CHEMICAL DIFFUSION ON SURFACES

FINAL REPORT

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The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.
Techniques have been developed enabling the measurement of the surface diffusive flux of one material on the surface of a chemically different material. These techniques involve the use of an Auger electron spectrometer system both to form an initial surface composition profile, and to measure the evolution of this profile with time. These techniques have been applied to a study of the surface diffusion of carbon on a Pt(111) surface.
STATEMENT OF THE PROBLEM

The phenomenon of surface diffusion plays a role in determining the overall rate of a number of processes, including stress corrosion cracking, the early stages of gas-phase corrosion, thin film formation and heterogeneous catalysis. In spite of this, virtually no systematic studies have been made of the rate of surface migration of one chemical species over the surface of a material of different chemical composition. This is due primarily to the difficulties involved in avoiding contamination of the surface under study, and to the difficulty of measuring surface concentration profiles over short distances and at low surface concentrations of diffusant. The problem attacked in the present work was that of developing techniques to measure this surface diffusion rate under conditions that would insure valid, reproducible results and of applying these techniques to determine surface diffusion rates in systems of practical and scientific interest.

SUMMARY OF RESULTS

1. A more-or-less standard ultrahigh vacuum system, containing a cylindrical mirror electron energy analyser (CMA) for the conduct of surface studies by Auger electron spectrometry (AES), was modified to permit the measurement of surface diffusivities. This modification consisted of the construction of a sample mounting and manipulating assembly which permitted the mounting of a metal ribbon sample so that it could be reproducibly heated to a given temperature over the range from room temperature to 1500°C, and so that it could be reproducibly positioned relative to the CMA to within 0.001 in. A system for admitting controlled pressures of a variety of gases to the system was also constructed and used.

2. A procedure was developed for reproducibly cleaning a single crystal Pt(111) surface in this system. The procedure involved exposure of
the surface to gaseous \( \text{O}_2 \) at a pressure of \( 10^{-6} \text{torr} \), at a surface temperature of 1200°C for a few minutes. After this treatment, AES spectra showed no observable peaks other than those attributable to platinum.

3. A procedure was developed for producing a uniform spot of carbon on this surface, having a diameter of approximately 0.5 mm, and of monatomic thickness. This procedure involved exposure of the cleaned surface to gaseous \( \text{CO} \) at a pressure of \( 10^{-6} \text{torr} \), concurrent to exposure of a spot on the surface to an electron beam of 50 \( \mu \text{amps} \), 2500 eV. The beam induced decomposition of adsorbed \( \text{CO} \) to form the carbon spot. \( \text{CO} \) was removed from the rest of the surface by heating the sample briefly to 800°C. Measurement of the profile of this spot, made by moving the sample relative to the CPA, while monitoring the carbon AES peak, indicated that the spot was circular and roughly 0.5 mm in diameter.

4. The rate of surface diffusion of carbon on Pt(111) was measured by observing the decrease in carbon AES intensity with time, while the sample was held at a temperature between 700°C and 800°C. Plots of the relative AES signal versus time yielded the surface diffusion coefficient.

5. Measured surface diffusion coefficients in the temperature range from 780 to 800°C ranged from \( 3 \times 10^{-7} \) to \( 1 \times 10^{-6} \text{ cm}^2/\text{sec} \). Scatter in the results was too great to permit calculation of the heat of diffusion. It is hoped that further work can reduce this scatter.

**Publications and Reports**

In addition to this Final Report, the results of this study have been reported in the following publications and reports:

1. "Chemical Diffusion on Surfaces", by John B. Hudson,
2. "Chemical Diffusion on Surfaces", by John B. Hudson, a report presented at the ARPA Materials Division Symposium on Surfaces and Interfaces, University of Pennsylvania, December 11-12, 1974, and published in the proceedings of that symposium.


PERSONNEL

The principal investigator, Dr. John B. Hudson, received partial support under this contract during the contract period.

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Michael T. Martin, a graduate student in the Materials Engineering Department at RPI, was wholly supported during the period of this contract. Mr. Martin will receive the M.S. degree from RPI in January, 1976.