Radiochimica Acta 60, 53–56 (1993)
 – 0033-8230/93 $ 3.00+0.00

Diffusion of I^- Ions in Near Surface Region of Molybdenum

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(Received February 14, 1992)

Diffusion / Molybdenum / Desorption / Diffusion-annealing / I^- ion / Activity

Abstract

Volume diffusion of I^- ions in molybdenum was studied over the temperature range 300–473 K, for different I^- surface coverages ($\theta = 0.75$, 1.25 and 2.0). The radiotracer technique of monitoring the residual activity on the molybdenum surface, subjected to successive sectioning by acid-etching, following the diffusion-anneal, was employed. Under these conditions, the diffusion coefficient varied from 10^{-18} and 10^{-16} m^2/s. These values are remarkably low compared with those for I^- diffusion in copper and silver, previously investigated. The low rate of diffusion in molybdenum is believed to be due to the effect of simultaneous evaporation and desorption proceeding side by side.

Introduction

As a refractory and corrosion resistant metal, molybdenum has been in use since long as the plant material [1] for breeder reactors. Due to this consideration and the fact that halogen atoms are produced in plenty during nuclear fission along with a wide range of other isotopes, the study of the interaction of halogens with molybdenum assumes significance. Though it is known [2] that molybdenum has excellent resistance to corrosion by halogens, data on halide ion uptake/diffusion in molybdenum are not available. It would, therefore, be of interest to study the adsorption behaviour of I^- ions from aqueous solution by molybdenum and of their diffusion in the metal.

Experimental

Molybdenum metal (99.9% pure) used in these experiments was provided in the form of a polished strip of width 6.37 mm and thickness 0.12 mm by The Goodfellow Metals, U.K. Small strips of 2 cm length each, were cut and were subjected to chemical polishing by dipping them in a mixture of 15 ml perchloric acid and 5 ml (1:1) HCl, for 2 sec. They were then washed thoroughly, dried and used immediately.

Surface area measurement

The actual surface area of the molybdenum strip was determined by the dye adsorption technique described below. The ratio of the real surface area to the geometric surface area is taken as the roughness factor.

Dye adsorption method

The actual surface area was obtained from the extent of the methylene blue molecules adsorbed from its aqueous solution onto the molybdenum strips of a given total geometric area (3.83 cm^2). The amount of the dye adsorbed was evaluated from the decrease in the absorbance, as recorded on the Beckmann DB spectrophotometer, after having verified that the absorbance varies linearly over the concentrations of the dye solution used. Three molybdenum strips were immersed in 25 ml of 5×10^{-6} M methylene blue solution, maintained at 303 K. The absorbance was recorded at regular intervals of time until a constant value was reached indicating the completion of monolayer adsorption of the dye molecules on the metal surface. Such a state is generally reached after about one and half hours. The real surface area was calculated assuming the cross-sectional area of methylene blue molecule to be 1.05×10^{-18} m^2 [3]. Assignment of surface coverage (θ) of I^- adions on molybdenum strips was based upon the surface roughness factor which was found to be 8.

Scanning electron micrographs of polycrystalline molybdenum surface before and after adsorption of I^- ions, are shown in Plates A, B and C.

Uptake of I^- ions

The pre-treated molybdenum strips, held erect on a perspex base, were immersed in 10^{-3} M NaI solution labelled with I-131, supplied by the Bhabha Atomic Research Centre, Bombay. The strips were removed from the solution, each after a particular time interval, washed in distilled water and dried. The activity on both the sides of each strip was recorded with an end-window G–M detector. Knowing the specific activity of the labelled NaI solution, the number of I^- ions adsorbed was calculated from this measured activity. From the knowledge of the actual number of molybdenum atoms present on the substrate surface (i.e. 1.08×10^{16} atoms per cm^2, as calculated from the known radius of Mo atom [4]), and assuming that each Mo atom adsorbed a single I^- ion, thickness in terms of I^- monolayers deposited or the I^- coverage (θ) was