Surface Structure of $Pd_3Fe(111)$ and Effects of Oxygen Adsorption

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ABSTRACT

Pd-Fe alloys have attracted attention in PEM fuel cell research because they were found to be comparable to Pt electrocatalysts in oxygen reduction reaction (ORR) kinetics at the cathode. In this study, the surface morphology of a $Pd_3Fe(111)$ single-crystal sample and oxygen reaction on the surface were investigated by low energy electron diffraction (LEED), low energy ion scattering (LEIS), x-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy (STM) under ultra-high vacuum (UHV) conditions. Strong segregation of Pd atoms was observed after annealing in UHV. Particularly, Pd single adatoms and dimers were found on the surface after high temperature annealing, which differs from most other well-studied binary alloy systems. Low free energy of Pd, strain relaxation, and interaction between Pd and Fe, are potentially responsible for the formation of this unusual surface. Adsorption of oxygen reversed the segregation trend and oxidized surface Fe. Ordered surface phases were observed after oxygen exposures at elevated temperatures. The reducing activity of Fe atoms in the alloy inhibited Pd oxidation, and weakened Pd-O interactions on $Pd_3Fe(111)$ are consistent with enhanced ORR kinetics.

INTRODUCTION

Pd-based bimetallic catalysts (Pd/M, M=Au, Ag, Fe, etc.) have been widely studied in heterogeneous reactions such as selective hydrogenation of unsaturated hydrocarbons [1], selective oxidation of alcohols to aldehydes [2] and as electrocatalysts in fuel cells [3]. Enhanced catalytic properties in bimetallic catalysts can arise from two different effects, an electronic effect and a geometric effect [1], and so, studying segregation in Pd-based alloys, including adsorption, is important [4].

Bimetallic catalysts are widely studied in fuel cells in terms of their performance as cathodes and anodes [5]. Recently, the study of non-Pt based electrocatalysts has become an increasing research focus. The cost is reduced when inexpensive metals such as Fe, Co and Ni are alloyed in the catalysts. Much higher electrocatalytic activity is also found when these bimetallic nanoparticles act as the support of a Pt or Pd monolayer [6]. To achieve fast oxygen reduction reaction (ORR) kinetics, the binding between oxygen and the active sites should be neither too strong nor too weak. Optimally, oxygen would bond to the surface strongly enough to enhance electron transfer, but weakly enough to allow facile desorption so that site-blocking does not hinder ORR kinetics.

To provide a better understanding of these newly developed Pd-based catalysts, it is

critical to fully characterize the surface composition and structure of these materials and to study their interactions with oxygen by applying modern experimental surface science techniques. In research, a well-defined $Pd_3Fe(111)$ single crystal bulk alloy has been studied extensively both in oxygen and under ultra-high vacuum (UHV) conditions. The segregation properties and surface structure have been probed by using techniques including low energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS), low energy ion scattering (LEIS) and scanning tunneling microscopy (STM). We report an unusual surface morphology with Pd adatoms segregated on the alloy surface. This surface structure is completely different from other well-studied (111) surfaces of the Cu_3Au type of 3d and 4d alloys such as Pd/M, M=Ni, Co and Pt/M, M=Fe, Ni, Cu, Rh, etc. [7], which are comprised of flat and complete terraces after high temperature annealing. This special surface structure may provide us with information leading to a new explanation of the origin of the enhanced electrocatalytic activity of Pd-Fe alloys.

EXPERIMENT

A $Pd_3Fe(111)$ single crystal (6 mm dia., 3 mm thick) was mounted on a sample holder in a UHV chamber with a base pressure of 1×10^{-10} torr. This UHV system was equipped with LEED, XPS, LEIS and STM. Cleaning of the sample was performed by 2×10^{-5} torr Ar^+ sputtering and annealing to 1100 K. Residual carbon was removed by annealing the sample at 700 K in 5×10^{-8} torr O_2 for 2 min. Then it was flashed to 1200 K to remove oxygen and achieve a long-range ordered surface. Cleanliness of the surface was evaluated by XPS, ensuring that no detectable amount of carbon, oxygen, sulfur or chlorine remained before experiments. XPS data was obtained using an Al Kα x-ray source with detection normal to the surface.

