CORROSION OF LANTHANUM UNDER ATMOSPHERIC CONDITIONS

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Tests on atmospheric corrosion of lanthanum [1-3] have taken little account of the effect of temperature, relative atmospheric humidity, and corrosive gases.

We have investigated atmospheric corrosion of lanthanum obtained by the calcithermic method and containing 99.9% La and the following impurities (%): Ca 0.03, Ce 0.035, and Nd 0.005. The content of Pr, Sm, Fe, and Cu (if present at all) was less than the sensitivity of the analytical method (0.01%). Metallographic and x-ray structural investigations revealed that the metal had a one-phase structure, namely α-La.

Before the tests the specimens (40 × 25 × 4 mm) were rubbed with emery paper 180, washed in ethyl alcohol, dried over $CaCl_2$ for several minutes, and then tested. All the experiments were performed in an apparatus enabling one to monitor both the relative humidity and the compositon of the atmosphere. The specimens were weighed together with the weighing bottles so as to take account of the partly crumbled corrosion products.

X-ray analyses were performed in a DRON-1 diffractometer in Fe–K_α radiation with a manganese filter. The IR spectra of the corrosion products in the form of suspensions in Vaseline oil were recorded in the range 400-4000 cm^{-1} in a UR-10 spectrometer. Differential thermal analysis (DTA) was performed in a Kurnakov pyrometer, designed by the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR, with simultaneous recording of the weight loss at a furnace heating rate of 20 deg/min.

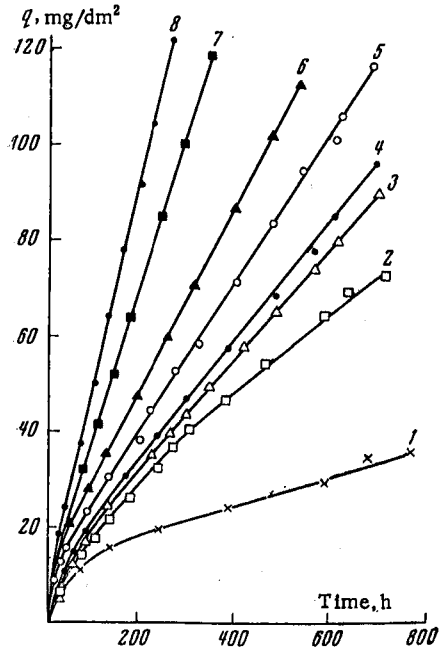

Fig. 1. Corrosion graph at 20°C in pure air with humidity (%): 1) 15; 2) 32; 3) 58; 4)80; 5)90; and in air with humidity 80% and 1 mg/liter of: 6) CO_2; 7) H_2S; 8) SO_2.

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TABLE 1. Electron-Diffraction Patterns of Primary Corrosion Products of Lanthanum

d, Å	Relative intensity, %	Identification of reflection
3,40	80	A — La_2O_3
2,27	100	A — La_2O_3; α — La
1,84	70	α — La
1,63	20	A — La_2O_3
1,41	20	α — La
1,30	20	A — La_2O_3
1,18	40	α — La

TABLE 2

Composition of atmosphere, additive, mg/liter	Content, %		
	H_2O (crystal.)	CO_2	$La(OH)_3$
Without corrosive gases	1,3	2,1	76.6
3 CO_2	2,5	3,0	58,1
1 H_2S	2,6	3,0	64,1
1 SO_2	2,6	2,8	62,3

It will be seen from the kinetic curves of atmospheric corrosion of lanthanum at t = 20°C in air with various different relative humidities (Fig. 1) that the process initially follows a decay law. An analysis of the initial sectors revealed that they are satisfactorily represented by a power function, the exponent of which decreases from two at low humidities to unity at high values. The lanthanum surface is initially covered by an thin dark blue film; after 20-30 h a bright deposit appears and then begins to crumble after 40-60 h. Regardless of the humidity, after roughly the same period the oxidation law becomes linear. Electron-diffraction analysis of the surface law after a test period of 30 h showed that in the initial period hexagonal lanthanum oxide is formed, not the cubic form, as stated by the authors of [4, 5] (Table 1).

From the data we may infer that in the initial period lanthanum is oxidized by atmospheric oxygen, leading to formation of an oxide film on its surface, thus retarding the process. However, as shown in [6], A-La_2O_3 readily absorbs water vapor from the ambient air and is converted relatively rapidly to $La(OH)_3$. This is accompained by a considerable increase in the specific volume, which leads to disintegration of the film and crumbling of the corrosion products. After disintegration of the oxide film the principal role is taken over by direct reaction of lanthanum with water. This is indicated by hydrogen evolution, established by gas analysis, and by formation of $La(OH)_3$ as the corrosion product, confirmed by x-ray analysis.

The partial pressure of water vapor, P_{H_2O}, has a marked effect on corrosion of lanthanum. It will be seen from Fig. 2 that the dependence of the reaction rate, calculated from the linear sectors, on P_{H_2O} is strongest at low relative humidities (15-32%), after which it is virtually linear. A similar dependence was observed in [7, 8] for other metals and was attributed to a change in the corrosion mechanism. If we bear in mind that with increasing relative humidity the parabolic dependence of the initial sectors becomes increasing linear, the data can be explained by the parallel course of oxidation and reaction of lanthanum with water. At low relative humidities the principal contribution is made by oxidation, whereas at higher humidities the role of the reaction with water becomes predominant.

