HEAT OF INTERACTION OF OXYGEN WITH DYSPROSIUM AND YTTRIUM

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Dedicated to Dr R. Zahradník on the occasion of his 60th birthday.

Heat of interaction of oxygen dosed to vacuum-evaporated films of dysprosium and yttrium were measured in a calorimeter at room temperature. The high and rapidly produced heat, and the attained oxygen-to-metal ratio indicate high reactivity of these rare earth metals towards oxygen molecules which obviously undergo dissociative sorption. The energy of bonding of the formed oxygen species to the metal was estimated to 723 kJ/mol (173 kcal/mol) and 780 kJ/mol (186 kcal/mol) for Dy and Y, respectively. A markedly higher sorption capacity of Y film compared to Dy film was observed. The heat produced by the first admitted doses of oxygen may suggest formation of a solid solution of oxygen species in Dy and Y at very low oxygen-to-metal ratios.

The rare earths metals include the IIIA Group elements Sc, Y, La, and the 14 elements of atomic number 58 through 71, designated as lanthanides. While the free atoms of lanthanides have the basic configuration of their outer electrons $4f^n6s^2$ or $4f^n5d^16s^2$, the valence band of lanthanides in the metallic state has predominantly d-character near Fermi level E_F and sp-character at the band bottom, the $4f$ levels being well below E_F (refs[1-3]). A similar hybridization occurs in the metallic Sc, Y, and La which lack f electrons. For example, $(4d5s)^3$ hybridization has been reported for the outer electron structure of metallic yttrium[4].

Knowledge of the properties of rare earths has advanced considerably in the last period[3,5]. Most recently, the attention paid to the rare earths has further increased in connection with their role in the high-T_c superconducting materials. The study of the interaction of rare earth surfaces with gases[3,6] has in general somewhat lagged behind the extensive research of other physical and chemical properties of these metals. Particularly little has been known about the energetics of the mentioned interactions.

The present paper reports on the heat of interaction of gaseous oxygen admitted in doses to films of Dy and Y. Dysprosium is a typical heavy lanthanide with an intensive band of f electrons which are located deep below E_F, nevertheless they

exhibit significant changes upon sorption of oxygen[7]. The present results are a continuation in the series of measurements dealing with the interaction energy of hydrogen[8], carbon monoxide[9], and hydrocarbons[10] admitted to clean Dy and to its alloys with Cu (ref.[11]). Yttrium has been chosen for the sake of comparison, because this rare earth lacks f electrons. In addition, its interaction with oxygen might be of some interest with regard to the presence of these two elements in the structure of high-T_c superconductors.

It is well known that all rare earths form stable trivalent sesquioxides M_2O_3, and some of them also lower or higher oxides. The mechanism of interaction of oxygen with Dy and Y is in general similar to each other[3,6]. The first step of the oxidation process probably consists in the dissociation of the oxygen molecule on the surface, followed by dissolution of the formed oxygen species into the subsurface region. The depth profile of oxygen concentration is strongly pressure dependent[3,6]. If a sufficiently high oxygen concentration in the subsurface region is attained, nucleation of an oxide likely sets on. The oxide film grows steadily deeper into the bulk. After a certain exposure the oxide film forms a protective layer which slows down the further oxidation[3,6]. Though the oxidation kinetics differ from one rare earth to an other one, most rare earth metals, including Dy and Y, are not attacked in air into a great depth at an appreciable rate[3,6,12]. The passive oxide film may be different from the known bulk oxide. The interaction of oxygen with Y surfaces has been discussed in ref.[13].

EXPERIMENTAL

The present results were obtained in a calorimetric device which was described jointly with the experimental procedure in earlier papers[8,14,15]. The heat measurements were performed at 295 K with films of the given metals evaporated onto the inner wall of the cylindrical glass vessel of the kalorimeter kept at about 285 K. The pressure in the calorimeter before the start of the film deposition, and during the deposition which took about 15 min, was of the order of 10^{-7} Pa. The films of Dy and Y weighed 8·3, 11·2, 5·9 mg; and 4·1, 3·0, 6·1 mg, respectively. After the film deposition, the calorimeter was closed by a ground-glass valve up to the beginning of the oxygen dosing. The films covered about 80 cm^2 of the vessel wall. Their average thickness calculated from the density of the metal disregarding the internal porosity of the film, ranged from approximately $0·85 . 10^2$ nm to $1·70 . 10^2$ nm both for Dy and Y. However, a strong inhomogeneity of the thickness along the film area and high internal porosity of the films should be expected. Oxygen was produced in the sorption apparatus by thermal decomposition of $KMnO_4$, and it passed before reaching the film through four traps cooled to 195 K. The used specimens of Dy and Y were prepared in the Institute of Metallurgy of the Academy of Sciences of the U.S.S.R., and their claimed purities were 99·99 and 99·96%, respectively.

