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Initial Oxidation of Cobalt

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The initial oxidation of pure cobalt has been studied by a manometric method in the range 320 to 520° C for 1 to 15 min using purified dry oxygen at 7.6 cm of mercury. The oxide thickness varies from 400 Å at the lowest to 5000 Å at the highest temperatures. Oxidation follows a direct logarithmic law and is independent of oxygen pressure. A typical Arrhenius plot shows an anomaly at the allotropic change point (~386° C) of cobalt, although the activation energies of oxidation of both the allotropes are very much the same. The modified model of Uhlig's mechanism on logarithmic oxidation [7] applies in the present case.

1. Introduction

So far very little attention has been paid to the kinetics of the initial oxidation of cobalt at low temperature. Only a few works [1, 2] have indicated deviations from the parabolic law in the early stages of oxidation. Uhlig, *et al* [3] have shown by graphical analysis of Gulbransen's results [2] that the initial oxidation of cobalt (at 400 and 500° C) could be logarithmic type. The present paper deals only with the initial oxidation of pure cobalt in the range 320 to 520° C at an oxygen pressure of 7.6 ± 0.1 cm mercury.

2. Experimental

2.1. Apparatus

The oxidation rate was studied using a manometric method. The apparatus is shown schematically in fig. 1. Each specimen was pushed into the reaction tube at room temperature by removing the detachable part L. Vacuum-tight brass fittings were used at both ends of the tube. Valves D_1, D_2, D_3 and D_4 were diaphragm types, while N was a needle valve. All these valves were of high vacuum type. The overall system was satisfactorily vacuum tight. The furnace temperature was maintained constant to within ± 1° C by means of a saturable reactor unit. Oxygen used was dried and cleaned by passing through a cylindrical brass filter F which was fitted with a porous stainless steel disc having pores 5 to 10 μm in diameter, on which was placed soda asbestos and magnesium perchlorate. The gas coming through the filter was admitted to the reservoir R by opening N. With D_1 opened and D_2 closed, the pressure of oxygen in this side of the apparatus was registered on the manometer.

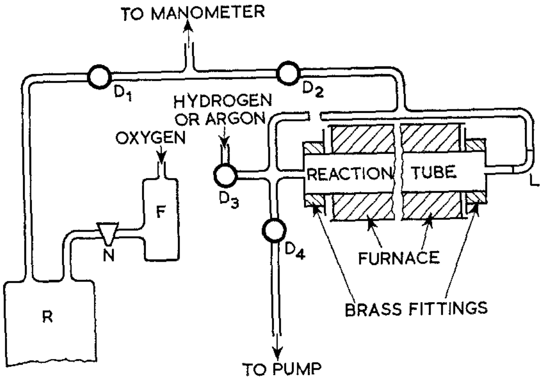

Figure 1 Apparatus for measuring oxidation.

2.2. Procedure

Spectrographically pure cobalt was supplied by Johnson Matthey & Co Ltd, in the form of rolled strips (0.05 cm thick). Specimens (5 × 2 cm) were cold sheared from the strips and were first degreased by washing in aqueous sodium carbonate followed by carbon tetrachloride. They were next given a surface polish as uniformly as possible by means of fine emery paper

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(4 grade). They were then re-washed in acetone, dried, weighed and were ready for the oxidation test.

