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OXIDATION CHARACTERISTICS
OF THE LANTHANIDE METALS

Technical Report

To

United States Atomic Energy Commission

Contract AT (30-1) - 2714

N. D. Greene

F. G. Hodge

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ABSTRACT

The oxidation rates and rate equations of the lanthanide metals have been determined in dry and moist air in the temperature range 100°- 800°C by precision weight gain measurements. Oxide structures have been examined by both metallographic and x-ray analyses.

The observed oxidation characteristics have been related to oxide structures and the physico-chemical properties of the rare earth metals.

OXIDATION CHARACTERISTICS
OF THE LANTHANIDE METALS

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This study is a part of a comprehensive investigation devoted to characterizing the corrosion and oxidation characteristics of the rare earth metals.⁽¹⁾ The rare earths or lanthanides are the fifteen elements between and including lanthanum (atomic No. 57) and lutetium (atomic No. 71).⁽²⁻⁸⁾ Before considering the oxidation behaviors of the lanthanides it is helpful to briefly review some of their pertinent chemical similarities and differences.

The most common oxidation state of the rare earth metals is trivalent and three of these are particularly stable.⁽⁹⁾ The first is the trivalent lanthanum configuration which is the same as the extremely stable xenon configuration. The second is the half-filled 4f configuration of trivalent gadolinium where there is one electron in each of the seven 4f orbitals so that further electrons are paired with one of those already present. Lastly is the trivalent lutetium configuration which has completely filled subshells. Different valence states do exist, however, and make possible the formation of several oxides which affect oxidation behavior. All the rare earth metals form sesquioxides, M_2O_3 .⁽¹⁰⁾ Cerium, praseodymium, and terbium, which exhibit tetravalency, normally form higher oxides of the general compositions CeO_2 ,⁽¹¹⁾ Pr_6O_{11} ,⁽¹²⁾ and Tb_4O_7 .⁽¹³⁾ Samarium and europium, which exhibit divalency,

normally form lower oxides of the general composition SmO ,^(14,15)
⁽¹⁵⁾ and EuO . The oxide TbO has been prepared but only under
⁽¹⁶⁾ conditions of reduced oxygen pressure (10^{-3} mm hg).

The published and limited distribution literature contain a small number of papers dealing with the oxidation characteristics of the lanthanide metals.^(1,8,11,17-22) Quantitative data from these papers and reports are summarized in Table I. As shown, information about many metals is limited or completely lacking (e.g., europium, thulium and lutetium) and there is considerable disagreement concerning oxidation rate laws. Moisture markedly increases the oxidation rate of the rare earths,^(1,5,8) and sometimes causes an unusual inverse temperature effect - oxidation rate decreases with increasing temperature.^(1,8) Thus, the discrepancies shown in Table I may be due to variations in gas phase water content.

The scarcity of quantitative oxidation data, together with increasing technological uses of the rare earth metals, suggest that a comprehensive oxidation study of all the lanthanide metals would be desirable, and should include the effect of moisture content.

EXPERIMENTAL

Fifteen metals (lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium and yttrium) were used

in this investigation. Promethium was not commercially available and yttrium was included because of its similarity to the lanthanide elements⁽²⁻⁸⁾. Metal purities ranged from 98.0% to 99.9% with other rare earth metals as the principal impurities.

Specimens were prepared by sectioning vacuum arc melted buttons into small rectangular blocks. Specimen weight was approximately 1.5 - 2.0 grams and surface area, measured to the nearest 0.001cm^2 , was $2-3\text{cm}^2$. Surface preparation generally consisted of polishing with 600A metallographic paper under mineral oil, degreasing in the condensing vapors of boiling trichloroethylene for 5 minutes and rinsing in ethyl alcohol. The specimen was then immediately placed in a platinum holder and inserted into the oxidation test apparatus. This procedure was not applicable to lanthanum, cerium, praseodymium and europium, since slight oxidation occurred at the boiling point of trichloroethylene, (80°C). These metals were prepared by polishing on 600A metallographic paper in air using vinyl gloves to exclude body acids and oils; wiped with a clean paper tissue and immediately inserted in the test apparatus.

