High Temperature Oxidation Kinetics of Dysprosium Particles

Brian J. Jaques
Boise State University

Darryl P. Butt
Center for Advanced Energy Studies

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Brian J. Jaques, Darryl P. Butt *

Department of Materials Science and Engineering, Boise State University, 1910 University Dr., Boise, ID 83725, USA
Center for Advanced Energy Studies, 995 University Blvd., Idaho Falls, ID 83415, USA

Abstract

Rare earth elements have been recognized as critical materials for the advancement of many strategic and green technologies. Recently, the United States Department of Energy has invested many millions of dollars to enhance, protect, and forecast their production and management. The work presented here attempts to clarify the limited and contradictory literature on the oxidation behavior of the rare earth metal, dysprosium. Dysprosium particles were isothermally oxidized from 500 to 1000 °C in N2–(2%, 20%, and 50%)O2 and Ar–20% O2 using simultaneous thermal analysis techniques. Two distinct oxidation regions were identified at each isothermal temperature in each oxidizing atmosphere. Initially, the oxidation kinetics are very fast until the reaction enters a slower, intermediate region of oxidation. The two regions are defined and the kinetics of each are assessed to show an apparent activation energy of 8–25 kJ/mol in the initial region and 80–95 kJ/mol in the intermediate oxidation reaction region. The effects of varying the oxygen partial pressure on the reaction rate constant are used to show that dysprosium oxide (Dy2O3) generally acts as a p-type semiconductor in both regions of oxidation (with an exception above 750 °C in the intermediate region).

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1. Introduction

Global interest in rare earth element production and management has significantly increased in the past few years. In the year 2008, nearly $190 million worth of rare earth materials were imported and used in the U.S. alone. Such “strategic materials” are sought after for use in metallurgical applications and alloys, electronics, catalysts, and cathode ray tubes [1]. Compared to the light rare earth metals, relatively little published literature exists for praseodymium, promethium, thulium, lutetium, and dysprosium (also known as the heavy rare earths) although scientific interest in these metals is on the rise. In the next forty years, Hoenderdaal et al. [2] project that the demand for dysprosia (Dy2O3) and other dysprosium compounds will increase to between 7 and 25 times (to 14–50 ktons) from the 2010 demand. Modern studies suggest that dysprosium is more abundant than 44 other elements in the earth’s crust (5.2 mg/kg) contrary to earlier perception, making its utility more available for emerging materials technologies [3].

According to Hoenderdaal et al. [2], the proposed increase in demand is due to the future of magnetic applications (electric motors) due to dysprosium’s exceptional magnetic moment of 10.8 Bohr magnetrons, which is second only to holmium [3], and its ability to induce coercivity as an alloying agent or dopant [3,4]. However, the demand for dysprosium has become more prevalent in other applications due to its many other interesting properties. For instance, dysprosium’s isotopes strongly absorb neutrons which lead to its use in nuclear reactor control rod moderator materials [3,5–7] and Dy2O3 has been considered as a substitute for SiO2 in high-k dielectric applications due to its large band gap (4.9 eV) and dielectric constant (14) [8,9]. Additionally, dysprosium mononitride (DyN) has been postulated as a suitable surrogate for americium mononitride (AmN) due to its similar physical and chemical attributes in studying its sintering and alloying effects in spent nuclear fuel reprocessing [10–15]. DyN has also been investigated as a material for ferromagnetic and semiconductor superlattice structures for spintronic applications [16–18].

Although a few manuscripts and reports were published in the late 1950s and 1960s on the oxidation behavior of dysprosium [19–22], the experiments were performed on monolithic samples (rather than powders or particles) and the results appeared to be contradictory. Of particular interest in this study is the high temperature oxidation kinetics of elemental dysprosium in the temperature range of 450–1000 °C in N2–(2%, 20%, and 50%)O2 and Ar–20% O2 using simultaneous thermal analysis techniques. An understanding of the oxidation kinetics of dysprosium has a wide
range of implications ranging from semiconductor and electronics applications, to “green” energy and electric motor (magnetic) applications, to nuclear power generation applications.

