CORROSION RESISTANCE OF Pd_{43}Cu_{27}Ni_{10}P_{20} BULK METALLIC GLASS

A thesis submitted in partial fulfillment of the requirements
for the degree of Master of Science in Chemistry

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Thank you Mom and Dad
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Abstract

Corrosion Resistance of Pd_{43}Cu_{27}Ni_{10}P_{20} Bulk Metallic Glass
By
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Master of Science in Chemistry

The corrosion behavior Pd_{43}Cu_{27}Ni_{10}P_{20} bulk metallic glass (Pd-BMG) was investigated in 1.00 M HCl, 1.00 M NaOH and Hanks’ solution, a simulated body fluid. The near-surface region has been quantitated by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), electrochemical voltammetry and x-ray photoelectron spectroscopy (XPS). The corrosion rates were calculated using an electrochemical method based on the linear behavior of current density in the region near open cell potential. Based on average corrosion rate, the Pd-BMG performed slightly poorer than either stainless steel 316 or Ti-6Al-4V in neutral or basic electrolyte solutions, but excelled in acidic media due to the formation of a Pd-dominated inactive surface. Anodic dealloying behavior of Pd-BMG in 1.00 M HCl solution was also investigated. A Pd-dominated porous black film was formed on the sample surface.
Chapter 1

Introduction

1.1 Overview of Bulk Metallic Glasses (BMGs)

Solid materials can be considered either crystalline or amorphous (glassy). The constituent atoms in crystalline materials are arranged in periodic order in three dimensions with the presence of some defects such as grain boundaries and vacancies. On the contrary, atoms in amorphous materials are randomly arranged indicating the periodicity is absent in their structures.

Metals and alloys were traditionally considered as crystalline materials. However, the discovery of metallic glass brought a revolution to the concept of metallic materials. Metallic glasses are amorphous alloys that exist in a metastable state. By rapid quenching of a Au-Si melt at rates about $10^6 \text{ K/s}$, Pol Duwez and his co-workers at Caltech synthesized the first metallic glass, a 10 μm thick Au$_{25}$Si$_{75}$ film, in 1960.\textsuperscript{1} The lack of any sharp peak on the x-ray diffraction (XRD) spectrum of Au$_{25}$Si$_{75}$ indicated this alloy was in a glassy state. Their work demonstrated that the process of crystallization could be kinetically bypassed by rapid quenching to preserve a frozen liquid configuration, that is, a metallic glass. Since then, a number of binary, ternary, quaternary and higher-order amorphous alloys have been produced by rapid quenching methods.\textsuperscript{2} However, the formation of the first prototypical metallic glasses by rapid quenching methods required a very high cooling rate, typically $10^5 \sim 10^6 \text{ K/s.}$\textsuperscript{2} Due to this high cooling rate, metallic glasses were limited to thin films, ribbons or sheets.
with casting thickness of a few tens of micrometers. This is because the interior of the material cools at a slower rate than the exterior, controlled by the thermal conductivity of the material. Removing the interior heat through a large distance is a slower process than a short distance and for this reason, thin films are less likely to crystallize when rapidly cooled. As a result, the applications of metallic glasses were severely restricted.³

The applications for metallic glass began to expand after the discovery of bulk metallic glasses. Bulk metallic glasses (BMGs) are those glassy alloys with critical casting thickness (maximum thickness to which a BMG can be cast without crystallizing) of at least a few millimeters. The origins of BMGs can be traced to 1974, when Chen and coworkers produced a ternary Pd-Cu-Si alloy by a water quenching method.⁴ The glassy alloy rod Chen et al. fabricated was 1-3 mm in diameter and several centimeters in length, cooled at a quenching rate of only 10³ K/s. In 1982, Turnbull and coworkers successfully prepared Pd-Ni-P glassy ingots with a casting thickness of 10 mm using a boron oxide fluxing method with an equivalent quenching rate of 10 K/s.⁵ During the late 1980s, the Inoue group in Sendai, Japan systematically investigated the ternary alloys of rare-earth metals with Al and ferrous metals.⁶ They found exceptional glass-forming ability (GFA: the tendency for a material to form a glass when quenched) in La-Al-Ni and La-Al-Cu alloys.⁷ Fully glassy cylindrical alloys with diameters up to 5 mm or sheets with similar thickness were fabricated by casting the alloy melt into Cu molds. The same group later discovered similar quaternary and quinary amorphous alloys (e.g. La-Al-Cu-Ni and La-Al-Cu-Ni-Co BMGs)
with a casting thickness of several centimeters at a quenching rate 100 K/s. In 1991, the Inoue group developed Mg-Y-Cu and Mg-Y-Ni BMGs along with a family of Zr-based (Zr-Al-Ni-Cu) BMGs possessing a high GFA and casting thickness up to 15 mm. In 1993, Johnson and coworkers at Caltech successfully developed a fully glassy BMG rod with the composition Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5} (commonly referred to as Vitreloy 1 or Vit 1) with a casting thickness of several centimeters.