Three different assemblies were used to conduct continuous weight gain oxidation measurements. Rapid oxidation rates (a) (large weight gain) were determined with both manual and automatic recording (b) semi-micro balances possessing accuracies

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(a) Mettler Balance Model H16

(b) Ainsworth Balance Model RV-AU-1

of ± 0.05 milligram. Slow oxidation rates were measured using an automatic recording balance^(c) with an accuracy of ± 0.01 milligram. Each assembly utilized a tube furnace with a control accuracy of $\pm 2^\circ\text{C}$ and temperature was continuously monitored with a chromel-alumel thermocouple positioned close to the test specimen.

Oxidation tests were performed in dry and moist air which was passed through the furnaces at about 80 cc/min., corresponding to a complete exchange approximately every two minutes. Dry air was prepared by passing water-pumped compressed air through a tower of 6-10 mesh Indicarb^(d) to remove CO_2 , through a tower of manganese dioxide to remove SO_2 , and through two towers of anhydrous calcium sulfate to remove water. Air with a constant water content was prepared by passing this dried and purified air through two columns of double distilled water. The dew point of the emergent gas was 21°C , which corresponds to a water content of 17.3 milligrams per liter at S.T.P.

Weight gain measurements were usually conducted for periods ranging between 8 to 12 hours. Longer periods were used for some of the slowly oxidizing systems to improve accuracy. After testing, specimens were microscopically

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(c) Cahn R.G. Recording Electrobalance.

(d) Trade mark for CO_2 absorbing material,
Fisher Chemical Company, New York.

examined and oxide scales were subjected to conventional x-ray diffraction analysis.

RESULTS

Oxidation in Dry Air

Table II summarizes, in terms of rate constants, the results of oxidation tests in dry air. In general, these data represent the average of two or more experiments which were usually reproducible to $\pm 10\%$. Due to the widely differing oxidation rates of the various metals, it was not possible to determine oxidation rate-time relationships at every temperature. As shown in Table II, parabolic and linear oxidation rate laws predominate. Typical parabolic behavior is shown in Figure 1, while typical linear oxidation is illustrated in Figure 2. Note that individual data points show little scatter over extended time periods. Cerium and terbium oxidize paralinearly (initially parabolic followed by linear kinetics after periods of 60-180 minutes) in certain temperature ranges. As a consequence, two rate constants are listed in Table II. The oxidation of yttrium is complex. It oxidizes according to a linear equation up to a temperature of 500°C. At 600°C it initially oxidizes linearly and then demonstrates a parabolic rate law. At 700°C only parabolic oxidation is

observed, while data at 800°C are best represented by a cubic law.

The data presented in Table II were used to calculate activation energies which are listed in Table III. In general, there is good agreement between these data and those data listed in Table I. The unusual minimum in activation energy occurring during the oxidation of gadolinium, observed by Vorres,⁽²⁰⁾ is confirmed here, although there is some discrepancy in the temperature ranges. This is probably the result of the continuous temperature increase technique employed by Vorres, which would be expected to cause positive temperature errors in his data.

With the exception of cerium, all the metals formed dark colored, adherent oxide coatings at 300°C. X-ray diffraction analysis showed that M_2O_3 type oxides were present on every metal except cerium. Other oxides identified by x-ray diffraction were CeO_2 , Pr_6O_{11} , SmO and EuO . At higher temperatures, non-adherent coatings cover these metals which oxidize linearly. At 700°C, erbium forms a loose, powder, rose-colored oxide, identified by x-ray analysis to be Er_2O_3 , and a loose, "cruciform" structure of Ho_2O_3 covers holmium. The oxide which forms of ytterbium above 500°C has a cracked

and porous appearance as shown in Figure 3.

After oxidation at 700°C, samarium possesses, in addition to a dual oxide layer, a second phase in the metal substrate as shown in Figure 4. Similar second phases were also observed in specimens of erbium and terbium but no determinations of the composition were attempted. It is possible that these second phases are due to internal oxidation by dissolved oxygen. The change in oxidation behavior of yttrium at 600°C is accompanied by a change in its oxide structure. Oxides formed at 500°C and 600°C show a change in the relative intensities of the Y_2O_3 peaks.

Oxidation in Moist Air.