2. Experimental details

The starting material used to study the high temperature oxidation kinetics of dysprosium was dysprosium particles (99.7 wt% purity, ESPI) sieved through a 40 mesh (420 μm) sieve (Fig. 1). The particles had a surface area of 0.20 ± 0.06 m² g⁻¹, as determined by nitrogen adsorption Brunauer–Emmett–Teller (BET) techniques. The particles were characterized using X-ray diffraction (XRD) with a Cu Kα source, as shown in Fig. 2. Additionally, minor concentrations of iron, yttrium, terbium, and tungsten (<3 ppm each) were identified in the starting material using a Thermo XSeries II quadrupole inductively coupled plasma mass spectrometry (ICPMS).

Oxidation experiments were performed using a high resolution simultaneous thermal analyzer (Netzsch STA 449) which is capable of collecting thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data simultaneously. Approximately 30 mg of the dysprosium particles (sealed and stored in an argon filled glovebox) was loaded into an 85 μL alumina combustion crucible which was immediately loaded in the STA furnace. In each case, a vacuum purge cycle was started using an oxygen-gettered ultra high purity (UHP) argon gas (<1 ppb oxygen). Once the chamber was fully purged, the thermal profile was started. The four process gases used for the oxidation studies presented in this manuscript were certified mixtures of N₂–(2%, 20%, and 50%) O₂ and Ar–20% O₂.

Non-isothermal oxidation data were first collected to determine suitable parameters to study the isothermal oxidation behavior. In the non-isothermal experiments, the furnace was ramped from 25 to 1100 °C at 20 °C/min in a gas flow rate of 100 mL/min while TGA and DSC data were collected. Each data set was replicated at least twice and the results were averaged. Isothermal oxidation experiments were completed in each of the atmospheres from 500 to 1000 °C. In each case, the temperature of the furnace was allowed to equilibrate for 5 min at the desired temperature prior to introducing the oxidizing atmosphere and the dysprosium particles were oxidized to completion. Each isothermal oxidation experiment was repeated 3–4 times. The isothermal oxidation data were averaged together and then the average mass gain was normalized by subtracting the initial mass gain (which was less than 0.1% in all cases). To account for geometry, the data was then divided by the maximum mass obtained and then multiplied through by the specific surface area (where the specific surface area is equal to the initial mass multiplied by the surface area of the particles obtained from B.E.T., as described above). This allowed for a direct comparison of data and accurate kinetics analysis using the specific mass gain with units of μg/cm².

3. Results and discussion

Dysprosium is reported to have a hexagonal close packed (HCP) crystal structure and a melting temperature of 1412 °C [3], although there also exists two other allotropes; a low temperature (<−187 °C) orthorhombic phase (Cmcm) and a high temperature (>1381 °C) face centered cubic (FCC) phase (Im3m) [3]. As seen in Fig. 2, the starting material for the oxidation studies presented here is primarily a HCP dysprosium phase (P63/mmc) with a small fraction of the high temperature FCC phase. The HCP and FCC cubic phases were identified using X-ray diffraction data from the International Centre for Diffraction Data (ICDD) database provided by Spedding et al. [23] and Curzon et al. [24], respectively. Additionally, it is important to note that the diffraction peaks were slightly shifted from the reported positions (depicted by the diamonds and circles in Fig. 2), which is discussed in more detail later in this manuscript. Although the authors understand that the geometry and morphology of the particles are not ideal for an oxidation kinetics study, the authors were unable to identify a vendor to provide single phase dysprosium particles (with minimal oxide). However, the dysprosium particles from ESPI were nearly single phase and had a low surface area which reduced unwanted oxidation during handling.

Fig. 2 also shows a typical diffraction pattern obtained from a fully oxidized dysprosium sample in each of the atmospheres and temperatures investigated. The particular diffraction pattern shown is the result of oxidizing the dysprosium particles completely in N₂–20% O₂ at 800 °C, which formed a cubic Dy₂O₃ phase (Ia₃), as compared to data in the ICDD database provided by Swanson et al. [25]. Additionally, as shown by the inverted triangles, the oxide diffraction peaks agree well with the published values for Dy₂O₃. It is also worth pointing out that there are peaks in all of the oxide diffraction patterns that were not able to be indexed, as shown in Fig. 2.

