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CORROSION CHARACTERISTICS
OF THE RARE EARTH AND YTTRIUM METALS

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Linda Lee

Norbert D. Greene

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CORROSION RESEARCH LABORATORY
DEPARTMENT OF MATERIALS ENGINEERING
RENSSELAER POLYTECHNIC INSTITUTE
TROY, NEW YORK

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ABSTRACT

The corrosion of rare earth metals in air, water, and aqueous solutions at different temperatures has been measured by conventional weight loss and weight gain tests. The metals oxidize slowly in air, corrode slowly in water and alkaline solutions, and are readily soluble in most acids.

Correlations of corrosion behavior with the electronic and physical properties of the rare earths are discussed.

Rare earths is a general name for a group of fifteen transition elements having similar chemical and physical properties. They include the element lanthanum, atomic number 57, and the following fourteen elements in the periodic table, to lutetium, atomic number 71. Although not a rare earth, the element yttrium is often included in this group because of its general similarity.^(1,2)

The physical properties of the rare earth and yttrium metals are shown in Table I.⁽³⁻⁷⁾ Promethium is not included because complete data is lacking. The chemical and physical characteristics of the elements and their compounds are closely related to the electronic structures of the atoms and ions from which they are derived. More specifically, these characteristics are determined largely by the electrons in the highest quantum levels.⁽⁸⁾ The 4f sublevel is filled after the 6s and 5d levels, and it can hold a total of fourteen electrons. Hence, there are fifteen elements (including lanthanum, which has no 4f electrons) in this transition series. The electronic structures of the rare earths are shown in Table II. Europium and ytterbium have only two valence electrons (i.e., 6s and 5d levels); they generally deviate from the trends in physical properties

exhibited by the other elements in this group,⁽⁹⁾ as shown in Table I.

Previously, the rare earth metals and their compounds were used in the glass and illuminating industries and as minor alloy additions. Recently, because of their availability in high purity, they have become increasingly important due to their nuclear, electrical and magnetic properties. For these reasons, it is probable that the rare earths will be utilized either as pure metals or as major components of an alloy. Hence, their corrosion resistance in various environments is of considerable technological importance. The transitional nature of the rare earths also suggests the possibility of relating chemical reactivity or corrosion behavior to electronic structure.

This paper describes an extensive study of the corrosion characteristics of the rare earths metals. Thirteen rare earths: lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, and ytterbium were chosen for this investigation because of their availability. Yttrium was also included for comparison.

EXPERIMENTAL

Corrosion tests were performed using high purity

(99.9%) rare earth metals obtained from the American Potash and Chemical Corporation. The metals were vacuum arc melted into buttons with a tungsten electrode in an argon atmosphere, and then sectioned into small rectangular specimens. Each specimen was polished with 00 emery paper, washed in acetone and dried prior to exposure.

Oxidation rates of the rare earths in air were determined in a thermostatically controlled oven ($\pm 1^\circ\text{C}$). Oxidation tests were also conducted in water-saturated air and air in equilibrium with 30% hydrogen peroxide at room temperature. All specimens were weighed immediately after exposure to minimize continued oxidation. The weight increases were calculated in terms of milligrams per square decimeter per day for each of five test periods of approximately 48 hours. For specimens with oxidation rates greater than 100 milligrams per square decimeter per day, only one test period was used. The accuracy of these tests was generally $\pm 1 \text{ mg/dm}^2/\text{day}$.

Aqueous corrosion tests were conducted by conventional techniques. (10) Five test periods (ranging from 20 hours to 60 hours for each period) were used to determine the corrosion rates of all specimens with corrosion rates less than 200 mpy (mils penetration per year). For specimens demonstrating rates

greater than 200 mpy, only one test period ranging from 10 minutes to 48 hours was used, depending on the corrosion rate. The accuracy of these measurements was, in general, ± 0.5 mpy.

RESULTS

Both oxidation and corrosion rates of the rare earths vary with time. To simplify the presentation of experimental data, all reported rates are those of the last test period. As noted previously, only one test period was used when oxidation or corrosion rates were excessive. The variations of corrosion and oxidation rates with time are discussed later.

Oxidation Tests.

Oxidation rates in air as a function of temperature are listed in Table III. The unoxidized surfaces of the rare earth metals have a bright metallic or silver luster and the surfaces of the more reactive metals quickly tarnish in air to dark colored oxide coatings. Lanthanum, cerium, and europium are very reactive and oxidize rapidly at room temperature; cerium has been reported to burn in the massive state (11) at low temperatures. Praseodymium and neodymium are also attacked by air, but at rates that are one to two orders of magnitude less than that of cerium. The remainder of the rare earths and yttrium are virtually unattacked by air at

temperatures up to 200°C.

