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DETERMINATION OF ELECTRIC POTENTIAL ACROSS THE OXIDE SCALE DURING OXIDATION OF TANTALUM, NIOBIUM, AND MAGNESIUM

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SUMMARY

According to Hauffe's theoretical treatment of the oxidation of metals, the oxide-gas interface is electrically negative with respect to the oxide-metal interface. The potential difference is considered to be one of the driving forces for oxidation. Experimental evidence, presented here, does not support this assumption. The polarity of measured potential is reversed and has a retarding effect on oxidation. The magnitude of the potential and its temperature dependence were determined for tantalum, niobium, and magnesium during oxidation in air. The magnitude of the potential does not depend upon oxide thickness. Features of the potential-temperature curves for tantalum and niobium correspond to significant changes in the oxidation rates of both metals.

INTRODUCTION

Although in various oxidation theories for metals and alloys (refs. 1 to 7) the electrochemical nature of the oxidation process was taken into account, experimental studies of this basic aspect of oxidation have been very limited. There are, therefore, few experimental data to test the validity of the assumptions concerning the electric potential, upon which the theories are based.

There are at least three theories which were proposed to describe the initial stage of oxidation. These electrostatic theories are based on different assumptions concerning the rate-controlling factor in this process. Cabrera and Mott (ref. 4) postulated that negatively charged oxygen ions when adsorbed on the oxide surface create an electric field within the oxide. This field induces migration of positive metal ions to the oxide surface, and the escape of metal ions into the oxide becomes the rate-controlling factor. Uhlig (ref. 5) assumed that the electron flow from metal to oxide determined the initial rate of oxidation. Boggio and Plumb (ref. 7) modified the

Cabrera-Mott theory by making several additional assumptions. Their theory is supposed to apply only at low temperature when the oxide film is about 20 Å (2×10^{-7} cm) thick.

In general, the oxidation studies of metals and alloys are performed by the gravimetric method. Such weight-increase determinations do not yield direct information concerning the mechanism of oxidation. The gravimetric determinations should be accompanied by electrochemical and physical experimental techniques if the proposed oxidation theories are to be tested. Such techniques have been used to determine thermodynamic properties of oxides (refs. 8 to 17), but only on rare occasions have they been applied to oxidation of metals. Uhlig and Brenner (ref. 18), Cismaru and Cismaru (ref. 19), and Lawless and Lombard (ref. 20) attempted unsuccessfully to influence the oxidation rates of metals by applying a potential difference between the sample and an electrode separated by a layer of air or oxygen. On the other hand, Schein, Le Boucher, and Lacombe (refs. 21 and 22) and Jorgensen (refs. 23 and 24) were able to demonstrate the effect of an externally applied electric field upon the oxidation of iron, silicon, and zinc.

The work reported here is a part of a larger program concerned with experimental studies of the electrochemical nature of oxidation. An electric potential which developed across the oxide layer during oxidation in air was measured for tantalum (Ta), niobium (Nb), and magnesium (Mg). The measured voltages were in the 1-volt range and were found to be a function of temperature and to be independent of the oxide layer thickness. The polarity of this potential is such that the metal is negative with respect to the oxide-gas interface, which is contrary to the one postulated by others in their oxidation theories.

EXPERIMENTAL PROCEDURE

Tantalum, niobium, and magnesium metals, 99.99 percent pure, were obtained in the form of 0.635 centimeter-diameter rods. They were cut into 1.27 centimeter-long cylinders, and a 7.62×10^{-2} centimeter-diameter-, 0.952 centimeter-deep concentric hole was drilled in each cylinder. Platinum wire 7.62×10^{-2} centimeters in diameter and 4.0 centimeters long was inserted into the concentric hole of the cylinder forming a so-called metal electrode. Tight contact between the wire and the cylinder was obtained by swaging. The "oxide electrode" was then formed by oxidizing Ta and Nb for 5 minutes at 900° C and Mg samples for 1 hour at about 530° C and wrapping 1.28×10^{-2} centimeter-diameter platinum wire around them (figs. 1 and 2). These oxidation conditions are not critical; the only requirement is that a thin and adherent oxide film be produced. Two platinum rings at the two ends of the cylinder held the