TGA and DSC data were simultaneously collected during non-isothermal oxidation of dysprosium particles in each of the

![Fig. 1. Images of the dysprosium particles used as the starting materials for the high temperature oxidation reaction study. The particles have a surface area of 0.20 ± 0.06 m² g⁻¹ as determined via gas adsorption techniques.](image-url)
atmospheres. The results are plotted in Fig. 3. From this figure, it is seen that the oxidation behavior in N\textsubscript{2}–20\% O\textsubscript{2} and Ar–20\% O\textsubscript{2} is very similar throughout the entire reaction although the onset of the reaction in the nitrogen carrier gas occurs at a slightly greater temperature (approximately 20 °C). Additionally, the TGA trace from oxidation in N\textsubscript{2}–2% O\textsubscript{2} follows similar behavior as the 20\% O\textsubscript{2} atmospheres but the onset of the reaction occurs at a slightly higher temperature: the onset of oxidation in 2\% O\textsubscript{2} occurs at 45 °C and 26 °C greater temperatures when compared to the argon and nitrogen carriers of 20\% O\textsubscript{2}, respectively. When comparing the DSC traces in each of the oxidizing atmospheres, there exists an exothermic peak at approximately 550 °C in all atmospheres except for the oxidation reaction in N\textsubscript{2}–2\% O\textsubscript{2}.

The results of the non-isothermal experiments informed and subsequently lead to the region of study for the isothermal oxidation temperatures reported in this manuscript. As previously stated, isothermal oxidation experiments of dysprosium particles were completed 3–4 times at each temperature and atmosphere to arrive at average behaviors, which was used for the kinetics analysis. Fig. 4 shows typical TGA data variability between duplicated oxidation experiments. In this figure, TGA data obtained from oxidizing dysprosium particles from 650 to 800 °C in N\textsubscript{2}–20\% O\textsubscript{2} are used to show the typical data variability, which is minimal. The variability that is present is due to the cumulative effects of several factors, including: irregular and non-uniform particle morphology (Fig. 1), the presence of a slight amount of secondary phase in the starting material (Fig. 2), the presumed presence of a native oxide and unquantified amounts of dissolved oxygen, the likelihood of residual stresses in the starting material due to vendor processing (as indicated by the slight leftward shift in the diffraction peaks when compared to the published values [23] shown in Fig. 2), as well as the sampling technique used (i.e. a scoop sampling technique was used whereas a more effective and representative sampling technique could have been used, such as powder riffling). However, since multiple data sets were averaged for all of the analysis, the assumption is that the results are representative. It should also be noted that although the effects of particle size distribution will influence the kinetics of thermal oxidation, no effort was made in this investigation to de-convolute such effects other than to account for the starting surface area and a nominal shrinking core.

Fig. 5 shows the isothermal oxidation behavior of dysprosium particles in N\textsubscript{2}–20\% O\textsubscript{2} from 500 to 950 °C. Two interesting observations from Fig. 5 are: there is a distinct inflection where the oxidation kinetics slow and the specific mass gain where the inflection occurs increases with isothermal oxidation temperature. The inflection, or transition from relatively rapid to slower oxidation kinetics, is seen more clearly in Fig. 5b, which focuses on the first two minutes of the oxidation reaction. Similarly, an inflection in the mass gain rate is observed in the TGA data of all of the oxidizing atmospheres, as discussed later. Additionally, each of the TGA traces in the initial region of oxidation exhibits nearly identical mass gain.
rates for each atmosphere; the primary difference being that the inflection, as previously discussed, occurs at a larger specific mass gain with increasing isothermal oxidation temperatures.

As seen by the inflections illustrated in the insets of Figs. 4 and 6 as well as in Fig. 5b, the mechanism for oxidation appears to change after some specific mass gain, which is affected by temperature as well as the oxidation atmosphere. Accordingly, a single oxidation model is not capable of describing the entire oxidation reaction and thus, each of the two regions were defined for individual kinetics assessment in each atmosphere and at each isothermal oxidation temperature. The two regions of differing oxidation behavior in each of the four oxidizing atmospheres are
quantified in Fig. 7 and labeled as the initial and intermediate regions, respectively. The initial region is defined by the onset of mass gain to the onset of the inflection and the intermediate region begins immediately after the inflection through a reaction extent of 95%, or a specific mass gain of $4.85 \times 10^8$ g/cm$^2$. Each data point in Fig. 7 corresponds to the average reaction extent, $\alpha$, defining the end of the initial region of oxidation and the beginning of the intermediate region of oxidation (resulting in a point nearly centered on the inflection in the mass gain data shown in the insets of Figs. 4 and 6 as well as in Fig. 5b). The reaction extent ($\alpha$) is defined as the ratio of mass gain at time $t$ divided by the total mass gain observed in the oxidation reaction.