The effect of moisture on the oxidation of cerium is shown in Figure 5. Oxidation rate increases and the rate law changes from parabolic to linear. Similar effects are also observed with praseodymium, europium and terbium (during its initial parabolic oxidation). The rate increases observed with praseodymium and terbium are, however, much less than those obtained with cerium and europium. At 100°C in air containing 17.3 mg H_2O /liter, europium oxidizes catastrophically. The surface is covered with a loose, yellow deposit of $Eu(OH)_2$ identified by x-ray analysis.

Figure 6 shows the effect of moisture on the oxidation of

lanthanum at 300°C. At a given temperature, oxidation rate increases, although the oxidation rate law (parabolic) is unchanged. Note the inverse temperature effect shown in Figure 6. At a constant water content, oxidation rate decreases as temperature is increased from 100°C to 300°C. Figure 6 is typical of all the rare earth metals except cerium, praseodymium, europium and terbium, as noted above.

The effect of moisture on the oxidation characteristics of the rare earth metals can be summarized as follows:

- 1) In the presence of 17.3 mg of water vapor per liter of dry air at standard temperature and pressure (STP), the oxidation of cerium, praseodymium, europium and terbium, transforms from parabolic to linear behavior with a corresponding increase in rate. At this moisture content, oxidation rate increases with increasing temperature.
- 2) In the presence of 17.3 mg H₂O/liter of dry air at STP, the oxidation rate laws (parabolic, linear) of the other lanthanides are unchanged, although their oxidation rates are increased. At a constant water content, oxidation rate decreases with increasing temperature.

DISUCSSION

As indicated above, the lanthanides oxidize according to different oxidation laws: parabolic, linear, paralinear, cubic and catastrophic. A parabolic rate law is observed when oxidation is controlled by the diffusion of a reacting species through an oxide layer of increasing thickness. The

rare earths which exhibit parabolic oxidation for the entire temperature range studied are lanthanum, praseodymium, neodymium, samarium, europium, gadolinium, dysprosium and lutetium. With the exceptions of praseodymium, samarium, and europium, these metals form only the M_2O_3 oxide. Praseodymium exhibits a tetravalent oxidation state in addition to the normal trivalent state, and as a result forms the oxide Pr_6O_{11} in addition to the sesquioxide Pr_2O_3 . The praseodymium tetravalent electronic configuration approaches the La^{3+} stable configuration but contains an extra 4f electron and is less stable than the normal trivalent configuration. Therefore, the sesquioxide Pr_2O_3 is probably the predominate form. Samarium and europium form both monoxides and sesquioxides. The sesquioxides, because of their greater specific volumes and higher oxygen contents, tend to form separate outer layers (see Figure 4). Thus, anion or cation diffusion through an M_2O_3 type oxide appears to be the cause of parabolic oxidation among the lanthanides.

Linear oxidation behavior is the result of diffusion through a barrier of constant thickness. Holmium, erbium, thulium and ytterbium oxidize linearly at all temperatures. Ytterbium oxidizes to the sesquioxide, Yb_2O_3 , which has a specific volume of 0.8 with respect to the metallic state. According to the Pilling-Bedworth rule,⁽²³⁾ such oxides do not

completely cover the metal surface which causes linear oxidation kinetics. This is supported by Figure 3, which shows that the oxide layer on ytterbium is severely cracked. Holmium, erbium and thulium have hexagonal crystal lattices possessing the lowest c/a ratios of all hexagonal metals.⁽³⁻⁵⁾ Epitaxial oxide growth on these compact, metal unit cells is necessarily accompanied by very high internal stresses because of the larger specific volumes⁽²⁴⁾ and lattice parameters⁽⁵⁾ of the rare earth oxides. Hence, the linear oxidation of these three lanthanides is most likely the result of oxide film rupture and/or stress-activated nucleation of their normal, large volume oxide structures.

Paralinear oxidation, first characterized by Loria⁽¹⁷⁾ for cerium and later expanded by Haycock,⁽²⁵⁾ is a combination of parabolic and linear rate laws and is usually associated with metals which form two oxide phases. Initially, parabolic behavior is observed due to the formation of a protective oxide layer. If this oxide transforms to a second oxide phase at a sufficient rate, a transition to linear oxidation kinetics occurs after a short time because the protective oxide layer reaches a constant thickness. Since paralinear oxidation rate depends on two competing reactions, it is usually associated with a narrow temperature region. At lower temperatures, parabolic oxidation is observed while higher temperatures yield linear oxidation kinetics. The oxidation characteristics of

cerium and terbium (Table II) are consistent with this hypothesis. In the tetravalent state, cerium has the same stable xenon configuration as La^{+3} and tetravalent terbium assumes the very stable Gd^{+3} configuration. Both metals therefore form the dioxides, CeO_2 and TbO_2 , in addition to the sesquioxides Ce_2O_3 and Tb_2O_3 , as shown here by x-ray examination.