The oxidation rates of lanthanum and europium at 200°C. are less than those at room temperature. Further, the oxidation rates of lanthanum, cerium, praseodymium, neodymium, and holmium decrease as temperature is increased from 100° to 200°C. This unusual effect has also been observed by Love, who (12) conducted similar oxidation studies in dry and moist air at temperatures up to 600°C. He postulated that this effect is due to moisture absorption by the rare earth oxides resulting in a less protective film. At high temperatures moisture absorption is not favored and more protective films are believed to form. This hypothesis is consistent with the results shown in Table III. The presence of moisture markedly increases oxidation rates. Air in equilibrium with a 30% aqueous solution of hydrogen peroxide is more corrosive than air in equilibrium with water at the same temperature (Table III). This is undoubtedly the result of atmospheric oxygen enrichment from the decomposition of the solution.

Oxidation rates usually vary with exposure time. Figure 1 illustrates typical oxidation characteristics. Lanthanum possesses a linear oxidation curve, while praseodymium shows exponential behavior in air. In moist air or air in equilibrium with hydrogen peroxide solutions, loosely

adhering oxide films are formed, producing the complex oxidation behavior shown in Figure 1.

Corrosion Tests.

Since there is little published information about the chemical reactivity of the rare earth metals in aqueous solutions, numerous exploratory tests were conducted in various media at ambient temperature, $(25 \pm 1^\circ\text{C})$. Five rare earth metals, gadolinium, dysprosium, holmium, erbium, and yttrium were chosen for these tests because of their resistant behavior, as evidenced by their retention of metallic luster when exposed to air. Table III summarizes the pertinent results of preliminary tests conducted in solutions made from reagent grade chemicals and triply-distilled water. The metals are very rapidly attacked by most acids and salt solutions at low concentrations. For those metal-corrosive systems demonstrating mild or negligible corrosive attack, more extensive measurements were made at various temperatures and concentrations.

Corrosion rates in distilled water and acids as a function of temperature are given in Table V. In water, europium first forms a yellow, water-soluble compound which oxidizes to white material which is probably hydrous europic
(13)
oxide. Its corrosion rate in distilled water at 30°C is over

10^6 mpy. Lanthanum, cerium, praseodymium, and neodymium show an increase in corrosion rates in boiling water, and the rest are not attacked at an appreciable rate either at ambient or boiling temperatures.

The behavior of rare earth metals in acids is rather complex and difficult to classify. All concentrated acids attack the rare earth metals severely, and the attack is generally very rapid even at concentrations of less than one normal (see Table III). Usually, europium is the most reactive with a corrosion rate of more than 10^4 mpy in all acid solutions at 30°C. There is one exception: a 1:1 mixture of concentrated nitric acid and 48% hydrofluoric acid which attacks europium at less than 100 mpy. Also, the heavy rare earths are attacked very slowly by this media, making this a useful metallographic etching reagent for these metals. (14)

In phosphoric acid, corrosion rates increase with increasing concentration. Lanthanum, cerium, praseodymium, and neodymium, which have higher corrosion rates in most media, showed lower corrosion rates than the others in 5N phosphoric acid at 30°C. However, they are more sensitive to temperature increases and have higher corrosion rates than the others in boiling normal phosphoric acid. The corrosion rates of gadolinium, dysprosium, holmium, erbium, thulium, ytterbium and yttrium

decrease with increasing temperature.

Metals with low atomic numbers (lanthanum, cerium, praseodymium and neodymium, show increasing corrosion rates with testing time and the others decrease with time in phosphoric acid. In chromic and oxalic acids, lanthanum, cerium, neodymium and gadolinium lost most of their weight during the 4th and 5th test periods; while praseodymium, samarium, ytterbium and yttrium had higher rates during the first period, followed by little or not weight decrease in later periods.

Table VI presents corrosion rates in bases at 30°C. The metals are resistant to alkali solutions and all had corrosion rates less than one mil penetration per year except europium, cerium, lanthanum and praseodymium.

Table VII summarizes corrosion rates in normal sodium nitrite as a function of temperature. In all neutral salts except sodium nitrite, the rare earths react rapidly (see Table III).

Corrosion rates generally varied with exposure time. A few representative curves are shown in Figure 2. Curve A is an example of constant corrosion rate (Y in boiling one normal chromic acid). Curve B represents a corrosion rate which increases with time (Ce in normal oxalic acid at 30°C). Curve C shows a rate which decreases with time (Sm in normal chromic

acid at 30°C). Curve D shows a corrosion rate which increases, then decreases with time (Nd in normal oxalic acid at 30°C).