An interesting observation from Fig. 7 is that the change in oxidation kinetics (from initial to intermediate reaction kinetics) occurs at lower reaction extents (i.e., the initial oxidation region is a smaller percentage of the overall reaction) in the Ar–20% O$_2$ oxidizing atmosphere when compared to the nitrogen carrier gases. Additionally, the oxidation reaction is nearly fully defined by the initial reaction region at temperatures equal to and greater than 900, 950, and 1000 °C in N$_2$–2% O$_2$, N$_2$–50% O$_2$, N$_2$–20% O$_2$.
respectively, whereas the initial reaction region comprises only 30–40% of the oxidation reaction at the same temperatures in Ar–20% O₂.

As previously stated, the published literature on the oxidation kinetics of dysprosium is limited; very few publications were found that describe the oxidation kinetics of bulk materials and
none were found describing the behavior of powders or finely distributed particles. Of the literature found, the mechanism of the oxidation reaction is presumed to remain constant over the entire reaction at each temperature, contrary to the results presented here. In a report written by Love [20] in 1959, the rate of dysprosium oxidation was best fit to linear kinetics from 200 to 600 °C in clean air (nearly 20% O2). However, in the late 1960s Pethe et al. [21] and Greene et al. [22] both reported that the oxidation kinetics follow a parabolic model. Greene et al. presents dysprosium oxidation in temperatures of 300–800 °C in clean air (N2–20% O2) and Pethe et al. from 500 to 800 °C in an atmosphere with an oxygen pressure of 100 Torr (13% O2 at 1 atm total pressure).

In the work presented here, the isothermal oxidation (TGA) data in the initial and intermediate oxidation regions (as defined in Fig. 7) at each temperature and atmosphere were individually fit to many different kinetic models to best determine the reaction rate constant (k). The models considered included various nucleation models, geometric contraction models, diffusion models, and reaction order models; many of which are described by Khawam et al. [27]. Each of the data sets were fit with each model and the model which best fit the majority of the isothermal oxidation data sets (as determined by a coefficient of determination, or R-squared parameter) was used for the kinetics analysis.

The initial regions of oxidation in each atmosphere was best fit using a contracting area model (also known as a contracting cylinder model), described by:

\[ k_p \cdot t = 1 - (1 - \alpha)^\frac{2}{3} \tag{1} \]

where \( k_p \) is the parabolic rate constant in \( \mu g/s \cdot cm^2 \), \( t \) is the isothermal oxidation time in seconds, and \( \alpha \) is the reaction extent. As previously discussed, the reaction extent (\( \alpha \)) was normalized to the maximum value observed after converting to a specific mass gain value with units of \( g/cm^2 \). The contracting area model assumes that nucleation occurs rapidly at the surface of the dysprosium particles and the rate of oxidation is controlled by the resulting reaction interface progressing toward the center of the assumed cylinder [27]. This is a significant assumption considering the morphology of the starting material, as shown in Fig. 1.

As seen in Figs. 5–7, the initial region of the oxidation reaction is confined to a relatively short time period, early in the progression of the overall reaction (less than 1 min in all but the 2% O2 atmosphere). Since the kinetics in this region are fast, some of the models could only be fit to a few data points, whereas other models (especially in the intermediate region) are defined by many thousands of data points. As seen in Table 1, this fact does not seem to effect the correlation coefficient in the N2–50% O2 atmospheres, but the correlation coefficient begins to decrease below 700 °C in the N2–20% O2 atmosphere and above 700 °C in the Ar–20% O2 atmosphere. This may suggest a breakdown of the contracting area kinetics model that was empirically chosen, as previously discussed. In the case of the initial region (below 700 °C) of oxidation in the N2–20% O2 atmosphere, the model that best fits the TGA data was a nucleation model (the Avrami–Erofeev (AE2) [27]). However, in the case of the initial region (above 700 °C) of oxidation in the Ar–20% O2, a better fit was not found.

