), it is possible to estimate the thermodynamic deoxidization limit. Calculated equilibrium oxygen concentrations in La, Pr, and Nd corresponding to Ca/CaO equilibrium at 1143 K are 180, 340, and 530 mass ppm, respectively. The values obtained from experiment are considered to be in fair agreement with the theoretical values, when considering the temperature difference between the experiment and theoretical estimation and the errors associated with the thermodynamic data.

Formation of oxide halide of lanthanide elements can be utilized (Corbett et al., 1986; Sano et al., 1997) for removing oxygen dissolved in lanthanide metals. In chloride-rich oxychloride melt, the activity of the oxide is considerably reduced. Oxygen concentrations ranging from 160 to 420 ppm have been achieved using this technique. The effectiveness of the process for oxygen removal increases with increasing initial oxygen concentration of the metal, because the deoxidation limit depends on the oxide ion concentration in the oxysalts. The stability field diagram for the Nd-O-Cl system at 1100 K, displayed in Fig. 5, is helpful for understanding the physico-chemical rationale of the oxychloride process. The thermodynamic data for NdO_2, NdCl_3, and NdOCl from Barin (1989) and for Nd-O solid solutions from this study were used in the construction of the diagram. When neodymium containing high concentration of oxygen is reacted with NdCl_3, oxygen in the metal will be transferred to the molten salt until the salt is saturated and NdOCl forms as a separate phase. The partial pressures of O_2 and Cl_2 are defined by power "b" on the diagram, when the metal coexists with oxide-saturated NdCl_3 and NdOCl. The corresponding equilibrium oxygen concentration in the metal is just above 100 mass ppm. If the initial oxygen content of the metal is relatively low and large amount of the salt phase is present, then there may not be enough oxygen to form NdOCl as a separate phase, and the activity of NdOCl in the fused salt may be less than unity. The lines corresponding to reduced activities (0.1 and 0.01) of NdOCl are also shown in Fig. 5. The equilibrium partial pressures for metal/fused-salt equilibrium are then defined by points "c" and "d", respectively. For each order of magnitude reduction in the activity of NdOCl, the equilibrium oxygen concentration in the metal is also reduced by an equal amount.

Solid state electrometallurgy (SSE) is effective for removing not only oxygen but also other impurities (Muirhead et al., 1976; Mattocks et al., 1977; Fort et al., 1987) from lanthanide metals; in this sense, the method appears to be one of

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Fig. 5 Stability-field diagram for the system Nd-O-Cl at 1100 K, illustrating the partial pressures and the limiting oxygen concentration achievable in the oxychloride deoxidization process for Nd.
Ln-O (Ln = La, Pr, Nd) 固体溶媒熟解法によるこれらの固体溶媒の脱酸

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酸化剤金属試料を研磨したカソードとグラファイトインアードを用いて溶媒CaCl₂を1,073 Kで脱酸した結果、それぞれ2,200、2,600、1,850 mass ppmの酸素を含むラジウム、プルオニウム、ネオジム試料中の固態酸素を20〜30 ppmレベルまで低減できた。電気化学的手法を用いて酸素のカルシウムを利用して熱分解し、反応生成物のCaOを溶融塩に溶解してアンドート地において酸素ガスとして系外に逃すことにより、効率的に脱酸反応を進行させた。また、脱酸限界を定量的に評価するため、脱酸実験に先立ってラジオアイドー酸素固体図の(Ln-O: Ln = La, Pr, Nd)熟解学的性質の測定実験も行った。LnO 固体溶媒試料を、酸素の活量係数が既知のイオンジウム−酸素固体溶媒とともに溶融塩中で平衡させ、参照金属の酸素の濃度よりLnO 固体溶媒中の酸素の活量係数を決定した。平衡実験には、主として、1,093 KのCaOの活量が低いカルシウム酸化物を用いたが、Y2O3−CaO平衡実験も行った。本研究により金属酸素の親和力は、Y > Ti > Nd とPr > La の順で小さくなることが明らかとなった。また、脱酸実験結果は、得られたLnO 固体溶媒の熟解学的性質とよい一致を示した。

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