Catastrophic oxidation is generally considered as a deviation from linear behavior resulting from non-isothermal conditions occurring at high reaction rates.⁽²⁴⁾ Under the conditions used in this investigation, cerium, terbium and erbium oxidized catastrophically at 300°, 400° and 700°C, respectively. As indicated in Table II, linear oxidation rates were observed for cerium and terbium prior to the onset of accelerating catastrophic oxidation.

Typically, oxidation rate laws follow the sequence: parabolic $\rightarrow$ paralinear $\rightarrow$ linear $\rightarrow$ catastrophic,⁽²⁴⁾ as temperature is increased.* With the exception of yttrium, all the metals investigated here oxidize according to this general rule (Table II). Yttrium is most unusual, since its oxidation kinetics follow an almost opposite sequence with

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* Less reactive metals (e.g., iron) often oxidize according to a logarithmic equation at low or ambient temperatures (24). The lanthanides, because of their high chemical activities, may possibly demonstrate logarithmic oxidation kinetics only at temperatures below ambient.

increasing temperature: linear $\rightarrow$ linear/parabolic $\rightarrow$ parabolic $\rightarrow$ cubic. The oxidation of yttrium at 900° and 1400°C has been studied recently by Borchardt⁽²¹⁾, who concluded that its high temperature behavior is controlled by two competing reactions; solution of oxygen in the matrix metal and oxide film formation. Initially the solution rate of oxygen in yttrium exceeds the rate of oxide formation. As oxygen saturation is approached, oxide formation becomes pre-dominate, and normal parabolic behavior is observed. The net effect of these two reactions is a weight gain-time curve which appears to be cubic, or possesses an exponent greater than two.

The results of this investigation generally support the Borchardt mechanism. At temperatures below 500°C, linear weight gain is observed indicating that oxygen solution in yttrium is the controlling reaction during the duration of the experiments. At 600°C, oxide formation rate becomes significant, which produces the peculiar linear/parabolic characteristics followed by a parabolic rate equation at 700°C. At 800°C the weight gain-time curve is most closely approximated by a cubic equation which is consistent with Borchardt's data obtained at higher temperatures⁽²¹⁾. However, the actual mechanism may be more complex since there is a change in oxide structure between 500° and 600°C, as noted above under Results.

The lanthanides oxidize more rapidly in the presence of water vapor due to the formation of less protective hydroxides. This effect becomes less pronounced at higher temperatures, since water adsorption and hydroxide formation are retarded, as discussed previously.^(1,8) Cerium, praseodymium, europium and terbium have multiple oxidation states, and the presence of moisture apparently promotes the formation of second oxide phases and causes a transition from parabolic to linear oxidation kinetics. For example, in the presence of moisture, europium forms the hydroxide $\text{Eu}(\text{OH})_2$ (or hydrated monoxide: $\text{EuO} \cdot \text{H}_2\text{O}$) in preference to the sesquioxide Eu_2O_3 .

Oxidation rate equations are functions of the physical and electronic properties of oxide scales. Therefore, correlations between overall oxidation kinetics and the physical characteristics of the lanthanides would not be expected.

Failure to find such correlations confirm this hypothesis. However, the initial oxidation rates of the rare earth metals should be very dependent on the physical properties of the individual metals. To verify this assumption, the initial oxidation rates of the lanthanides were calculated from weight gain-time curves measured at 300°C^* by constructing tangent

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* The excessive oxidation rate of europium necessitated the use of data obtained at 250°C (see Table II). Ytterbium and lutetium oxidize too slowly to be accurately measured at 300°C as shown in Table II and data measured at 400° and 350°C , respectively, were used to determine initial rates.