In a similar manner as described above for the initial region kinetics, the best fits kinetics model in the intermediate region of the oxidation reaction in each of the atmospheres is the Ginstling–Brounshtein diffusion model (a deviation of the Jander model [27]), described by:

\[ k_{p,int} = 1 - \frac{2}{3} \alpha - (1 - \alpha)^\frac{2}{3} \tag{2} \]

As seen in Table 2, the Ginstling–Brounshtein model correlates well to the oxidation data (TGA) in all atmospheres except for N2–2% O2, where geometric contraction models (in particular, a contracting area model) best fit the data.

Similar to the contracting area model used to describe the initial region of oxidation, the Ginstling–Brounshtein model is also a deceleratory model, suggesting that the rate of reaction slows as the reaction extent increases or the available area for reaction decreases. The reaction rate decreases due to the fact that the product layer increases with reaction extent and results in an increasing diffusion distance for cations and/or anions, and thus, slowing the reaction.

In each case, the parabolic rate constant (\( k_{p,i} \) and \( k_{p,int} \)) was determined by plotting the kinetics model (Eqs. (1) and (2)) versus the isothermal reaction time and extracting the slope from a linear relation. As noted previously, the parabolic rate constants for each temperature and atmosphere are listed in Table 1 for the initial oxidation region kinetics and Table 2 for the intermediate oxidation region kinetics.

In order to determine an activation energy for the oxidation reaction in each of the oxidizing atmospheres, the rate constants were plotted using the Arrhenius relation:

\[ k_{p,i, int} = A e^{-\frac{E_a}{RT}} \tag{3} \]

where \( A \) is a pre-exponential factor, \( E_a \) is the activation energy for the rate limiting mechanism(s) of the oxidation reaction, \( R \) is the universal gas constant (8.3145 J/mol K), and \( T \) is the absolute temperature in Kelvin. The Arrhenius behavior describing the oxidation of dysprosium particles in the four atmospheres investigated is shown in Fig. 8 for the initial region of oxidation and in Fig. 9 for the intermediate region. As shown in Fig. 9b, unusual oxidation behavior was observed in the N2–50% O2 oxidation atmosphere.

### Table 1

Parabolic rate constants (\( k_p \)) and correlation coefficients (R-squared values) for the fits of the oxidation kinetics in the initial oxidation region for all atmospheres using a contracting area model.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>N2–2% O2 ( k_p ) ( 10^{-7} g^2/cm^4 s )</th>
<th>R²</th>
<th>N2–20% O2 ( k_p ) ( 10^{-7} g^2/cm^4 s )</th>
<th>R²</th>
<th>N2–50% O2 ( k_p ) ( 10^{-7} g^2/cm^4 s )</th>
<th>R²</th>
<th>Ar–20% O2 ( k_p ) ( 10^{-7} g^2/cm^4 s )</th>
<th>R²</th>
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<td>–</td>
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<tr>
<td>950</td>
<td>–</td>
<td>–</td>
<td>36.6</td>
<td>0.999</td>
<td>–</td>
<td>–</td>
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<tr>
<td>900</td>
<td>55.1</td>
<td>0.994</td>
<td>34.0</td>
<td>0.999</td>
<td>71.7</td>
<td>0.991</td>
<td>36.9</td>
<td>0.987</td>
</tr>
<tr>
<td>850</td>
<td>3.96</td>
<td>0.997</td>
<td>34.6</td>
<td>0.999</td>
<td>75.1</td>
<td>0.991</td>
<td>35.9</td>
<td>0.980</td>
</tr>
<tr>
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<td>0.999</td>
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<td>60.2</td>
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<td>29.8</td>
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<td>0.998</td>
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<td>0.990</td>
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<td>6.96</td>
<td>0.979</td>
<td>–</td>
<td>–</td>
<td>9.27</td>
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where there exists a discontinuity in the reaction kinetics between 650 and 800 °C.

The oxidation rate constants in the initial region of the oxidation reaction were found to be much greater (5–6 orders of magnitude) with a lower apparent activation energy than those found for the intermediate region in each atmosphere. The activation energies in the initial region of oxidation for all of the atmospheres (except the N2–2% O2 atmosphere) were found to be approximately 24 kJ/mol (Fig. 8). The value might be compared to the 38 kJ/mol reported by Greene et al. [22], who reported the oxidation of monolithic dysprosium between 300 and 550 °C, but experimental details are lacking which make comparisons difficult. Another interesting trend in Fig. 8 is that samples in the N2–50% O2 atmosphere have a rate constant that is nearly twice that of those oxidized in the (Ar, N2)–20% O2 atmospheres and more than 10 times that of those oxidized in the N2–2% O2 atmosphere. However, the activation energy in the initial reaction region in the 2% oxygen atmosphere was significantly lower, at 8 kJ/mol.