Research in the area of bulk metallic glasses has been growing rapidly worldwide since these fundamental studies, and a wide variety of new multicomponent BMGs systems have been discovered. The Pd-Cu-Ni-P family is the metallic system with the highest GFA known to date, and the largest diameter of 72 mm was obtained for a Pd-based BMG with a composition Pd_{40}Cu_{30}Ni_{10}P_{20}. The critical casting thicknesses (θ) as a function of year in which the metallic glasses/bulk metallic glasses were synthesized are presented in Figure 1.1.

Figure 1.1: Critical casting thickness (θ) of metallic glasses as a function of year.
As Turnbull pointed out in his work, metallic glasses are fundamentally no different from non-metallic glasses such as silicate and ceramic glasses. A glass is formed by continuous cooling from the liquid state. When the temperature of a liquid metal (melt) is reduced, the volume decreases gradually as the temperature approaches its melting/freezing point, $T_m$. At the melting point, the volume of a liquid metal (melt) can either drop abruptly as it transforms into a crystalline solid or continue at the same rate as it becomes undercooled (the liquid state maintained without crystallization) due to a high quenching rate or removal of heterogeneous nucleation sites. The volume continues to drop in the undercooled region and the viscosity increases. At a temperature far below $T_m$, the viscosity becomes so large (small volume) that the liquid metal turns into a frozen-in state referred to as a glass. The temperature at which the viscosity of an undercooled liquid (melt) reaches to a value of $10^{12}$ Pa·s is traditionally defined as the glass transition temperature, $T_g$ as shown in Figure 1.2.

![Figure 1.2: Variation of specific volume with temperature for crystal and glass formation.](image)

Figure 1.2: Variation of specific volume with temperature for crystal and glass formation.
The ratio \( T_g/T_m \), which is referred to as the reduced glass transition temperature, \( T_{rg} \), can be used as a criterion to determine the glass forming ability (GFA) of an alloy. The larger the \( T_{rg} \) value, the higher is the viscosity, thus the easier it is for a melt to be solidified into a glass.\(^3\) According to Turnbull’s research, at an empirical value \( T_{rg} \geq 2/3 \) crystallization of a liquid metal is completely suppressed.\(^{14}\) However, not all alloys are good bulk glass formers. The GFA is also strongly related to critical cooling rate, \( R_c \) (the minimum quenching rate to obtain the glassy phase), and the lower the \( R_c \) value, the larger the GFA. The time-temperature-transformation (T-T-T) curve (Figure 1.3) is a useful tool to determine the value of \( R_c \). The T-T-T curve can be constructed by graphing the logarithm of the time-to-nucleation as a function of temperature.

![Figure 1.3: Schematic of T-T-T curve.\(^3\)](image)

The critical cooling rate, \( R_c \), to form the glassy phase is obtained by

\[
R_c = \frac{\Delta T}{t_n}
\]

where \( \Delta T \) is the undercooling, and \( t_n \) is the value of time at the minimum temperature (nose) of the T-T-T curve. BMGs are known for their high glass forming ability, for instance, Pd\(_{40}\)Cu\(_{30}\)Ni\(_{10}\)P\(_{20}\) has a critical cooling rate as low as 0.1 K/s.\(^{15}\)
1.2 The Thermodynamics and Kinetics of Bulk Metallic Glass Formation