With D_2 closed, the tube with the specimen in it was evacuated by opening D_4 (the left side of the apparatus was not affected since D_2 was closed and thus the oxygen gas which was admitted beforehand remained intact). After evacuation, hydrogen gas was admitted through D_3 with D_4 closed, in order to reduce any air-formed film on the metal. The furnace was then switched on and the temperature was raised slowly to the desired figure. Hydrogen treatment was followed by annealing in argon to remove any hydrogen left in the tube after evacuation at the end of the treatment. After argon annealing, the tube was again evacuated. With D_3 and D_4 closed, the specimen, inside the tube *in vacuo* at the right temperature, was ready for the oxidation test. This was carried out by opening D_2 with D_1 closed. Oxygen enclosed between D_1, D_3 and D_4 (which includes the reaction tube, the manometer and the connecting brass tubing) was gradually used up by the cobalt as the oxidation proceeded. Progress of oxidation was measured from the decrease in the pressure of oxygen in the manometer. Readings were taken using a cathetometer from which a change in pressure, as low as 1/200 mm, can be noted. The volume of oxygen (435 ml) enclosed between the valves D_1, D_3 and D_4 was determined by allowing oxygen of known volume and pressure between valves D_1 and D_2 to expand into the evacuated system, and noting the final pressure.

3. Results

An X-ray analysis of the as-received metal was carried out because of the possible existence of two kinds of cobalt crystal structure at room temperature [1, 4, 5]. The structure thus found was entirely of hexagonal close packed (hcp) form. In view of decreasing pressure during a run, it was necessary to estimate the effect, if any, of oxygen pressure on the oxidation rate. Several runs were carried out at different temperatures with oxygen pressure varying from 2.5 to 25 cm. Oxidation rates were found to remain the same (within experimental error) despite a tenfold change in the pressure. Results at various temperatures, e.g. at 470, 386 and 335° C are plotted in fig. 2, the initial pressure of oxygen was 7.6 cm in all cases. (Two sets of curves at 386° C are shown to illustrate the two types of results obtained at that temperature.) The data fall on smooth curves in fig. 2, but when re-plotted semi-logarithmically as in fig. 3 they conform to linear plots, hence to a direct logarithmic law. The final film thickness is estimated to vary from 400 to 5000 Å with increasing temperature. The logarithm of the rate constant K_0 decreases linearly with the reciprocal of absolute temperature in accordance

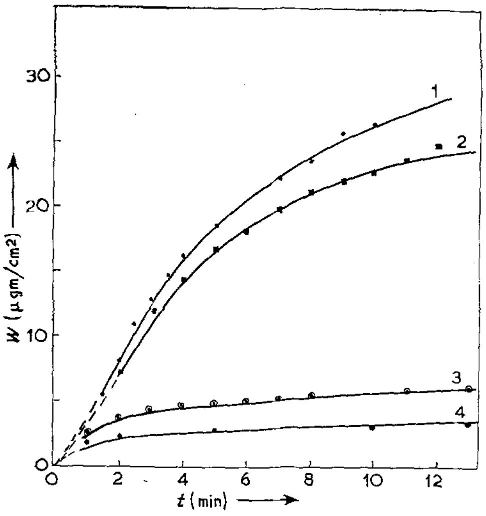

Figure 2 Isothermal plots of weight of oxide per unit area (W) against time (t) at various temperatures. Ordinate W (μgm/cm²); abscissa t (min). Curve 1 (470° C), 2 and 4 (386° C), 3 (335° C).

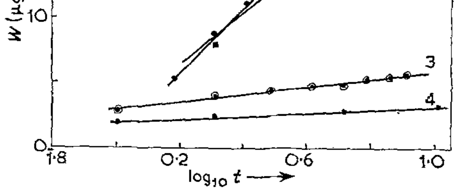

Figure 3 Isothermal plots of weight of oxide per unit area (W) against logarithm of time ($\log_{10} t$) at various temperatures. Ordinate W (μgm/cm²); abscissa $\log_{10} t$. Curve 1 (470° C), 2 and 4 (386° C), 3 (335° C).

with the Arrhenius equation (fig. 4). There is a break in the Arrhenius plot at 386° C which is due to the allotropic transformation of hcp cobalt to fcc (face centered cubic) form. A dialatometric curve of the as-received metal also confirmed such a transformation.