lines at the origin (time = 0). The results are plotted as a function of atomic number in Figure 7. Initial oxidation rate decreases continuously with atomic number except for cerium and europium. This observation is virtually identical to the aqueous corrosion characteristics of these metals, reported previously,⁽¹⁾ and shown in Figure 8. The gaseous and aqueous reactivities of the lanthanides are related to solid state bonding. Except for cerium and europium, metallic bond strength increases continuously with atomic number, as reflected by melting point, density, and atomic radii.⁽¹⁻⁸⁾ Cerium and europium are less strongly bonded than their adjacent neighbors, and are therefore more reactive.⁽¹⁾

SUMMARY

1. The oxidation characteristics of fourteen lanthanide metals and yttrium have been examined in detail in dry and moist air at temperatures between 100° and 800°C. Oxidation rates and rate equations have been determined, together with activation energies.
2. In dry air, oxidation generally proceeds according to linear or parabolic oxidation kinetics. At intermediate temperatures, cerium and terbium oxidize parabolically, and at higher temperatures, together with erbium, they are catastrophically oxidized. Yttrium possesses unusual oxidation characteristics

which are apparently related to oxygen solubility in the matrix metal.

3. Water vapor generally increases oxidation rates as a result of less protective hydroxide films. This effect becomes less pronounced as temperature is increased, since water adsorption is retarded.
4. Initial oxidation rates of the lanthanides are a function of metallic bonding. Strong metallic bonding decreases chemical reactivity.

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FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7

FIGURE 8

TABLE I

SUMMARY OF PRIOR OXIDATION DATA

Element	Oxidation Rate Law	Temperature Range °C	Reported Rate Constant	Activation Energy (kcal)	Observer
La	P ⁽¹⁾				Loriers
	P	35-600			Love
	P	330-450		17 ± 1	Vorres
	P	450-670		18 ± 1	"
	P ⁽²⁾	670-1179		28 ± 1	"
	L	25-200			Lee & Greene
Ce	P ⁽³⁾	30-125		12	Loriers
	P-L	125-200			and
	L	200-320		12	Cubicciotti
	Ignition Above 320				
	L	600-750 (4)	5.0-40.0 mg/cm ² -hr	7.4	Phillips
		(55% RH Air)			
Pr	P	60-187		13 ± 1	Vorres
	L	187-269		15 ± 1	"
	L	269-320		29 ± 1	"
	L	25-200			Lee & Greene
	L	600-800	8.6-39.5 mg/cm ² -hr	7.4	Phillips
		(55% RH Air)			
Nd	P	66-260		4 ± 1	Vorres
	P	260-449		27 ± 1	"
	P	449-504		68 ± 2	"
	P	25-200			Lee & Greene
	L	200-600			Love
	L	100-1000	3.2-45.1 mg/cm ² -hr	7.4	Phillips
Nd		(55% RH Air)			
	P	Below 530		Variable	Vorres
	P	530-860		25 ± 1	"
	P	860-1150		32 ± 2	"
	P	35-600			Love

(continued)

Table I
(continued)

Element	Oxidation Rate Law	Temperature Range °C	Reported Rate Constant	Activation Energy(kcal)	Observer
Sm	L	750-1000	5.0-40	7.4	Phillips
		(55% RH air)	5.6-36.0 mg/cm ² -hr		
	P	350-590		Increasing	Vorres
	P (5) Log	590-1155 35-600		41 ± 1	" Love
Gd	L	800-1200	1.0-20.0	7.4	Phillips
		(55% RH Air)	mg/cm ² -hr		
	P	550-614		84 ± 4	Vorres
	P	614-800		14.8 ± 0.4	"
	P	800-934		0	"
	P	934-1082		15 ± 1	"
	P	1082-1135		41 ± 1	"
Tb	P	35-600			Love
Tb	L	800-1200	0.65-10.4	7.4	Phillips
		(55% RH Air)	mg/cm ² -hr		
	P	335-600			Love
Dy	L	200-600			Love
Ho	L	800-1200	0.5-7.4	7.4	Phillips
		(55% RH Air)	mg/cm ² -hr		
	P	200-400			Love
Er	L	600			"
	P	200-400			Love
Yb	L	600	720 mg/dm ² -day		"
	P	R.T.-630		11 ± 1	Vorres
		400	170 mg/dm ² -day		Love
Y	P	900 and 1400°C		44.5	Borchardt