In order to understand the formation of bulk metallic glasses, one needs to take the thermodynamic and kinetic aspects into consideration. From a thermodynamic point of view, BMGs are in a metastable state, but possess a low driving force to crystallize in the undercooled liquid region. The low driving force to crystallization indicates that the glassy phase is more thermodynamic favorable than the crystalline phase in bulk metallic glasses. The thermodynamic stability of a system at constant temperature and pressure is governed by its Gibbs energy, \( G \), defined as

\[
G = H - T \cdot S
\]

where \( H \) is the enthalpy, \( T \) is the absolute temperature, and \( S \) is the entropy. Thermodynamically, a system will be at stable equilibrium if it has achieved the lowest possible Gibbs energy. Hence, a glass becomes more stable when the free energy of the glass phase is lower than that of the competing crystalline phase(s) at some specific temperature. In other words, a negative value of \( \Delta G (G_{\text{glass}} - G_{\text{crystal}}) \) is attained. The \( \Delta G \) can be calculated according to the equation:

\[
\Delta G = \Delta H_f - T \cdot \Delta S_f
\]

where \( \Delta H_f \) and \( \Delta S_f \) are the enthalpy and entropy of fusion, respectively. A negative value of \( \Delta G \) can be obtained by either decreasing the value of \( \Delta H_f \) or increasing the value of \( \Delta S_f \) or both. However, it is difficult to directly control these two parameters simultaneously. The most convenient way to decrease free energy for the amorphous state
relative to the crystalline state is to increase $\Delta S_f$ by introducing a large number of components into the alloy system with large variation in atomic sizes: a difference between the largest and smallest atom size of at least 12%. The large $\Delta S_f$ implies the higher the degree of disorder present in a given system, the more components an alloy possesses and hence the more random arrangements of atoms that can occur in the alloy system. Thus, a higher degree of disorder and larger value of $\Delta S_f$ result. Moreover, the increase in $\Delta S_f$ leads to an increase in the degree of dense random packing in the liquid state due to the large atomic size ratios between constituents, which favors a decrease in $\Delta H_f$ and increase in solid/liquid interfacial energy.\(^\text{16}\)

From the perspective of kinetics, the greater the viscosity at the melting point, the easier it is for the glass to form because of reduced atomic motion, a necessary factor in crystallization. The variation of viscosity ($\eta$) with temperature can be described using the modification of the Vogel-Fulcher-Tammann (VFT) relation:

$$\eta(T) = \eta_0 \cdot \exp\left[\frac{D^* \cdot T_0}{T - T_0}\right]$$

where $D^*$ is the fragility parameter ($1 \leq D^* \leq 100$) that controls how closely the system obeys Arrhenius behavior ($D^* = \infty$),\(^\text{17}\) $T_0$ is the temperature at which the liquid ceases to flow, and $\eta_0$ is a constant ($\sim 10^{-5}$ Pa·s).\(^\text{3}\)

Liquids with large $D^*$ values ($D^* \geq 20$) are classified as strong liquids and those with small $D^*$ values ($D^* \leq 10$) as fragile liquids. Strong liquids are good glass formers since they possess high viscosity at the melting point. On the contrary, fragile liquids are
marginal glass formers because they have a low viscosity at the melting point. The available viscosity data of BMG forming liquids demonstrates fragility close to 20. The strong liquid behavior of BMG-forming liquids indicates that their high viscosity and sluggish kinetics in the undercooled liquid region retards the formation of stable crystal nuclei in the melt and hence inhibits growth of the crystalline phase.

Based on the data obtained from synthesis of bulk metallic glasses, Inoue et al. proposed three empirical rules for the formation of bulk metallic glasses: (1) the alloy must contain at least three components; (2) the alloy must be made of atoms with a significant difference in size (> 12%) among the three main constituent elements; (3) the alloy must have a negative enthalpy of mixing among the three main constituent elements. These rules serve as a successful framework to predict alloy compositions that produce bulk metallic glasses, even in spite of several notable exceptions, for example binary Cu_{50}Zr_{50} BMG.

1.3 Application of Bulk Metallic Glasses

The physical properties of BMGs differ from their crystalline counterparts. The high strength, hardness, toughness and potential corrosion resistance of BMGs make them promising candidates for some commercial and industrial applications.