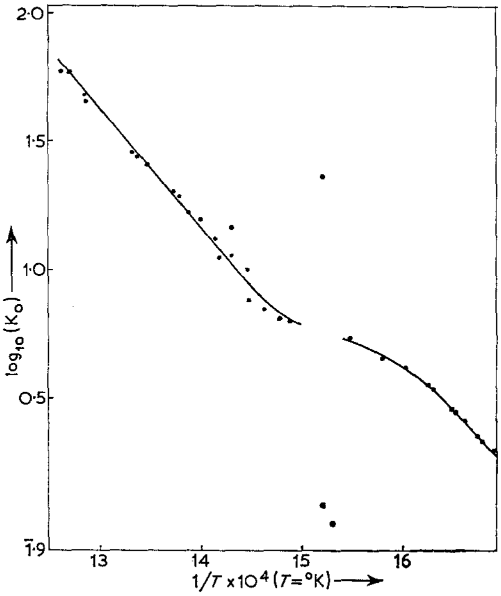

Figure 4 Arrhenius plot of logarithm of the reaction rate constant ($\log_{10} K_0$) against reciprocal of the absolute temperature ($1/T$). Ordinate $\log_{10} K_0$; abscissa $1/T \times 10^4$ (T = °K).

Besides the kinetics of oxidation, a study on the oxide films by transmission electron micrography has also been made [6]. Thus it has been shown [6] that the oxide formed from fcc cobalt has higher dislocation density than that from hcp-phase.

4. Discussion

Linear semi-logarithmic plots (fig. 3) suggest the oxidation law to be the direct logarithmic law in the present case. The Arrhenius plots of $\log_{10} K_0$ against $1/T$ and $\log_{10}(K_0/T)$ against $1/T$ were almost identical. Only the former type of Arrhenius plot is shown here (fig. 4). The ΔE values (i.e. the activation energies of oxidation) are given in table I. It becomes evident from the table that the ΔE values for the two allotropes do not differ much. In fig. 4 there is an indication of a higher K_0 value for the oxidation of hcp cobalt than that of the fcc-phase. This could be attributed to the different pre-exponential terms in the Arrhenius equation for the two cases, since the ΔE values are the same in both cases.

TABLE I Activation energy of oxidation, ΔE (kcal/mol)

Cobalt	ΔE values as obtained from the plot of $\log_{10} K_0$ against $1/T$	ΔE values as obtained from the plot of $\log_{10}(K_0/T)$ against $1/T$
hcp	18.5	18
fcc	20	19

Interpretation of any activation energy value basically depends upon the type of mechanism that has been adopted to explain the oxidation process. Thus according to the proposed mechanism of the direct logarithmic oxidation [7], the activation energy of oxidation is given by,

$$\Delta E = e(\phi_m - V_a - V_s) \qquad (1)$$

where, e is the electronic charge, ϕ_m is the thermionic work-function of the metal, V_a and V_s are the potentials due to the electron affinity of oxygen and the surface state charge at the metal/oxide contact respectively. The ϕ_m values of hcp and fcc cobalt are nearly equal, and with the other terms in (1), remaining unaltered, one can expect identical ΔE values for the logarithmic oxidation of both the forms of cobalt.

The reason for the break in the Arrhenius plot (fig. 4) at the allotropic change point is not clearly known. But since the plot originates from an oxidation law whose mechanism is based upon some electronic factors [7], the most likely explanation for the break would be, therefore, to correlate it with any change in electronic phenomena, such as the Fermi surface behaviour, which are involved at the onset of allotropic transformation.

5. Conclusions

(i) The initial oxidation of pure cobalt has been shown to follow the direct logarithmic law for 1 to 15 min in the range 320 to 520° C.

(ii) The process is independent of oxygen pressure.

(iii) The Arrhenius plot has an anomaly around the allotropic change point (386° C). The reason for this is probably associated with the Fermi surface behaviour at the onset of allotropic transformation. The activation energies of oxidation of both the allotropes are however identical. This is to be expected from the proposed model of logarithmic oxidation [7].

(iv) From transmission electron micrographs it has been found that the oxide formed above

386° C has higher dislocation density than that formed below 386° C.

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