LEIS spectra were taken using He^+ at 1000 eV and 3.0 nA ion current at an incident angle 50° from the surface normal with a 130° scattering angle. Annealing of the sample was carried out for 2 min.

STM images were taken at a base pressure of 6.0×10^{-11} torr. After the sample was cleaned, it was annealed at 1100 K for 2 min. Only room tempertature STM images were taken. The LEED pattern was examined before the sample was transported to the STM chamber. STM images were acquired with an electrochemically etched tungsten tip at a voltage of -1.0 – +1.0 V with a tunneling current of 0.3–2.5nA.

Oxygen gas was exposed on the sample surface by using a leak valve and directed gas doser.

DISCUSSION

A sharp and bright (1×1) hexagonal LEED pattern, as shown in Figure 1-A, is characteristic of the clean $Pd_3Fe(111)$ surface. This pattern indicates that the surface atoms are in an ordered structure, although the Fe and Pd atoms are not in a particular intermetallic 2D geometry. This is similar to the surface of the $Pd_{25}Ni_{75}(111)$ alloy [8], but different from the $Pt_{80}Fe_{20}(111)$ alloy, which showed a (2×2) superstructure caused by an ordered atomic

arrangement in the second layer [9]. Similar to the Pd-Fe polycrystalline alloy, Pd tends to segregate to the surface of $Pd_3Fe(111)$. In Figure 1-B, the Pd concentration is normalized so that a value of 1.0 defines one monolayer of Pd atoms. The Pd concentration at the surface, as determined by LEIS (Figure 1-A), increased as the annealing tempeature was increased before it reached the highest coverage of 0.90 ML at ~1130 K. Segregation is expected to disrupt order and break energetically favorable Pd-Fe bonds. Further increasing the annealing temperature lowered the Pd concentration slightly, showing Langmuir-McLean behavior as the phase-transition temperature was reached [7]. Pd/Ni(111), one of the most-studied models of segregation, was found to have Pd segregate to the surface and Ni-enrichment in the second layer. This oscillating interlayer chemical ordering is caused by attractive Ni-Pd interactions [10].

A   **B**
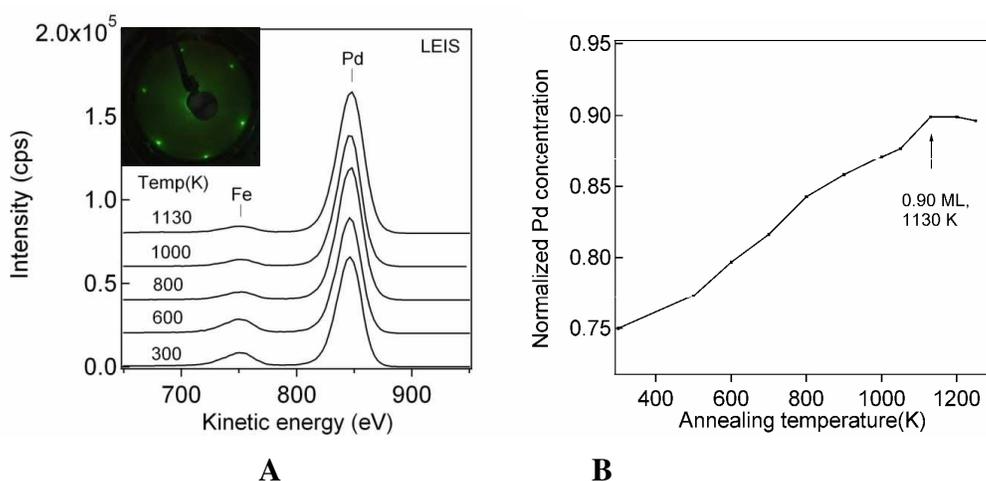
Figure 1. (A) LEIS of $Pd_3Fe(111)$ after annealing at several temperatures. Insert: LEED pattern at $E_p = 55$ eV. (B) Surface Pd concentration determined by LEIS after annealing.