Additionally, the oxidation kinetics in the intermediate region of the oxidation reaction were all found to have an apparent activation energy between 80 and 90 kJ/mol over the temperature range studied, with the exception of the discontinuity observed in the 50% oxygen atmosphere (Fig. 9). The fact that the activation energy in the 2% oxygen atmosphere is slightly higher (90 kJ/mol versus 80 kJ/mol) suggests that the mechanism for oxidation requires slightly more energy (e.g., temperature) than the higher oxygen concentration environments. In any case, these values are fairly similar to those presented by Greene et al. [22] and Pethe et al. [28] who described the overall kinetics of dysprosium oxidation using parabolic kinetics and determined an activation energy of approximately 105 kJ/mol. The discontinuity observed in the 50% oxygen atmosphere, which suggests an apparent activation energy of zero, is indicative of a spontaneous oxidation reaction but is suspected to be anomalous, but repeated, behavior.

In both of the initial and intermediate regions of the isothermal oxidation reaction, it appears that the carrier gas (containing 20% O2) has minimal effects on the oxidation rate of dysprosium based on similar oxidation rate constants (argon results in a rate constant nearly double that observed in nitrogen) and apparent activation energies. However, by comparing the non-isothermal oxidation behavior (Fig. 3) and the selected isothermal behavior (Fig. 6), it is clear that the argon carrier gas promotes more rapid overall oxidation kinetics. This is likely due to the fact that the argon carrier gas induces a transition into the intermediate stage of oxidation at

### Table 2

Parabolic rate constants \( k_{p,\text{int}} \) and correlation coefficients (R-squared values) for the fits of the oxidation kinetics in the intermediate oxidation region for all atmospheres using the Ginstling–Brounshtein diffusion model.

<table>
<thead>
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<th>Temp (°C)</th>
<th>N2–2% O2</th>
<th>N2–20% O2</th>
<th>N2–50% O2</th>
<th>Ar–20% O2</th>
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<td></td>
<td>( k_{p,\text{int}} \times 10^{-12} ) g²/cm⁴ s</td>
<td>( k_{p,\text{int}} \times 10^{-12} ) g²/cm⁴ s</td>
<td>( k_{p,\text{int}} \times 10^{-12} ) g²/cm⁴ s</td>
<td>( k_{p,\text{int}} \times 10^{-12} ) g²/cm⁴ s</td>
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an earlier reaction extent (Fig. 7) than nitrogen atmospheres. Being 
that the transition occurs at a lower reaction extent suggests that 
the initial oxidation layer is thinner, reducing the diffusion length 
of the oxygen ions, and resulting in faster kinetics in the interme-
diate region, as observed in Table 2.

A brief, additional study investigating the effects of gas flow 
rate on the oxidation reaction was performed. In the study, the 
gas flow rate was increased from 100 to 250 mL/min in an isother-
mal oxidation temperature range of 650–850 °C. The intermediate 
region reaction rate and the transition reaction extent (Fig. 7) 
remained constant, but an effect on the initial region oxidation rate 
was observed. Although the trends were similar for the initial 
region oxidation rates, the reaction onset occurred quicker and 
the rate of oxidation reaction increased with increased gas flow 
rate. The findings suggest that there is a time delay for the furnace 
reaction chamber to reach the nominal oxygen concentration of 
the gas stream. However, the fact that the transition reaction 
extent remained constant suggests that a critical volume or surface 
area must be consumed in order for the reaction mechanism to 
change.