RESULTS AND DISCUSSION

The heat produced by doses of oxygen admitted to the Dy film weighing 8·3 mg is shown in Fig. 1. The average heat in the central region of the $Q(n)$ curve (the range

of the O/Dy ratio from 0·039 through 0·138) was 956·4 $\pm$ 20·9 kJ/mol, i.e. 228·8 $\pm$ $\pm$ 5·0 kcal/mol (Grubbs T test and Student distribution were used with the significance level of 0·05). The two other experiments of a preliminary nature[16] gave an average heat of 989 $\pm$ 87 kJ/mol (237 $\pm$ 21 kcal/mol) and 941 $\pm$ 63 kJ/mol (225 $\pm$ 15 kcal/ /mol). No clear-cut dependence of the heat Q on the consumed amount n of oxygen appeared in the given region. By contrast, XPS measurements[7] showed an increase in the O $1s$ binding energy and development of a second peak at the increasing exposure of a polycrystalline Dy film to oxygen. A detailed comparison of the O/Dy ratio reached in the two kinds of experiments would be necessary to clarify this point.

Again three experiments were performed with Y films. In the experiment shown in Fig. 1 (the film weight was 4·1 mg), the average heat in the range of the O/Y ratio from 0·023 through 0·277 amounted to 1 107·5 $\pm$ 20·1 kJ/mol, i.e. 264·7 $\pm$ 4·8 kcal/ /mol (Grubbs test and Student distribution were applied in the same manner as with Dy). No distinct trend in the $Q(n)$ curve was apparent over the given range of the O/Y ratios. The two other experiments were in a fairly good agreement with these findings. They gave an average heat of 1 023·8 $\pm$ 12·1 kJ/mol (244·7 $\pm$ 2·9 kcal/mol)
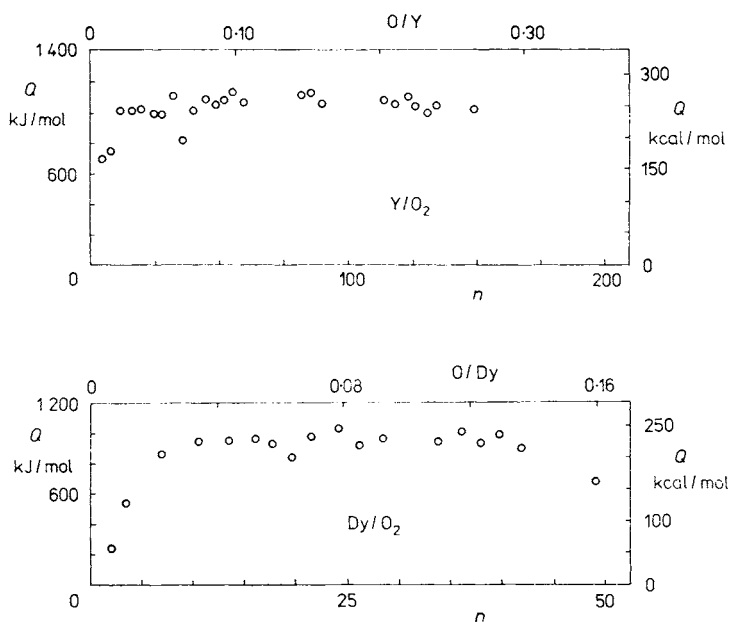

FIG. 1

Heats of interaction of oxygen admitted to yttrium and dysprosium film at 295 K in dependence on the amount of oxygen adsorbed n (10^{-6} mol O_2 per 100 mg of the metal); 1 kcal/mol = = 4·1868 kJ/mol

and 1 041·0 ± 18·0 kJ/mol (248·8 ± 4·3 kcal/mol), respectively. The average value from the three experiments is 1 057·3 kJ/mol (252·7 kcal/mol).

