A quantitative kinetic study on low temperature oxidation and hydroxidation of rare earth elements

Hirohisa UCHIDA, Daisuke KATSUYA and Fujio SUZUKI

Department of Applied Physics, Tokai University

Kitakaname 1117, Hiratsuka, Kanagawa 259-1292, Japan

Tel: +81-463-58-1211(EX.4136) Fax: +81-463-58-9461 e-mail: 0aasm007@keyaki.cc.u-tokai.ac.jp

(Received 15, October 2001 Accepted 7, December 2001)

We measured the oxidation kinetics of rare earth elements at room temperature. Until present, most work on oxidation of metals have been concerned for high temperature oxidation. We report that the surface of rare earths becomes oxidized and/or hydroxidized even at room temperature. This information is of great importance for materials conservation.

Keywords: oxides, hydroxides, surface process, low temperature, rare earth elements

I. INTRODUCTION

As well known, rare earths form various functional intermetallic compounds with transition metals such as hydrogen storage alloys (LaNi₅, Mm (mish metal) Ni₅) and magnetic materials (TbFe₂, Nd₂Fe₁₄B). However, rare earths included in the compounds have high reactivity with O₂ and H₂O even at room temperature.^{1,2,3} Actually, the surface oxidation of Nd₂Fe₁₄B type magnet is well known. In addition, the loss of such valuable materials is a serious problem for our future. In this study, we measured the oxidation kinetics of rare earth elements at room temperature. Until present, most work on oxidation of metals have been concerned for high temperature oxidation. We report that the surface of rare earths becomes oxidized and/or hydroxidized even at room temperature. This information is of great importance for materials conservation.

II. EXPERIMENTAL CONDITION

An ultra high vacuum system was used for the measurements of the reaction probability *r* of gases of O₂ and H₂O with rare earth elements and the reacted gas amount *N*. Details of the measurement are reported elsewhere.^{4,5} After degassing treatment of metal samples, the samples were evaporated onto reaction vessel until the sample film thickness attained to 100 nm. The purity of used gases were 99.99% (O₂ gas) and 15MΩ cm (H₂O gas). Reaction gases were introduced to reaction vessel through receiver, capillary.

III. RESULT

III-A. Ln – O₂ systems

In this study, the reacted gas amount of *N* is expressed in molecules cm⁻² or monolayers (ML), where 1 ML = 10¹⁵ molecules cm⁻². And the reaction probability *r* is defined as the ratio of the rate of gas adsorption of gas molecules to the impinging rate of gas molecules on the metal surface.

Fig.1. O₂ reactivity with each rare earth(La, Ce, Nd, Dy, Tb).

Table 1. Heat of solutions in kJ/mol O.

La ₂ O ₃	Ce ₂ O ₃	Pr ₂ O ₃	Nd ₂ O ₃	Sm ₂ O ₃	Dy ₂ O ₃	Tb ₂ O ₃
-598.3	-599.0	-603.5	-602.9	-611.1	-609.6	-622.2

Table 2. Activation energy of oxygen in kJ/mol O.

CeO _{1.818}	Pr ₇ O ₁₂ (low temp)	Pr ₇ O ₁₂ (high temp)	Nd ₂ O ₃	Sm ₂ O ₃
41.9	34.4	79.74	130	98.4

In Ln (La, Ce, Pr, Nd, Tb, Dy) – O₂ systems (Fig. 1), reaction probability $r_{O_2} = 1$ is shown at the initial stage. These results mean that Ln – O₂ systems have high reactivity of O₂ with rare earths films with a clean surface even at low temperature. This means that the clean surface of Ln (La, Ce, Pr, Nd, Tb, Dy) can readily exchange electrons with the covalent O₂ molecules to dissociate the molecules into O atoms. The length of region of the highest reactivity $r_{O_2} = 1$ differs for each rare earth element respectively. Based on the Fromm – Mayer model, the length L of the region of the highest reactivity is proportional to the ratio of heat of reaction of oxygen solution ΔH_S in a metal to activation energy A_D of oxygen atom in a metal: $L = |\Delta H_S| / A_D$.^{6, 7} This model argues that L should become longer with negatively increasing heat of solution, and shorter with increasing activation energy for diffusion. In fact, the penetration of oxygen atoms into a metal at low temperature cannot be explained simply by conventional diffusion mechanisms of oxygen at high temperatures over 500 K. The formation of oxide layers on the metal surface by actual occurrence of oxygen atoms in the surface region is explained by complex mechanisms of the changing flow rates of electrons and ions between the metal surface and oxide layers as the layers grow.^{8, 9} Reported ΔH_S and A_D are given in Table. 1 and 2.¹⁰ For each rare earth used in this study, ΔH_S values are similar, however, A_D has quite different values. From these, the different values of A_D seem responsible for the different length of L.