Liquidmetal Technologies (USA) has already commercialized some Zr-based BMGs in sporting goods, for example golf club heads and tennis racket frames. BMGs have
also been developed as cases for electronic devices and wristwatches. Liquidmetal Technologies materials have been chosen for handheld ultra-personal computer screen casings by OQO, Inc., and casings for digital still cameras by Sony. In 2002, Liquidmetal Technologies cooperated with TAG Heuer to produce a special edition Microtimer Concept wristwatch featuring Zr-based BMGs as the scratch- and dent-resistant, high-gloss casing. In addition to sporting goods and protective cases, BMGs are being considered for application in motors and precision gears due to their high wear-resistance and ease of formation (casting or extrusion) of complicated shapes.

The absence of grain boundaries in BMGs make them potentially corrosion resistant and hence good candidates for biocompatible medical applications, such as reconstruction devices, fracture fixations and spinal implants. It has been reported that Zr-based BMGs have been manufactured as knee-replacement and pacemaker casings by Depuy Orthopedics, Inc. Moreover, the application of BMGs has been expanded to defense and aerospace industries. Liquidmetal Technologies has received a series of contracts from the Department of Defense to develop military materials including environmentally benign BMGs-composite KEPS (kinetic energy penetrator) to replace the conventional depleted uranium penetrators and the casings for lightweight fragmentation bombs for the US Navy. Meanwhile, Liquidmetal Technologies is cooperating with Lockheed Martin Missiles and Fire Control to develop lighter and stronger ceramic-BMG composite armor tiles. Additionally, NASA’s Genesis spacecraft, collected samples of the solar wind
using a collector plate that was coated with Zr-Nb-Cu-Ni-Al BMG (formulated by Charles C. Hayes at Caltech and prepared by Howmet Corporation). The collector plate successfully absorbs and retains noble gases like He and Ne.\textsuperscript{19}

While BMGs have some unique features, the high cost of BMGs, both raw materials and fabrication, has deterred their widespread use in consumer goods.\textsuperscript{3} However, as BMG research deepens, it is expected that low-cost BMGs will be developed to replace some conventional materials in the near future.

\section*{1.4 Corrosion of Bulk Metallic Glasses}

Corrosion is defined as the deterioration of material properties due to reaction with the environment.\textsuperscript{20} Metallic corrosion in aqueous solution is almost always an electrochemical process that usually consists of the release of metal ions into solution as the result of oxidation reactions and the reduction of species in the aqueous solution. Uniform corrosion, localized corrosion and Galvanic corrosion are three types of corrosion that usually occur at the metallic material surface. Uniform corrosion corresponds to a homogenous, regular loss of metal from the corroding surface. Localized corrosion, such as pitting and crevice corrosion, is a result of the local breakdown of a surface passive (protective) film resulting in metal loss occurring at discrete areas. Galvanic corrosion occurs by localized redox reactions due to the electrical contact between dissimilar materials when placed in an electrolyte.\textsuperscript{21}
Metallic glasses are expected to possess higher corrosion resistance than their crystalline counterparts due to the lack of grain boundaries and other crystalline defects.\textsuperscript{3} The corrosive behavior of metallic glass ribbons produced by the rapid quenching method has been studied since 1974.\textsuperscript{22} The rapid quenching rates applied during metallic glass synthesis are believed to promote chemical homogeneity of glassy materials, although this assertion may not hold for BMGs due to the relatively slow quenching rates.\textsuperscript{3} In addition, the presence of specific atoms may contribute to high corrosion resistance.\textsuperscript{3} For example, it was reported that Cr-containing Fe-based glassy ribbons showed much greater corrosion resistance than their crystalline counterparts.\textsuperscript{23} The high corrosion resistance of these particular glassy alloys can be partly ascribed to the formation of a protective hydrated chromium oxyhydroxide that prevents the occurrence of corrosion, in the same way that conventional stainless steels are protected.

