

Convenient Procedure For Preparation of Copper-Platinum Surface Alloy

H. Matsui and Y. Matsunaga

Department of Chemical Science and Technology,
Faculty of Engineering, The University of Tokushima,
Minamijosanjima, Tokushima 770-0814, Japan

INTRODUCTION

Surface alloys can be formed by annealing a very thin overlayer on different kind of substrate [1]. Many applications have been reported for the improvement of corrosion resistance, mechanical properties, etc. Particularly, an application to electrocatalysts is attractive, because high catalytic activity can be obtained by the formation of a very thin catalyst layer of surface alloy. A well-defined surface alloy has been prepared on single crystal substrate, and confirmed with the aid of some expensive apparatus, e.g., for low energy electron diffraction and X-ray photoelectron diffraction. Furthermore, the experimental conditions with single crystal substrate were seriously limited due to its instability. In order to overcome these difficulties, the present authors used polycrystal substrate for the surface-alloy preparation. The obtained data with single crystal substrate [2] revealed that the surface alloying was caused by mutual diffusion of overlayer atoms and substrate atoms in the solid phase. Therefore, surface alloy is expected to be formed also on polycrystal substrate, though the obtained overlayer is probably comprised of many grains of well-defined surface alloys.

In the present work, a copper-platinum system was selected for an example of surface-alloy preparation on polycrystal substrate, because of the facility of alloying due to similar atom size and strong interaction between both atoms.

EXPERIMENTALS

Pure polycrystal platinum substrate was used for the preparation of copper-platinum surface alloy. A very thin copper overlayer was formed by the electrodeposition at a constant potential in the buffer solution of pH 5.3 containing a small amount of copper sulphate. The obtained overlayer was immediately characterized by an anodic stripping method in the same solution, and some samples by an electron spectroscopic method for chemical analysis. The thickness of the overlayer was evaluated from the stripping charge, and expressed by the number of copper atom layers. For comparison, relatively thick surface alloys also were formed by an annealing method.

RESULTS AND DISCUSION

Simple copper deposition on platinum metal: Up to approximately monolayer, the overpotential of copper dissolution increased by about 0.3 V without annealing, while at thicker layers than bilayer it was practically not influenced by platinum substrate (Fig. 1).

Complex copper deposition on platinum metal: Copper overlayer was formed in the presence of an excess of nickel ions, i.e. in a simplified Watt bath containing a small amount of copper sulfate. As shown in Fig. 2 the behavior of copper dissolution was quite different from that of Figure 1. The dissolution wave at lower potentials revealed that the copper at the solution side of the overlayer dissolved like bulk metal, while the second wave at higher potentials its dissolution overpotential explicitly increased. This result suggests the alloying to occur at the platinum side of the overlayer. Figure 3

shows the ESCA pattern of copper overlayer after about several-atom layers were removed by argon etching. Copper and platinum spectra was explicitly confirmed, supporting the suggestion about the alloying. The data of thick overlayers will be presented at the day.

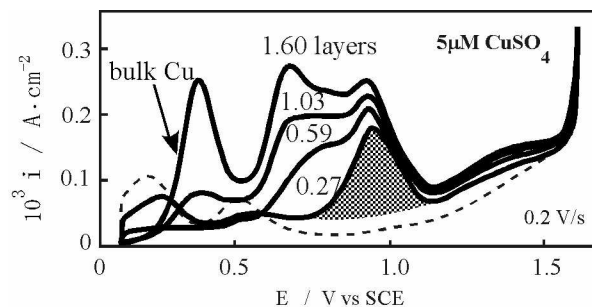


Fig. 1. Stripping curve of simply deposited Cu on Pt.

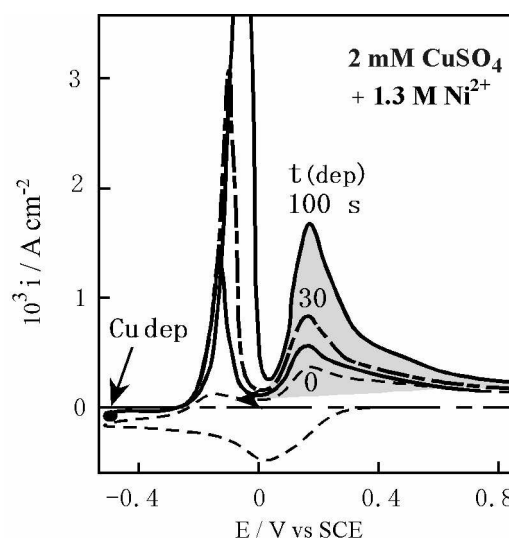


Fig. 2. Anodic stripping of Cu-deposit on Pt in the presence of an excess of Ni^{2+} ions.

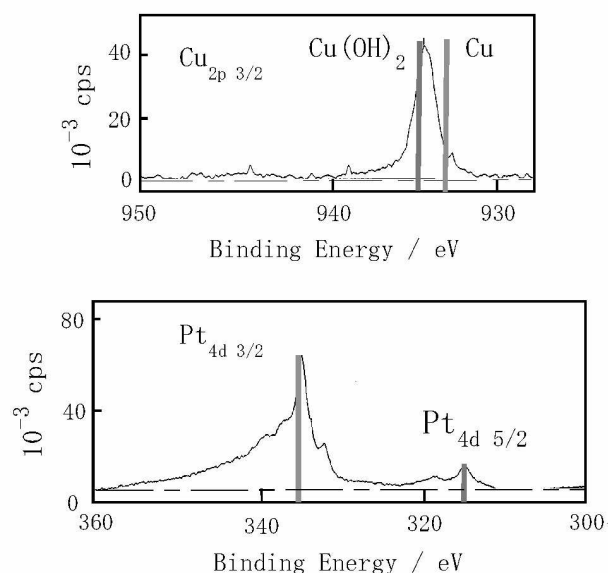


Fig. 3. ESCA pattern of Cu deposit on Pt in the presence of an excess of Ni^{2+} ion, after Ar etching.

- 1) J. S. Tsay, T. Mangan, and K. Wandelt, *The Solid Films*, **397** (2001) 152.
- 2) R. C. Yeates and G. A. Somorjai, *Surface Science* **134** (1983) 729.