The corrosion rate of lanthanum increases with temperature; the reaction rate of the linear sector closely obeys the Arrhenius equation. Analytical and graphical calculations gave virtually coinciding values of the apparent activation energy (21.3 ± 0.5 kcal/mole).

An investigation of the effect of corrosive gases showed that the corrosion rate increases in their presence, their corrosiveness increasing in the sequence $CO_2 < H_2S < SO_2$ (Fig. 1), i.e., increasing with the acid properties of the gas. The composition of the corrosion products was complex, but, as in a pure atmosphere, they consist mainly of lanthanum hydroxide. The IR spectra of the corrosion products formed in the presence of SO_2 exhibits a broad band at 1000 cm^{-1}, attributable to stretching vibrations in SO_4^{2-}, SO_3^{2-}, or S^{2-}, but chemical methods did not reveal these compounds.

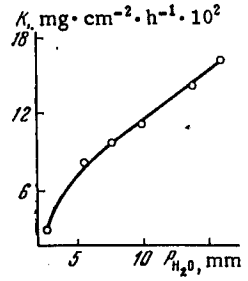

Fig. 2. Corrosion rate of lanthanum plotted vs P_{H_2O} at 20°C.

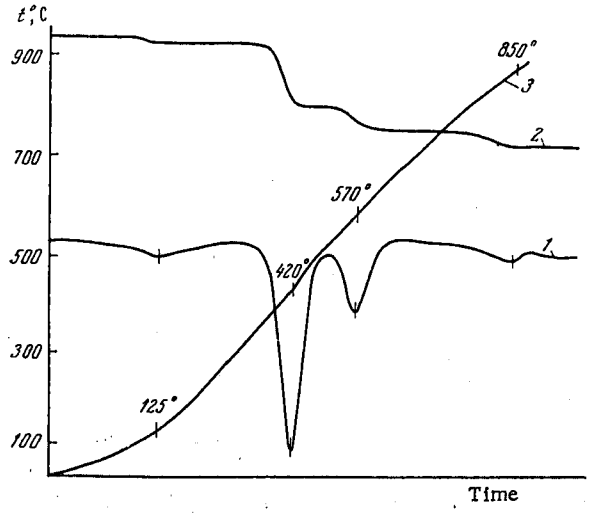

Fig. 3. Thermograms of the corrosion products of lanthanum: 1) differential thermal curve; 2) thermogravimetric curve; 3) heating curve.

X-ray phase analysis revealed that the products of corrosion in the presence of H_2S consist largely of $La(OH)_3$ and of a certain compound which we were unable to identify; however, the IR spectrum did not have additional bands in comparison with that of $La(OH)_3$.

In the case of atmospheric corrosion of lanthanum in the presence of CO_2, IR spectroscopy and DTA revealed formation not only of $La(OH)_3$, but also of a carbonate similar in composition of $La_2(CO_3)_3.8H_2O$ (if one investigates the effect of corrosive gases in air from which CO_2 has not been removed, in all cases the corrosion products contain carbonates). The thermograms of the products of corrosion in the presence of corrosive gases are not essentially different from those obtained under ordinary conditions (Fig. 3).

The first endoeffect (t = 125°C) is due to the removal of crystallization water from the carbonate. The next two effects at 420 and 570°C are due to decomposition of $La(OH)_3$ [6], and the effect at 850°C corresponds to evolution of CO_2 from the anhydrous carbonate [9].

The content of crystallization water, CO_2, and $La(OH)_3$ was calculated from the change in weight. As follows from Table 2, the presence of corrosive gases and an increase in the CO_2 content reduce the $La(OH)_3$ content and increase the carbonate content.

Table 2 shows that in an ordinary atmosphere corrosive gases promote formation of carbonates, the protective properties of which are apparently poorer than those of $La(OH)_3$. Therefore the accelerating effect of corrosive gases on corrosion of lanthanum is attributable both to acceleration of the cathodic process of hydrogen evolution and to a change in the compositon of the corrosion products.

LITERATURE CITED

1. B. Laves, in: Metallurgy of Rare Earth Metals [Russian translation], IL, Moscow (1962).
2. L. Lee and N. Green, Corrosion, 20, 145 (1964).
3. N. D. Tomashov and T. V. Matveeva, in: Corrosion and Protection of Metals [in Russian], Nauka, Moscow (1970), p. 70.
4. V. B. Glushkova, Polymorphism of Rare Earth Oxides [Russian translation], IL, Moscow (1962).
5. L. N. Komissarova, Wang Kên-shih, and V. I. Spitsyn, Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 3 (1965).
6. B. N. Rybakov, A. F. Moskvicheva, and G. D. Beregovaya, Zh. Neorgan. Khimii, 14, 2904 (1969).
7. J. T. Weber and G. E. Sturdy, J. Electrochem. Soc., 101, 583 (1954).
8. B. N. Rybakov, G. V. Maslova, and D. I. Zalkind, Zashchita Metal., 6, 444 (1970).
9. I. S. Morozov, Zh. Neorgan. Khimii, 1, 791 (1956).