High-Temperature Oxidation of Pt–45Pd–10Rh

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The surfaces of Pt–45Pd–10Rh foils oxidized over the range 875–1075 K in a 20% \( \text{O}_2 \)-Ar mixture at atmospheric pressure were examined by Auger electron, X-ray photoelectron, and Raman spectroscopy. The composition of the oxide formed on the surface was found to vary with temperature from predominantly PdO at 875 K to PdRhO\(_2\) at 1075 K. Only a few atomic percent Pt was observed, present in both the metallic and (apparently) +1 oxidation states at 875 K and in the metallic state at 1075 K. The formation of PdRhO\(_2\) (and no Rh\(_2\)O\(_3\)) at 1075 K was found to persist upon reoxidation following a low-temperature reduction cycle in which the increased Rh concentration on the surface was retained. An oxidation-induced Rh enrichment of the surface of the alloy foil beyond 50 at.% does not appear likely within the temperature/pressure regime investigated.

KEY WORDS: Alloy; oxidation; platinum; palladium; rhodium.

INTRODUCTION

Studies of the oxidation-induced changes in the surface composition of bulk binary alloy foils containing either Pt and Rh or Pd and Rh have previously been performed with the aim of obtaining insight into possible small particle surface enrichment effects in supported mixed-metal catalysts in which alloying might occur.\(^1\text{-}^5\) In the case of Pt–10Rh, air oxidation in the range 1025–1175 K was found to cause a rhodium oxide layer to form on the surface of the foil, a result understood in terms of the stability of the simple oxides.\(^1\) In the case of Pd–15Rh, air oxidation was found to cause a PdO layer to form on the surface of the foil in the range 875–1000 K and a mixture of PdO and PdRhO\(_2\) to form in the range 1075–1125 K.\(^4\text{-}^5\)

The results of the present investigation of the oxidation of the bulk ternary alloy, Pt-45Pd-10Rh, are consistent with the combined results for the two binary systems, i.e., formation of an oxide consisting largely of PdO at low temperatures in the range 875-1075 K and PdRhO$_2$ at the highest temperature in the range.

**EXPERIMENTAL DETAILS**

The Pt-45Pd-10Rh (wt.%) alloy was prepared by Engelhard Industries in the form of a polycrystalline foil approximately 0.2 mm thick. Samples of approximately $2 \times 10 \, \text{mm}$ were cut from the foil, washed, lightly etched in HCl, rinsed, washed in solvents, dried, and then inserted into a preheated tube furnace under a flowing gas consisting of 20% O$_2$ in Ar at atmospheric pressure (i.e., at an O$_2$ partial pressure of 152 torr) for a given period of time in the range 0.5-4 hr. Temperature was measured with a Chromel-Alumel thermocouple located adjacent to the samples.

The near-surface composition of the foils was obtained by sputter depth profiling using Auger electron spectroscopy (AES). These measurements were performed with a computer-controlled Physical Electronics model 545 scanning Auger microprobe using a rastered 2-keV Xe$^+$ ion beam for sputtering and a rastered 200-nA 3-keV electron beam to excite the Auger transitions. Four transitions—Pt (64 eV), Rh (302 eV), Pd (330 eV), and O (510 eV)—were monitored during the course of sputtering. Complete spectra were also recorded occasionally in order to check for the presence of impurities.

The unsputtered sides of the foils were subsequently examined by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The XPS measurements were performed with a Surface Science Laboratories SSX-100 spectrometer that used monochromatized Al-K$_\alpha$ excitation. Core-level binding energies were referenced to the adventitious carbon 1s level, the binding energy of which was taken to be 284.6 eV. The Raman measurements were done using an Ar$^+$ ion laser, SPEX Triplamate spectrometer, and an EG&G PAR model 1420 intensified solid-state array detector as more fully described elsewhere.

**RESULTS**

Depth profiles obtained with AES for foils heated at 875 and 1075 K for 4 hr are shown in Fig. 1a, b, respectively. As in the case of the binary alloy, Pd-15Rh, the foil heated at 875 K exhibits a Pd-rich oxide on the surface. The thickness of this oxide layer, corresponding roughly to the width of the plateau in the oxygen portion of the profile in Fig. 1a, is