DISCUSSION

In solution, the rare earth ions are quite similar since they all possess three valence electrons. Further, they have a great affinity for water and an adhesive hydration shell surrounds them and tends to mask the negligible differences between them.⁽¹⁵⁾ In the metallic state, however, strong differences in physical and chemical properties often occur. Figure 3 illustrates a plot of melting point versus atomic number. (See Table I). In general, melting point increases with atomic number with three exceptions: cerium, europium, and ytterbium. Similar deviations are observed when density, atomic volume, atomic radius, number of valence electrons, and thermal expansion coefficients are plotted against atomic number. All of these parameters reflect metallic bonding strength which increases with increasing atomic number. The deviations at cerium, europium and ytterbium indicate that these metals are less strongly bonded than their immediate neighbors. It would be expected that the chemical reactivity of the rare earth metals should depend on their individual metallic bond strengths (or those physical properties which

are related to bond strengths). This assumption is qualitatively confirmed by the results presented in Tables III, V, VI, and VII, and illustrated in Figures 4 and 5. The corrosion resistance of this transition series generally increases with increasing atomic number. Cerium and europium are usually attacked more rapidly than their immediate neighbors in all tests except those in acid solutions, where no trends are evident (Figure 6).

Figures 5 and 6 show systems in which deviations do occur: a) metals other than cerium, europium and ytterbium corrode faster than expected (Figure 5); b) cerium corrodes more slowly than expected (Figure 5); c) no general trends are observed (Figure 6). Ytterbium, although its physical properties indicate weak metallic bonding, is attacked at approximately the same rate as the other metals adjacent to it in these experiments. In most of the media studied, ytterbium and the other heavy rare earths corroded at very low rates which were close to the limit of experimental error, which may explain this lack of correlation.

The above correlations, although qualitatively correct, are only approximations. Other factors, such as oxide film formation, interactions between the kinetics of oxidation and reduction processes, and specific catalysis by ionic species

in solution may obscure the effects of metallic bond strength.

SUMMARY

1. Lanthanum, cerium, and europium are rapidly oxidized in air at room temperature. All the other rare earths are not appreciably attacked by dry air at 200°C. Oxidation rates are markedly increased by the presence of water vapor and they tend to decrease with increasing temperature.
2. Except for lanthanum, cerium, praseodymium, neodymium, and europium, the rare earths are corroded at rates less than 1 mpy by distilled water at temperatures up to the boiling point, and by dilute sodium and ammonium hydroxide solutions. Dilute acid and salt solutions usually produce severe corrosion.
3. In general, corrosion resistance increases with increasing atomic number. However, it is shown that better, although qualitative, correlations are achieved by relating corrosion resistance to parameters which reflect metallic bond strength (e.g., melting point and density).

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TABLE I

Physical Properties of Rare Earth and Yttrium Metals *

Metal	Atomic Number	Atomic Weight	^o A Atomic Radius	C.C. Atomic Volume	Density g/cc (Xray)	M.P. °C
La	57	138.42	1.870 (1.872)	22.43	6.162 (6.180)	920 _{±5}
Ce	58	140.13	1.81	20.7	6.768	804 _{±5}
Pr	59	144.92	1.824 (1.821)	20.79	6.769 (6.805)	935 _{±5}
Nd	60	144.27	1.818	20.60	7.007	1024 _{±5}
Sm	62	150.43	1.804	20	7.54	1052 _{±5}
Eu	63	152.0	1.9841	29.00	5.245	826 _{±10}
Gd	64	156.0	1.794	19.79	7.868	1350 _{±20}
Tb	65	159.2	1.773	19.11	8.253	1450 _{±50}
Dy	66	162.46	1.769	18.97	8.565	1485 _{±20}
Ho	67	164.94	1.759	18.65	8.799	1500 _{±25}
Er	68	167.2	1.748	18.29	9.058	1500 _{±25}
Tm	69	169.4	1.742	18.12	9.318	1600
Yb	70	173.04	1.933	24.75	6.959	824 _{±5}
Lu	71	174.99	1.737	17.96	9.849	1700 _{±50}
Y	39	88.92	1.814	19.7	4.472	1500 _{±25}

* Data from references (3-7)

TABLE II

Electronic Structure of the Rare Earth Metals *

<u>Metal</u>	<u>Electronic Structure</u>		
	<u>Bonding Electrons</u>		
	6s	5d	4f
La	2	1	0
Ce	2	1	1
Pr	2	1	2
Nd	2	1	3
Pm	2	1	4
Sm	2	1	5
Eu	2	0	7
Gd	2	1	7
Tb	2	1	8
Dy	2	1	9
Ho	2	1	10
Er	2	1	11
Tm	2	1	12
Yb	2	0	14
Lu	2	1	14