The corrosion behavior of BMGs is important when considering their application in corrosive environments. Several corrosion studies of BMGs based on Cu,\textsuperscript{24} Fe,\textsuperscript{25} Ni,\textsuperscript{26} and Zr\textsuperscript{27} have been performed in acidic and electrolyte solutions using immersion and electrochemical methods combined with surface analytical techniques such as XPS (X-ray Photoelectron Spectroscopy). It is worth noting here that the mechanisms developed for one alloy system are not necessarily applicable to other alloy types due to the different compositions. But common to all the materials studied, XPS measurements revealed that oxides are formed on the surface of BMGs. These oxides are believed to serve as a passive
layer that reduces the corrosion rate. Additionally, the introduction of alloying components such as P, Mo, Nb or Ta seems to improve the corrosion resistance by assisting the formation of passive film.\textsuperscript{28}

Specific electrolyte anions, such as chloride, are found to accelerate and exacerbate the corrosion process for conventional and glassy alloys. Studies have indicated that chloride assists in the initiation of the breakdown of surface passive layers.\textsuperscript{29} In addition, chloride interferes with the repassivation that occurs after the dissolution of any passive layers, and this can ultimately lead to pitting corrosion. The studies of chloride-containing media are of distinct interest due to the fact that chloride is ubiquitous in the environment.

While there have been some studies of the corrosion of metallic glasses and bulk metallic glasses in acidic media, corrosion studies of metallic glasses in basic solution, such as NaOH, are non-existent. There is no paper focused on the behavior and corrosion mechanism of BMGs in basic solutions.

Of all the BMGs that have been fabricated to date, Pd-based BMGs have some superior properties. They are known for their low critical cooling rate and large critical casting thickness.\textsuperscript{15} A \textit{Pd}_{40}\textit{Cu}_{30}\textit{Ni}_{10}\textit{P}_{20}\text{BMG} developed in 1996 by the Inoue group currently holds the record for the lowest $R_c$ of the order of 0.1 K/s and highest critical casting thickness of 72 mm. This composition is similar to the composition of BMG that is the focus of the current work ($\textit{Pd}_{43}\textit{Cu}_{27}\textit{Ni}_{10}\textit{P}_{20}$). Extensive studies on the physical properties of Pd-based BMGs have
been conducted, however, a systematic corrosion study of Pd-based BMGs has not been performed so far.

In this current work, a corrosion study was carried out on Pd$_{43}$Cu$_{27}$Ni$_{10}$P$_{20}$ BMG to determine the corrosion rates and investigate the corrosion mechanisms in 1.00 M HCl, 1.00 M NaOH and Hanks’ solution (a simulated body fluid, see Appendix A). A dealloying study of Pd$_{43}$Cu$_{27}$Ni$_{10}$P$_{20}$ BMG was conducted to examine the electrochemical polarization behavior in 1.00 M HCl solution. Multiple analytical techniques were used in the studies of this thesis, including electrochemistry to determine the corrosion rates, SEM (Scanning Electron Microscopy) to detect the topographical changes together with EDS (Energy-dispersive X-ray Spectroscopy) and XPS to study the surface compositional changes.

The structure of this thesis is as follows. Chapter 2 is a brief background and introduction to the materials and each of the principle analytical techniques used in this thesis, together with experimental conditions and parameters. Chapter 3 is a compilation of results obtained from the corrosion and dealloying experiments described in Chapter 2. A discussion of the results is presented in Chapter 4. This thesis concludes in Chapter 5 with a summary of the results and remarks for future work.
Chapter 2

Materials and Methods

2.1 Sample Preparation

Pd$_{43}$Cu$_{27}$Ni$_{10}$P$_{20}$ bulk metallic glass (Pd-BMG), stainless steel 316, and Ti-6Al-4V (Ti$_{86}$Al$_{10}$V$_{4}$) cylindrical samples, together with three Pd-BMG coupons were supplied by Dr. Robert Conner from Department of Manufacturing System Engineering of California State University, Northridge (see Appendix B). Smooth sample surfaces were obtained by polishing with 5-micron alumina powder (Buehler Company) suspended in MetaDi Fluid (Buehler Company) followed by 1-micron alumina powder (Buehler Company). The samples were rinsed with Millipore water and isopropanol after polishing to achieve flat, clean surfaces.