Atomic resolution STM image in Figure 2-A shows bright spots assigned as adatoms, mostly monomers or dimers, with only a very small amount of trimers or tetramers. The STM image is independent of the bias on the tip (-1.0 - +1.0 V). The distance between the bright spots is twice the nearest neighbor distance of $Pd_3Fe(111)$ (0.273 nm), and the distance between two dimer spots is 0.273 nm. Thus, the bright spots in the STM images are single atoms, even though they appear larger than the Pd atomic diameter. Short range (2×2) ordering was found. Single Pd adatoms are sometimes observed to move across the surface, jumping to the next adsorption site (atoms labeled with an arrow in Figure 2 A-B) as it followed the trajectory of the tip ("pulling mode") [11]. Examination of these STM images showed that these bright spots are located at the 3-fold hollow sites of the first layer (Figure 2-C), which eliminates the possibility that these bright spots are embedded into the first layer. Therefore, we have assigned the bright spots to single adatoms. Statistical analysis of the STM images reveal that the surface adatom coverage is 16.5%, which is higher than the surface Fe coverage (9.20%), but much smaller than the Pd surface coverage (90.8%), as determined by LEIS. The 0.90 ML Pd concentration determined by LEIS includes Pd both in the first layer and Pd adatoms. Atoms in the first layer can be seen by

He$^+$ due to the open structure of the adatom layer. Thus, the 0.165 ML adatoms observed by STM must be from Pd adatoms. Figure 2-D is a proposed model of this surface, which also proposes that the preferred location of Pd adatoms is above Fe sites in the first layer. The low surface coverage of Fe determined by LEIS is likely due to a shadow effect of the Pd adatoms adsorbed above the Fe atoms. Therefore, an unusual structure is formed on the clean, annealed Pd$_3$Fe(111) surface: 0.17 ML Pd adatoms segregated on the outermost layer.

A   B   C   D
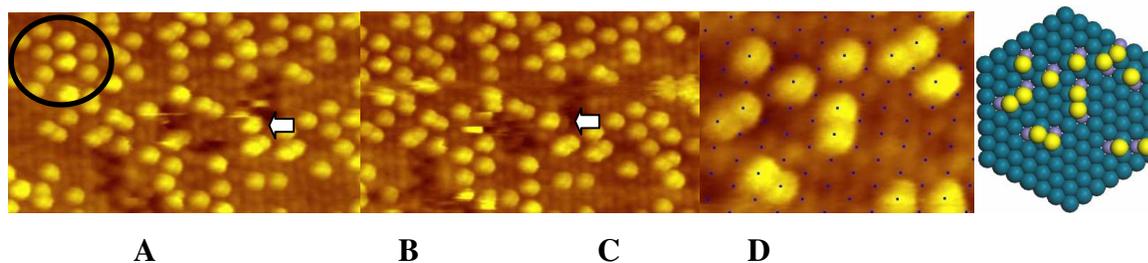
Figure 2. (A) and (B): Atomic resolution images of Pd$_3$Fe (111). The atom labeled by an arrow shifted to a neighboring site during scanning. Short range ordering of Pd adatoms forms (2×2) structures, as associated by a circle at the upper-left corner. (Image size: 8 nm × 5 nm) (C) STM image of 14 Pd adatoms (6 monomers, 4 dimers) with a superimposed lattice showing that their positions maintain an interatomic spacing (0.273 nm) correlated with the FCC lattice. (Image size: 2.5 nm × 1.5 nm) (D) A proposed schematic model of an incomplete adlayer accounting for the STM image in (C).

The presence of Pd adatoms is surprising. At high temperatures, the mobility of metal adatoms might be expected to cause diffusion on terraces to form islands or localization at edges. Sputtering roughens the Pd$_3$Fe(111) surface, but high temperature annealing smooths the surface, as seen by STM, creating large flat terraces. Thus, it is interesting to consider why adatoms still survive high temperature annealing, and why high temperature annealing causes formation of adatoms. This is not an isolated case, because it was reported that high temperature annealing (1000 K) of bulk Pt$_3$Sn(111) causes Sn adatoms to appear at the surface [12]. In that case, the formation of a stable ordered (2×2) structure is able to push some extra Sn atoms out of the (√3×√3)R30° surface. Theoretical calculations of the adsorption energy of adatoms may help identify the ideal geometrical configuration of adatoms on the surface, and also may help to explain how the local composition and electronic properties of the Pd adatoms on the top alloy layer may play an important role to maintain the unique surface structure.