* Data from reference 9

TABLE III

Oxidation of Rare Earth and Yttrium Metals

Metal	Weight Gain (Milligrams per square decimeter per day)				
	Air			Water Saturated Air at 40°C	Air in Equilibrium with 30% H ₂ O ₂ at 40°C
	25°C	100°C	200°C		
La	2	48	<1	16	6
Ce	4	2020	570	37	25
Pr	<1	11	<1	13	25
Nd	0	3	<1	6	11
Sm	0	0	0	5	20
Eu	1550	230	560	3370	4560
Gd	0	0	0	<1	0
Tb	0	0	0	<1	2
Dy	0	0	0	<1	0
Ho	0	2	<1	<1	0
Er	0	0	0	<1	1
Tm	0	0	0	<1	<1
Yb	0	0	0	<1	<1
Y	0	<1	0	0	0

TABLE IV

Exploratory Corrosion Tests of
Gadolinium, Dysprosium, Holmium, Erbium, and
Yttrium at 25°C.

Media	Corrosion Rate (MPY)
98% H ₂ SO ₄	Dissolved [*]
37% HCl	"
70% HNO ₃	"
70% HClO ₄	"
1N H ₂ SO ₄	Over 10 ⁶
1N HCl	"
1N HNO ₃	1-9x10 ⁵
1N HClO ₄	"
1N HCOOH	"
0.1N H ₂ SO ₄	1-9x10 ⁴
0.1N HCl	"
1N KCl	"
1N CuCl ₂	"
3.6% Fe ₂ (SO ₄) ₃	"
99.9% CH ₃ COOH	1-9x10 ³
85% H ₃ PO ₄	"
48% HF	1-10

* Specimens had surface areas of approximately 3 cm² and were completely dissolved within 10 minutes.

TABLE V

Corrosion Rates of Rare Earth and Yttrium Metals in Distilled Water and Acids
as a Function of Temperature

Corrosion Rate, mpy Media	$1-9 \times 10^6$	$1-9 \times 10^4$	$1-9 \times 10^3$	$1-9 \times 10^2$	10-100	1-10	≤ 1
Distilled Water 30°C	Eu					La, Ce	Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Y
Distilled Water 100°C			Ce	La, Pr, Nd			Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Y
1N H ₃ PO ₄ 30°C	Eu				La, Ce, Nd, Gd, Dy, Tm, Yb, Y	Pr, Ho, Er	Sm, Tb
1N H ₃ PO ₄ Boiling		Ce	La, Pr	Nd			Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Y
5N H ₃ PO ₄ 30°C	Eu		Sm, Gd, Tb, Dy, Ho, Tm, Y	Pr, Nd, Er, Yb	La, Ce		
1N CrO ₃ 30°C		Eu	La, Tm	Tb, Nd, Ho, Er	Ce, Yb	Pr, Sm, Gd, Dy	Y
1N CrO ₃ Boiling	La	Ho, Er	Ce, Pr, Tb	Nd, Sm, Tm, Yb	Gd, Dy, Y		
1N H ₂ C ₂ O ₄ 30°C	Eu				Ce, Nd	La, Er, Tm, Yb	Pr, Sm, Gd, Tb, Dy, Ho, Y
1N H ₂ C ₂ O ₄ Boiling			La, Ce, Pr, Nd, Sm, Er, Y	Dy, Ho		Tb, Tm, Yb	Gd
1:1 HF-HNO ₃ 25°C		Sm	Nd	La, Ce, Pr	Eu	Tb, Ho, Yb	Gd, Dy, Er, Tm, Y

TABLE VI

Corrosion Rates of Rare Earth and Yttrium Metals
in Bases at 30°C

Corrosion Rate, mpy Media	$1-9 \times 10^5$	$1-9 \times 10^4$	$1-9 \times 10^2$	10-100	<1
1N NaOH		Eu	Ce	La, Pr	Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Y
1N NH ₄ OH	Eu		Ce	La, Pr	Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Y

TABLE VII

Corrosion Rates of Rare Earth and Yttrium Metals
in Sodium Nitrate Solutions

Corrosion Rate, mpy Media	$1-9 \times 10^3$	$1-9 \times 10^2$	10-100	1-10	<1
1N NaNO_2 , 30°C		Eu		Nd, Tm	La, Pr, Ce, Sm, Gd, Tb, Dy, Ho, Er, Yb, Y
1N NaNO_2 Boiling	La, Ce, Eu	Pr	Nd	Yb	Sm, Gd, Tb, Dy, Ho, Er, Tm, Y

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FIGURE I

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6