To gain insight into the mechanism of dysprosium oxidation, it 
is helpful to understand the type of defects present in the oxide. 
Accordingly, Brouwer diagrams (also referred to as Kroeger–Vink 
plots [29]) were constructed in each of the identified oxidation
regions using the three partial pressures of oxygen used to oxidize dysprosium. As seen in Fig. 10a, the log–log plot in the initial region of oxidation shows a nearly linear dependence of oxygen partial pressure on the rate constant for each temperature studied (600–800 °C). The slope gradually changes from +3/4 to +1 with increasing temperature. Due to the positive slopes over the entire range of temperatures, it is presumed that the oxide behaves as a p-type semiconductor and suggests that the oxidation mechanism is either due to diffusion of oxygen through interstitial sites or dysprosium through vacancies. However, the effects of oxygen pressure on the rate constant in the intermediate region of oxidation is more complicated. As seen in Fig. 10b, which also shows nearly linear correlations, the slope changes from +1/5 to −1/5 from 550 to 850 °C, respectively, with a near zero slope at 750 °C. As was
observed in the initial oxidation region, the positive slope suggests that the oxide acts as a p-type semiconductor in the lower temperature range and as an n-type semiconductor in the high temperature range, with competing defects counteracting each other’s charge near 750 °C. An n-type semiconductor suggests that the oxidation mechanism is either due to diffusion of dysprosium through interstitial sites or oxygen through vacancies. Oxygen diffusion is more likely due to the very large size of the dysprosium ions. The n-type behavior was also observed by Tare and Schmalzried [30] from 667 to 860 °C while a later report by Lal et al. [31] suggests that Dy2O3 is a p-type semiconductor at 627 °C with a 0.011 cm−2 V−1 s−1 mobility and 0.010 cm−2 V−1 s−1 electron mobility. Pethe et al. [21] also notes that the parabolic rate constant remains constant (within the experimental error) from 1% to 13% O2 at 600 °C. However, it is known that minor concentrations of impurities in the starting materials can significantly alter the semiconducting behavior of the oxide. Since impurity concentrations were neither identified nor quantified in previously reported oxidation behavior, comparisons with the work presented here may not be valid. Further work in this area needs to be completed.

To provide further insight into the mechanism of oxidation and to eliminate possible rate limiting defect mechanisms, an inert marker experiment was performed. A thin gold wire was fixed to a nearly 2 mm thick monolithic dysprosium sample which was subsequently oxidized in N2–20% O2 at 850 °C for 45 h. The gold marker remained at the oxide/gas interface after oxidation, suggesting that growth occurs at the metal/oxide interface. This observation is consistent with the work of Pethe et al. who found similar behavior via an inert (silver) marker experiment at 800 °C. The results of the marker experiments suggest that when the oxide behaves as a p-type semiconductor, the primary defect mechanism is most likely the diffusion of oxygen via dysprosium vacancies in the oxide and when the oxide behaves as an n-type semiconductor, the primary defect mechanism is likely oxygen diffusion through oxygen vacancies in the oxide.

4. Conclusions

The high temperature oxidation of dysprosium particles in 2–50% oxygen atmospheres in both nitrogen and argon carrier gases was studied from 450 to 1000 °C using both non-isothermal and isothermal techniques. The results of this study have identified two distinct regions of oxidation in each of the four atmospheres investigated, termed the initial and intermediate stages. The reaction rates at 800 °C in the initial oxidation region in N2–2% O2, N2–20% O2, Ar–20% O2, N2–50% O2, were found using a contracting area model as 10−7 (3.77, 32.8, 31, and 60.2 g/cm3 s), respectively. The reaction rates at 800 °C in the intermediate oxidation region in N2–2% O2, N2–20% O2, Ar–20% O2, N2–50% O2, were found using the Ginstling–Brounshtein diffusion model as 10−11 (15.5, 17.2, 33.2, and 9.87) g/cm3 s, respectively. The apparent activation energy was found to be much lower in the initial stages (8 kJ/mol in 2% oxygen and 25 kJ/mol in the 20 and 50% oxygen atmospheres) than in the intermediate stages (80–90 kJ/mol).

Insight into the defect mechanism limiting the kinetics of the oxidation reaction was provided by an inert marker experiment as well as identifying the effects of oxygen pressure on the kinetics rate constant via Kroeger–Vink diagrams. It was determined that oxide growth occurs at the metal/oxide interface, most likely via oxygen diffusion. With the exception of above 750 °C in the intermediate oxidation region, the oxide behaves as a p-type semiconductor. The conclusion drawn from the evidence provided is that the rate limiting oxidation mechanism is oxygen diffusion via dysprosium vacancies to grow at the Dy/Dy2O3 interface. In the cases where the oxide behaves as an n-type semiconductor, oxidation is primarily rate limited by oxygen ion diffusion via oxygen vacancies to the Dy/Dy2O3 interface. However, further studies are needed to better understand the effects of impurity types and concentrations on the semiconducting properties of the oxide layer.

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References