The XPS peaks at 710.2 eV binding energy in Figure 3 are due to Fe oxidation. In addition, the total Fe 2p$_{3/2}$ intensity increased as the oxidation temperature increased from 300 to 950 K. This reversed segregation is caused by a stronger interaction between Fe and oxygen than that between Pd and oxygen. No chemical shift was found for Pd 3d peaks. The reducing ability of Fe atoms in the alloy inhibited Pd atom oxidation, which decreased the interaction between Pd and oxygen. This provides a possible explanation of the enhanced ORR of Pd$_3$Fe(111) at the cathode. The LEED patterns in Figure 3 show different surface structures under different oxidation
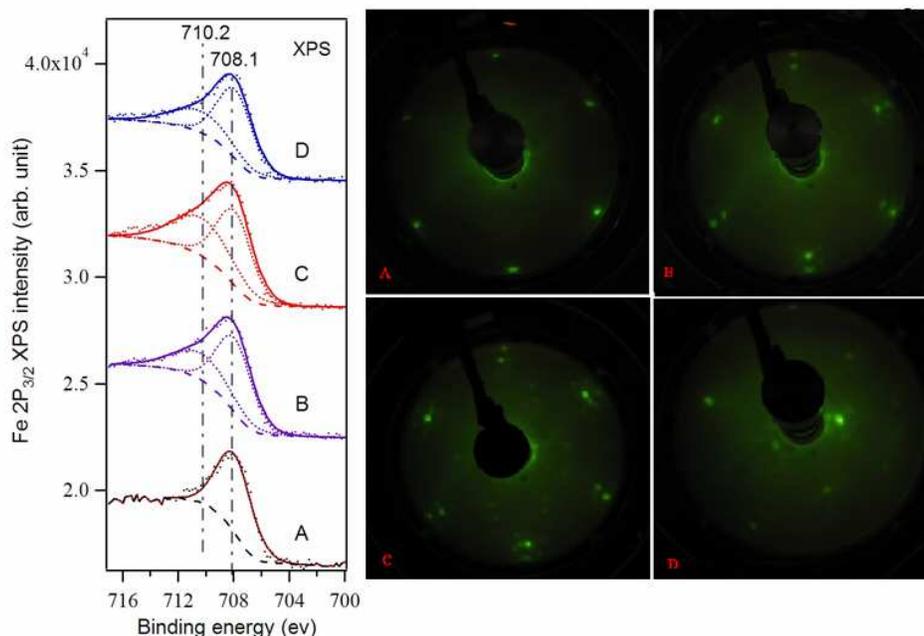
Figure 3. XPS and LEED of (A) clean surface (B) (7×7)R21.8° after 15L O_2 at 800 K; (C) (√3×√3)R30° + (7×7)R 21.8° after 15L O_2 at 950 K; (D) (√3×√3) $Pd_3Fe(111)$ surface after 15L O_2 at 800 K, and flashed to 1000 K.

conditions. The surfaces are characterized by ordered patterns described as (7×7)R21.8° at 700-800 K, a mixture of (√3×√3)R30° and (7×7)R21.8° at 800-950 K, and (√3×√3)R30° at 950-1000 K. However, structural details of these ordered surfaces and the oxygen adsorption sites are unknown, but important to study because of their relevance to an explanation of the origin of enhanced ORR kinetics.

CONCLUSIONS

We report on surface structures of a Pd-Fe alloy and the initial oxidation of that surface. On the clean, annealed $Pd_3Fe(111)$ surface, Pd atoms segregate to the surface and form 0.17 ML of Pd single adatoms and dimers sitting in FCC sites. The first layer is likely still alloyed with 0.17 ML Fe and 0.83 ML Pd. Lower surface energy of the Pd atoms, strong interactions between Pd and Fe, and electronic structure changes may all play a role in forming this structure. Adsorption of oxygen reversed the segregation trend and oxidized surface Fe. Ordered surface phases were observed after oxygen exposures at elevated temperatures. Additional STM investigations and DFT calculations supporting the elucidation of these structures will be reported later.

ACKNOWLEDGMENTS

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