

Geiss and Lutz<sup>4</sup>. These authors have also discussed the application of such investigations to the question of the size of the meteoroid and the problem of space erosion.

The presence of neutron-capture <sup>36</sup>Cl which can be washed away from the chips points to a possible source of uncertainty in calculations of the cosmic-ray exposure ages of iron meteorites. The experimental results that are used for those calculations are the <sup>36</sup>Ar concentration and <sup>36</sup>Cl specific activity in adjacent specimens. Generally the latter is measured by dissolving a compact mass and includes both the spallation and the neutron-capture <sup>36</sup>Cl. The <sup>36</sup>Ar is measured on a small metal chip after thorough cleaning. Any <sup>36</sup>Ar resulting from the decay of the neutron-capture <sup>36</sup>Cl would reside with the natural chlorine and would probably be removed during sample preparations. This would result in a low value for the <sup>36</sup>Ar concentration and hence in a low value for the apparent cosmic-ray exposure age of the meteorite.

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P. S. GOEL\*

Department of Chemistry,  
Carnegie Institute of Technology,  
Pittsburgh, Pennsylvania.

\* Present address: Indian Institute of Technology, Kanpur, India.

<sup>1</sup> Goel, P. S., *Cosmogenic Carbon-14 and Chlorine-36 in Meteorites*, thesis, Carnegie Institute of Technology, U.S.A.E.C. Rep. NYO-8922 (1962).

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## METALLURGY

### Oxygen Diffusion in Tungsten

INFORMATION concerning oxygen diffusion in tungsten is technologically valuable for many reasons. One such reason is its important role in the development of the structural properties of tungsten for high-temperature applications.

Because direct measurements are difficult, indirect assessments of oxygen diffusion in tungsten have recently been made, but the results seem somewhat confusing. For example, assuming the frequency factor  $D_0$  as  $10^{-2}$  cm<sup>2</sup>/sec, Stringer and Rosenfield<sup>1</sup> estimated the activation energy for oxygen diffusion in tungsten as 2.7 eV by using Cottrell's equation which was established on the basis of the Portevin-Le Chatelier effect. This value of activation energy agrees with those for oxygen diffusion in some transition metals in which the solubility of oxygen is smaller than 1 per cent. On the other hand, Jacobs<sup>2</sup> obtained a value of the frequency factor as 1.3 cm<sup>2</sup>/sec and the activation energy as 24,000 cal/mol for oxygen diffusion in tungsten by means of internal friction measurements. His results agree with those for oxygen diffusion in some transition metals in which the solubility of oxygen is greater than 1 per cent. Regardless of the empirical relation between diffusion and solubility for oxygen in transition metals, the two estimations yield serious disagreement on the rates of oxygen diffusion in tungsten.

The purpose of this communication is to deduce a diffusion coefficient of oxygen in tungsten at a convenient temperature from a direct measurement of the variation of oxygen concentration with time of diffusion and to compare with the estimations mentioned previously.

Examining the effect of the interstitial impurities on the recrystallization of tungsten, Allen, Maykuth and Jaffee<sup>3</sup> doped high-purity tungsten crystals with oxygen by means

of a diffusion process. In their experiment, the boundary condition of the diffusion equation for diffusant from a constant surface concentration into an infinite cylinder is closely fulfilled. Although the experimental uncertainties due to the analytical procedure appeared for single crystalline specimens, the variation of the dopant concentration with time for polycrystalline specimens seems meaningful, that is, the average concentration of oxygen in tungsten is 33 p.p.m. for 6 h of diffusion at 1,700° C and 39 p.p.m. for 12 h at the same doping condition. Should the most reliable value of the solubility of oxygen in tungsten at 1,700° C be about 40 p.p.m.<sup>3,4</sup>, the fractional saturation from the doping process is about 83 per cent for 6 h and 98 per cent for 12 h. Knowing the dimensions of the polycrystalline specimens, the diffusion coefficient of oxygen in tungsten can be estimated as  $3 \times 10^{-7}$  cm<sup>2</sup>/sec at 1,700° C. From the results of the single crystalline specimens, the diffusivity is calculated to have a value between  $7 \times 10^{-8}$  cm<sup>2</sup>/sec and  $5 \times 10^{-7}$  cm<sup>2</sup>/sec at the same temperature.

According to the Arrhenius relation for the temperature dependence of diffusivity, the diffusion coefficient of oxygen in tungsten at 1,700° C can also be assessed from the other two estimations of the activation energy and the frequency factor. The values are  $3 \times 10^{-3}$  cm<sup>2</sup>/sec and  $1 \times 10^{-9}$  cm<sup>2</sup>/sec from the internal-friction measurements and the Cottrell's equation respectively. Because of the serious disagreement of these two estimations, one should make an approximation based on the observations from the dosing experiment. Should  $3 \times 10^{-3}$  cm<sup>2</sup>/sec be the expected value, the time for saturation with oxygen at 1,700° C would take as short as 0.5 min. It is obvious that this value is too large for the diffusivity at the temperature. On the other hand,  $1 \times 10^{-9}$  cm<sup>2</sup>/sec would be too small for dosing to about 90 per cent of saturation within a few hours. It is therefore our opinion that the  $D$  value should be of the order of  $10^{-7}$  cm<sup>2</sup>/sec at 1,700° C as estimated from the dosing experiment.

C. H. LEE

Franklin Institute Laboratories,  
Philadelphia 3, Pennsylvania.

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### Decomposition Pressure Hysteresis in the Zirconium-Hafnium-Hydrogen System

A RECENT investigation<sup>1</sup> of the Zr-Hf-H equilibrium system at pressures less than one atmosphere of hydrogen gas revealed the presence of hysteresis. Although this was not unexpected<sup>2</sup>, it was somewhat disconcerting and demanded further elucidation. Results presented here will show that: (1) decomposition pressure hysteresis must be considered when dealing with equilibrium between gases and multi-component alloy systems; (2) hysteresis always involved a region of more than one phase and was most prominent at lower temperatures where diffusion was slowest; (3) no evidence for an interfering surface film was found; (4) internal factors such as stress and large surface area accompanying a martensitic reaction are prominent in the hysteresis reactions of the Zr-Hf-H system.

Hysteresis in metal-hydrogen systems has been found by a number of workers as far back as the early 1900's, and the subject has been reviewed in recent publications<sup>3-7</sup>. Most explanations involved internal solid-state properties of the hydrided alloys. On a pressure-composition plot different paths were followed on absorbing or desorbing hydrogen when crossing a multi-phased region because either: (1) the two paths represented different statistically predictable metastable states of long duration; or