2.2 X-ray Diffraction (XRD)

2.2.1 Principle of Operation

X-ray diffraction (XRD) is an analytical technique used for identification and structural analysis of organic, inorganic and metallic crystals. The wavelengths of X-rays in the range 0.01 nm to 10 nm are similar to the interatomic distances in crystals and crystal lattices can act as diffraction gratings for incident X-rays. Scattered X-rays will interfere constructively if they are in phase or destructively if they are out of phase, which produces a diffraction pattern. Constructive interference will only occur when Bragg’s law is satisfied,
\[ n \cdot \lambda = 2 \cdot d \cdot \sin \theta \]

where \( n \) is the diffraction order, is an integer, \( \lambda \) is the wavelength of the incident X-ray, \( d \) is the spacing between planes in the atomic lattice, and \( \theta \) is the scattering angle with respect to the surface normal.

By scanning an X-ray detector through a range of \( 2\cdot\theta \) angles (angle between the X-ray source and the detector axes), typically \( 0^\circ \) to \( 170^\circ \), the intensities of the scattered X-rays at all scattering angles will be obtained and each of these angles is associated with a different atomic spacing in the crystal. A unique diffraction pattern or “fingerprint” of every crystalline material is generated by plotting scattering intensity versus \( 2\cdot\theta \). A database is used to identify the material and its crystal structure.

The diffraction pattern of an amorphous material is fundamentally different from that of a crystalline material. Due to the absence of long-range periodicity in an amorphous substance, a diffraction pattern with a single broad peak distributed over a wide range of \( 2\cdot\theta \), caused by a large variability of nearest-neighbor distances, will be observed instead of high intensity sharp peaks. Hence, the diffraction pattern is one useful analytical technique to distinguish crystalline and amorphous materials. The sampling depth of XRD using Cu K\(_a\) incident radiation is \( \sim 2-200 \) micrometers, depending on the material.
2.2.2 Experimental Procedure

X-ray diffraction was conducted at Getty Museum using a Bruker-AXS D5005 powder diffractometer equipped with a Cu Kα X-ray tube (wavelength = 0.15406 nm). The polished Pd-BMG sample, with a surface area approximately 0.30 cm² was examined by XRD for crystalline characteristics.

2.3 Scanning Electron Microscopy (SEM)

2.3.1 Principle of Operation

Scanning electron microscopy (SEM) is a useful method to obtain high-resolution images of solid surfaces. Topographical images obtained by SEM are vital in corrosion studies. The resolution of optical microscopy is restricted by diffraction at optical wavelengths. This means the minimum size of object that can be resolved in optical microscopy is approximately 250 nm. However, SEM uses a focused beam of high-energy electrons to bypass this limitation since the de Broglie wavelength of an electron can be made smaller than that of an optical photon. A modern SEM achieves an image resolution close to 1 nm, which is 200 times higher than the best light microscope.\(^{35}\)

The sample surface is scanned in a raster pattern in which a high energy electron beam is swept in two perpendicular directions until a desired area of surface has been covered. During this scanning process, signals produced by irradiation of solid materials by high-energy electron beams are collected to develop SEM images.\(^{36}\) Among various signals generated by
the interactions between the incident electron beam and sample surface is secondary electron (SE) emission that can be used for SEM imaging. Secondary electrons are low energy (< 50 eV) inelastically scattered electrons originating within the top few nm of the sample surface. The SE detection mode is sensitive mostly to the topography of the surface. Collection of backscattered electrons (BSE), elastically or near-elastically scattered electrons from the incident beam, produces a signal that is primarily dependent on composition, since the scattering is a strong function of atomic number. Large Z elements scatter BSE more efficiently and so regions of the sample where large Z elements are concentrated appear bright in a BSE image. Finally, X-ray emission can be used for surface compositional analysis. When high-energy electrons collide with a solid, core or valence electrons can be ejected from the target atoms. Internal rearrangement of the electrons in the target atom causes ejection of a second electron (Auger electron) or a photon (X-ray fluorescence). Each element emits Auger electrons or X-rays of characteristic energies. Energy dispersive X-ray spectroscopy (EDX or EDS) coupled with SEM provides qualitative and quantitative information on the chemical composition of a sample by collecting and analyzing the emitted X-rays. The X-ray photons can travel relatively large distance in solids and so the sampling depth of SEM-EDS is ~1-2 μm. Unfortunately, X-ray fluorescence is an improbable process in low Z elements and the low energy photons produced (<1 keV) are detected with low sensitivity by a conventional Si (Li) detector. Consequently, SEM-EDS is unreliable for Z <11.
2.3.2 Experimental Procedure