The high heats indicate that the oxygen molecules undergo dissociative sorption. Auger spectra have shown that a covalent bond is formed between the Y and O atoms[13]. Energy of bonding of the oxygen atoms to the metal can be approximately estimated if the produced heat Q is taken equal to the difference between the sum of energies of the formed oxygen-to-metal bonds, and dissociation energy of the oxygen molecule. In this way, 723 kJ/mol (173 kcal/mol) and 774 kJ/mol (185 kcal/mol) result for the energy of bonding of O atoms to metallic Dy and Y, respectively (the average heat of 1 057·3 kJ/mol was taken in the calculations with Y). In ref.[17], 602·2 kJ/mol (144·1 kcal/mol) and 702·4 kJ/mol (168·0 kcal/mol), respectively, are given for dissociation energies of the diatomic molecules DyO and YO in their ground states. In ref.[18], 144 ± 5 kcal/mol (601·9 ± 20·9 kJ/mol) and 170 ± 3 kcal/mol (711·8 ± 12·5 kJ/mol) can be found for the respective dissociation energies.

Similarly as in a number of other gas–metal systems[19], the two or three initial doses in the Dy/O_2 and Y/O_2 system gave markedly lower heats. This might be due either to an artifact (partial adsorption in cold traps and on the outgassed tubing of the apparatus, and/or displacement of impurities from the film), or − at least partially − to a process characteristic for the gas–metal system under study[9,14,19]. Since heat of solution is in general lower than the heat of oxide formation, solution of oxygen atoms in the Dy and Y film at very low O/Dy and O/Y ratios might be partially responsible for the lower heats observed. A similar tentative explanation involving formation of a solid solution of the dissociated species was suggested for the initial heats in the Gd/H_2 system[14].

The rate of heat production after admission of an oxygen dose to the Dy and Y film was high over a large range of the oxygen-to-metal ratios; the major portion of heat was produced within some 20 s. However, minor protracted heat effects likely followed the rapidly produced heat, particularly in the later doses, both in the Dy/O_2 and Y/O_2 system. This was indicated by changes in the effective cooling constant calculated from the temperature–time trace of the particular doses (cf. ref.[20]). Such heat effects might be connected with progressive penetration of oxygen species into the subsurface region of the metal resulting in a slow oxidation process. The used technique was not suitable for a detailed study of such effects.

When the uptake of oxygen reached approximately 42 . 10^{-6} mol per 100 mg of the Dy film, which corresponded to an O/Dy ratio of about 0·14, the subsequent doses of oxygen were sorbed with a progressively decelerating heat production and a decreasing heat (Fig. 1). This continued up to an O/Dy ratio of approximately 0·20; then the process became too slow to be monitored in the used device. With Y, rapid uptake of the dosed oxygen occurred up to an amount of approximately 155 . 10^{-6} mol per 100 mg of the Y film, i.e. up to an O/Y ratio of about 0·28 (Fig. 1). A fall in the heat and deceleration of its production took place in the next

doses. When an O/Y ratio of approximately 0·33 was attained, further consumption of oxygen proceeded at a rate hardly detectable with our instrument. The surprisingly high O/Y ratio which was achieved could be due to a developed porous structure and high internal surface of the Y film, so that a large portion of the Y atoms were exposed to the gas phase. The Dy film was probably less porous.

CONCLUSION

The high and rapidly produced heat, and the attained high oxygen-to-metal ratio show that both Dy and Y are very reactive toward admitted gaseous oxygen. Oxygen molecules are first dissociated on the surface, and the atomic species thereafter penetrate into the subsurface region where they ultimately form strong bonds to the metal. Energies of these bonds are estimated to 723 kJ/mol and 774 kJ/mol with Dy and Y, respectively. The initial part of the observed $Q(n)$ curve might be tentatively ascribed to the formation of a solid solution of dissociated oxygen species in Dy and Y at low oxygen-to-metal ratios. Sorption capacity of the Y film was higher than that of the Dy film under the given conditions.

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Translated by the author (S.Č.)