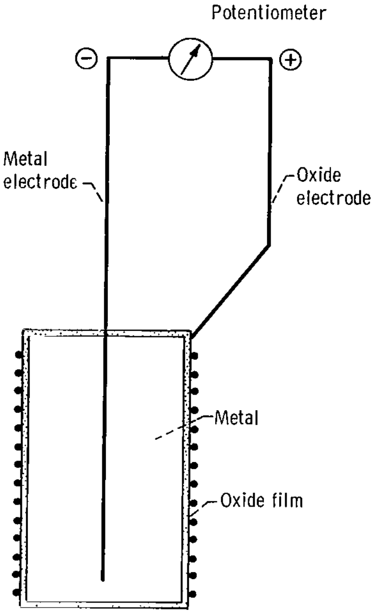

Figure 1. - Schematic diagram of experimental cell.

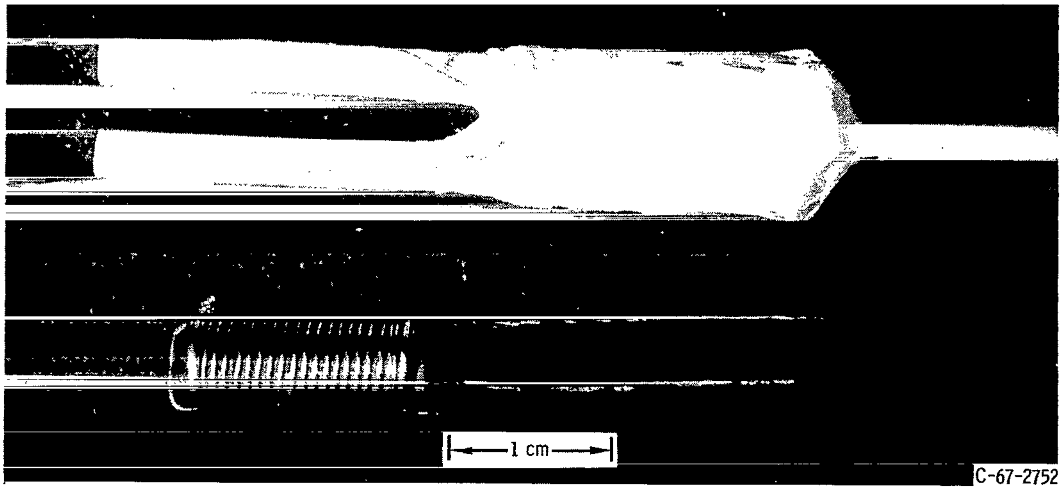

Figure 2. - Oxidation cell and its holder.

platinum spiral in place throughout the experiment.

The cells were supported by an alumina holder, shown in figure 2. The cell was cradled between the two prongs of the alumina fork. The lead wires from the cell were connected to two platinum wires which were threaded through two holes in the 30 cm-long alumina tube. The oxide electrode lead was connected to the positive pole of the recording potentiometer (Graphicorder 10) and the metal electrode to the negative one. The cells were oxidized in air in a platinum-wound resistance tube furnace open at both ends, and their temperatures were recorded with the aid of a platinum - platinum-13-percent rhodium thermocouple attached to a dummy cell. The effectiveness of temperature determination on a dummy cell was verified with a fine platinum - platinum-13-percent rhodium thermocouple attached to one of the investigated cells. The desired oxidation temperatures were obtained by changing the temperature of the furnace. In this manner the electric potential across the oxide scale, developed during oxidation, was measured as function of temperature. Three Ta, two Nb, and two Mg cells were used in the experiment. Experimental points were obtained on heating and cooling with satisfactory reproducibility.