With increasing N, the value of r_{O_2} decreases differently for each rare earth. This different behaviors in decreasing in r_{O_2} are surely influenced, firstly, by the length of the initial stage $r_{O_2}=1$, and secondly, by decreasing metallic features of each rare earth element as surface oxidation proceeds. The Ce surface can exhibit a higher oxidation state, Ce⁺³. This may exhibit a prolonged oxidation even at lower reactivities than $r_{O_2}<10^{-3}$. The Nd surface exhibits a very low reactivity compared with other elements. A high A_D value may be responsible for the low activity (Table 2).

III-B. Ln – H₂O systems

In metal – H₂O systems, we define the following relation

where β which is the dissociation rate of the H atoms from H₂O, is estimated from the measurement of the increasing H₂ partial pressure.^{1, 11}

In Ln (La, Ce, Pr, Nd, Tb, Dy) - H₂O systems, the initial reactivity of H₂O is $r_{H_2O} = 1$ (Fig.2 and Fig.3).

This means that dissociated atoms (H, O and OH) from H₂O are reacted with the surface of rare earths. As oxide and hydroxide layers grow, r_{H_2O} (Fig.2) and r_{2H/H_2O} (Fig.3) decrease. This argument is demonstrated also by the change in the β factor. β is decreased as the reactivity of the H atoms from H₂O decreases. At $r_{H_2O}<1$, r_{H_2O} is higher than r_{2H/H_2O} , meaning that oxidation or hydroxidation by O or OH from H₂O proceeds at higher rates than that of H uptake into metal.

Fig.2. H₂O reactivity with each rare earth s films.

Fig.3. H from H₂O reactivity with each rare earths films.

IV. CONCLUSION

This study quantitatively revealed that each rare earth can be easily oxidized or hydroxidized even at

room temperature, and demonstrated that each rare earth has different reactivity with O₂ and H₂O molecules. These facts should be taken into account in practical use and saving of rare earths.

V. REFERENCES

- ¹ H. Uchida and E. Fromm, J. Less-Common Met. 95 (1983) 147.
- ² N. Hosoda, H. Uchida, Y.Ohtani, T. Takahashi and E. Fromm, Z. Phys. Chem. N. F., 164 (1984) 103.
- ³ M. Hadano, N. Urushihara, T. Inoue and H. Uchida, J. Alloys & Comp., 293 (1999) 403.
- ⁴ S. Wagener, Br. J. Appl. Phys., 1 (1950) 225.
- ⁵ E. Fromm and H. G. Wulz, J. Less-Common Met., 101 (1984) 469.
- ⁶ E. Fromm and O. Mayer and W. Nickerson, Surface Sci. 57 (1976) 776.
- ⁷ E. Fromm and O. Mayer, Surface Sci., 74 (1978) 259.
- ⁸ O. Kubaschewski and B. E. Hopkins, Oxidation of Metals and alloys, 2nd ed., Butterworths, London, (1962).
- ⁹ N. Cabrera and N. F. Mott, Rept. Phys. 12 (1949).
- ¹⁰ L. Eyring, Handbook on the Physics and Chemistry of Rare Earths, Vol. 3, edited by K. Gschneider Jr.
- ¹¹ N. Hosoda, H. Uchida, Y. Ohtani, T. Takahashi and E. Fromm, Z. Phys. Chem. N. F., 164 (1989) 1129.

Presented at the 5th International Conference on
ECOMATERIALS Oct. 2-4, 2001, Honolulu, Hawaii