LEGEND: (1) P - Parabolic
(2) L - Linear
(3) P-L - Paralinear
(4) RH - Relative Humidity
(5) Log - Logarithmic

TABLE II
OXIDATION RATE CONSTANTS* FOR THE LANTHANIDE METALS

	100°C	150°C	200°C	250°C	300°C	350°C	400°C	450°C	500°C	550°C	600°C	650°C	700°C	800°C
La				4.8×10^{-5}	1.3×10^{-4}	3.8×10^{-4}	7.5×10^{-4}							
Ce	1.1×10^{-4}		9.9×10^{-4} 4.4×10^{-3} (L)	1.5×10^{-2} 1.6×10^{-2} (L)	5.9×10^{-2} (L) Catas- trophic									
Pr			2.8×10^{-5}	6.4×10^{-5}	1.1×10^{-4}									
Nd				3.1×10^{-6}	2.2×10^{-5}		1.1×10^{-4}			1.9×10^{-3}			1.9×10^{-2}	
Sm					8.5×10^{-6}		3.0×10^{-4}	8.8×10^{-4}	3.8×10^{-3}				3.6×10^{-1}	
Eu	1.5×10^{-4}	1.5×10^{-3}	3.4×10^{-2}	4.0×10^{-1}										
Gd					2.2×10^{-5}	6.1×10^{-5}		6.6×10^{-5}		8.5×10^{-5}			5.2×10^{-4}	2.3×10^{-3}
Tb				1.0×10^{-6} 5.1×10^{-5} (L)	3.8×10^{-4} (L)	2.5×10^{-3} (L)	9.4×10^{-3} (L) Catas- trophic							
Dy					1.7×10^{-5}			7.0×10^{-5}		1.8×10^{-4}			5.1×10^{-4}	2.0×10^{-3}
Ho					2.8×10^{-4} (L)	5.2×10^{-4} (L)	9.4×10^{-4} (L)		1.5×10^{-2} (L)				5.8×10^{-1} (L)	
Er				1.1×10^{-4} (L)	2.6×10^{-4} (L)	3.8×10^{-4} (L)	9.0×10^{-4} (L)		2.4×10^{-3} (L)				Catas- trophic	
Tm			6.4×10^{-5} (L)		3.4×10^{-4} (L)		5.0×10^{-4} (L)		6.8×10^{-4} (L)				2.2×10^{-3} (L)	
Yb							1.5×10^{-4} (L)	3.2×10^{-4} (L)	4.0×10^{-4} (L)		6.3×10^{-4} (L)	1.5×10^{-3} (L)	2.4×10^{-3} (L)	
Lu						2.5×10^{-5}	4.4×10^{-5}		1.9×10^{-4}				1.3×10^{-3}	
Y					1.0×10^{-4} (L)	2.0×10^{-4} (L)	3.9×10^{-4} (L)		1.3×10^{-3} (L)		1.3×10^{-4} 1.8×10^{-3} (L)		3.0×10^{-3}	2.4×10^{-2} (C)

* Parabolic rate constants ($\text{mg}^2/\text{cm}^4\text{-min}$) unless denoted as linear (L) or cubic (C)
 (L) Linear rate constant: $\text{mg}/\text{cm}^2\text{-min}$.
 (C) Cubic rate constant: $\text{mg}^3/\text{cm}^6\text{-min}$.

TABLE III
ACTIVATION ENERGIES FOR OXIDATION⁽¹⁾

Metal	Oxidation Rate Law	Temperature Range (°C)	Activation Energy (Kcal)
La	P	250-400	13.5
Ce	L	100-300	14.3
Pr	P	200-300	7.9
Nd	P	250-700	19.1
Sm	P	300-700	30.0
Eu	P	100-250	19.1
Gd	P	300-350	13.9*
	P	350-550	1.6*
	P	550-800	27.0*
Tb	L	250-400	24.1
Dy	P	300-550	9.0
	P	550-800	22.9*
Ho	L	300-400	9.6
	L	400-700	28.6
Er	L	250-500	13.5
Tm	L	250-300	19.9*
	L	300-700	3.1
Yb	L	400-700	10.9
Lu	P	350-700	13.5
Y	L	300-600	10.7

P: parabolic; L: linear.

(1) Except where noted by an asterisk (*), activation energies were calculated from 5 or more data points obtained at 3 or more temperatures.