RESULTS AND DISCUSSION

Experimental results representing the relation between the measured potential and the temperature for Ta, Nb, and Mg during oxidation in air are shown in figure 3. For

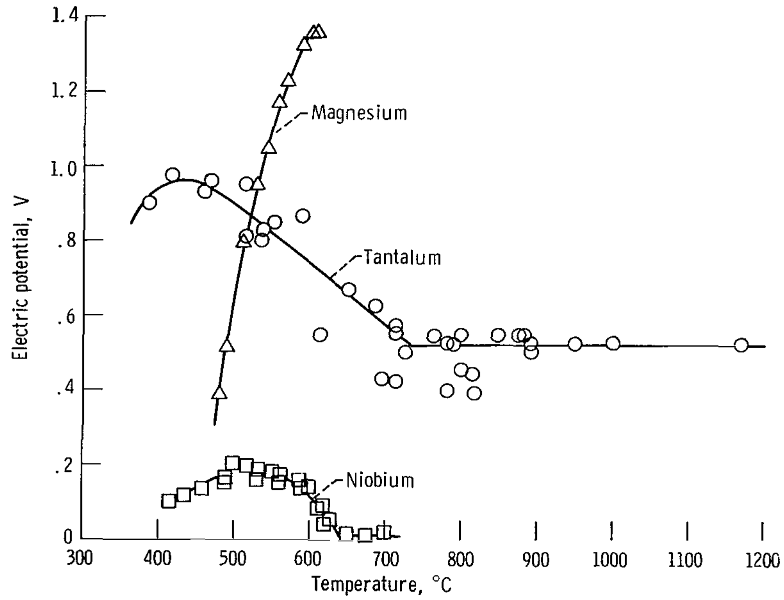

Figure 3. - Electric potential measured across oxide scale during oxidation of tantalum, niobium, and magnesium in air.

Nb, the potential increases with temperature, goes through a maximum, and then decreases to a constant level. Tantalum exhibits a similar behavior. A comparable curve for Mg could not be obtained, because the samples ignited at about 610° C.

At the present it is not possible to discuss the quantitative aspects of these results. However, several qualitative observations, which are basic to an understanding of the oxidation mechanism, can be made. One important observation is concerned with the polarity of the measured potential. The metal electrode was negative with respect to the oxide electrode for all three materials. Also, it was established that, at constant temperature, the potential does not change with time; therefore, it is independent of the oxide-layer thickness. It can be seen from figure 3 that at temperatures above 750° and 640° C for Ta and Nb, respectively, the electric potential becomes constant. In relation to this observation, it should be noted that Kofstad (ref. 25) and Arbuzov and Chuprina (ref. 26) observed a significant change in the oxidation behavior of Ta and Nb in similar temperature ranges. This change appeared as a maximum on the Arrhenius plot of the linear rate constant of oxidation.

Considering the fact that the polarity of the potential, as determined in this study, is not in agreement with the polarity assumed by Hauffe (ref. 6, pp. 97 to 143) in his oxidation theory, one can question whether the measured potential is indeed due to the oxidation process. In order to answer such questions, additional experiments were performed, the results of which are as follows:

(1) In the case of the tantalum cells, the measured potential depends upon oxygen pressure. The potential decreases as the pressure becomes lower.

(2) Tantalum cells, measured under complete electrostatic shielding, produced the same potential as the nonshielded cells.

(3) In the case of a tantalum cell in which the platinum lead wire (metal electrode) was replaced with a tantalum rod, thus eliminating the Ta-Pt interface, results identical to those of the regular Ta cells were obtained.

(4) An oxidation cell, made of chromium, in which the metal electrode was made equipotential with the oxide electrode by connecting them together, oxidized at a faster rate than a similar cell with electrodes not connected.

A similar experiment was reported by Ilschner-Gensch (ref. 27), who observed that nickel covered by a borate melt under an oxygen atmosphere did not oxidize at 780° C. If, however, the nickel sample was in electrical contact with a platinum wire, which extended up to the melt-oxygen interface, the nickel oxidized rapidly. These two experiments indicate clearly that the potential across the oxide layer retards the oxidation, and in order to do so, the metal has to be negative with respect to the outermost oxide surface.

Thermoelectric effect in metals and their oxides should be negligible because the cells were at uniform temperature. Even if there were significant temperature differences between different points in a cell, the thermoelectric electromotive force would be considerably smaller than the observed potential.

SUMMARY OF RESULTS

A simple experimental technique was used to measure the electric potential across the oxide scale which developed during oxidation of tantalum, niobium, and magnesium. The potential was independent of the oxide-scale thickness, but its magnitude changed with temperature. Its polarity opposed the ionic transport (oxidation) contrary to the commonly accepted notion that it is one of the driving forces for oxidation as expressed in Hauffe's theory.

Lewis Research Center,
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