Effect of High Temperature and Low Pressure on the Stability of Rhodium

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At the Seventh International Congress on Metallic Corrosion held at Rio de Janeiro in October 1978 one of the papers related to work on rhodium which was similar, in some respects, to earlier experiments on iridium recently reported in this Journal (1). This work on rhodium is now summarised.

The investigation was carried out on pure rhodium discs and prior to each experiment they were annealed for 15 minutes at 1400°C in vacuum (1×10^{-5} torr). Experimental details may be found in the earlier iridium paper.

The specimens were subjected to atmospheres of oxygen, nitrogen or air, at temperatures between 1400 and 1800°C and pressures in the range 0.001 to 760 torr. The weight change of the specimens, as function of time, illustrated the comparatively high stability of rhodium to oxidation and sublimation which led to losses in weight by the formation of the volatile oxide RhO_2. The solid oxides of rhodium, Rh_2O_3 and RhO_2, are unstable above 1127°C and the weight losses, which were linear with time, increased strongly with temperature and pressure. The maximum weight loss at the higher temperatures was observed at the higher pressures of oxygen. The sublimation rate at temperatures between 1700 and 1800°C exceeded the rate of oxidation in oxygen or air. In vacuum the sublimation rate of rhodium increased with increasingly higher temperatures. The affinity of rhodium to air or oxygen was very low, particularly at low temperatures where its oxides are less volatile and so may be expected to protect the surface. During cooling of the rhodium below the decomposition temperature of its oxides, 1140°C at atmospheric pressure for RhO_2 (2), a stable oxide film covered the surface. Specimens heated in vacuum and then cooled always had bright surfaces while those heated in oxygen showed a dark grey surface film of oxides.

The main conclusions are: (a) The stability of rhodium is particularly sensitive to temperature, as at low temperature the oxide film formed on the surface is relatively stable and its sublimation is slow. At about 1600°C the rate of oxidation and the rate of sublimation are equal while above 1600°C the rate of sublimation exceeds that of oxidation. (b) Air and nitrogen atmospheres decrease the sublimation of rhodium at 1800°C, and on cooling dark grey reaction products form on the surface. These have a dull appearance and are mainly oxides. (c) The effect of pressure is not selective and the stability of rhodium seems to be less dependent on pressure, although in oxygen the weight loss increases with pressure. At 1800°C the specimen heated in vacuum (10^{-3} torr) shows a high sublimation rate and a bright recrystallised specimen results. However, the magnetic flux resulting from induction heating of the rhodium discs may affect the rate of mass transfer of the high temperature-ionised rhodium ions from the metal substrate to the surface, and then to the atmosphere.

Acknowledgements

Valuable discussions with Professor Dr. E. Gebhardt and Dr. H. Jehn (Max-Planck-Institute, Stuttgart, West Germany, where this work was carried out) are greatly acknowledged. The technical assistance provided by Mr. R. Volker is appreciated.

References

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