SEM images were collected using a FEI Quanta 600 microscope equipped with a tungsten hairpin filament electron gun (0-30 keV), Everhart-Thornley detector (for SE collection), a radial segmented semiconductor detector (for BSE collection) and an Oxford EDS system based on a liquid nitrogen cooled Si (Li) detector. A Quanta xTM version 2.4 interface was used to control electron gun, imaging potential and all the other parameters. Samples were mounted onto stainless steel sample holders and a working distance of approximately 10 mm was used to acquire images. Unless otherwise noted, all images were constructed by SE emission.

EDS analysis was carried out using Aztec software suite developed by Oxford Instruments. Default settings were used for quantitation (standardless quantitation) and EDS map construction.

2.4 Ultraviolet-Visible Spectroscopy (UV-Vis)

2.4.1 Principle of Operation

Ultraviolet-visible spectroscopy (UV-Vis) is an important analytical method used to identify and quantitate organic and inorganic species. The absorption of ultraviolet (200-400 nm) or visible (400-700 nm) radiation by substances can promote electrons located in various molecular orbitals. The absorption bands can be used to identify different types of bonds or functional groups. The application of UV-Vis can be extended to study transition metal
complexes, which is of great importance to corrosion. According to crystal field theory, the five d orbitals in octahedral complexes can be split into two groups with different energy levels, t_{2g} and e_g, due to the interactions with ligands. The electronic transitions of transition metals occur among the partially filled d orbitals. The magnitude of the energy gap (Δ) between t_{2g} and e_g, is determined by the identity of the parent element, the complex symmetry and ligand field strength. The value of Δ dictates the wavelength of absorption peaks allowing qualitative and quantitative analysis of different complexes.

2.4.2 Experimental Procedure

UV-Vis analysis was conducted using a Hewlett Packard 8453 diode array spectrophotometer. A solution made by mixing equal volumes of 1.00 M copper (II) chloride and 1.00 M hydrochloric acid, the yellow solution that resulted after anodic polarization of Pd-BMG in 1.00 M hydrochloric acid, and a 1:20 Millipore water diluted yellow solution were used for UV-Vis detection. 1.00 M hydrochloric acid was used as a blank for UV-Vis measurement. Wavelengths from 190 to 1200 nm were measured to construct all UV-Vis spectra.

2.5 Cyclic Voltammetry and Potentiodynamic Polarization

2.5.1 Principle of Operation:

Voltammetry is an electroanalytical method used to derive information about a redox active analyte by measurement of a current, I, that develops in an electrochemical cell as a
function of applied potential, \( E \). A typical electrochemical cell consists of a working electrode, a reference electrode and a counter electrode (Figure 2.1).

![Schematic of a three-electrode cell.](image)

Figure 2.1: Schematic of a three-electrode cell.

The working electrode is the electrode at which the reaction of interest occurs. The counter electrode is used in conjunction with the working electrode so that the majority of electrical current flows between them. An electronic device named a potentiostat regulates the potential difference between the working and reference electrode. A reference electrode has a stable and well-known electrode potential, and the potential of the working electrode can be determined by comparison with the reference electrode. The voltammogram, a graph of current versus working electrode potential, is obtained. In corrosion science and engineering, potentiodynamic polarization and cyclic voltammetry are two voltammetric methods widely used to study corrosion mechanisms, determine the corrosion rate of a material in a given corrosive medium, and examine the anodic polarization behavior of a material. In anodic polarization, the potential of the working electrode is swept in the anodic or more positive direction relative to the reference
electrode. Electrons flow from the working electrode as the components of the electrode undergo oxidation reactions.

In potentiodynamic polarization, the material of the interest, acting as the working electrode, is submerged in the corrosive medium and the working electrode potential is changed while monitoring current through the electrode. Potentiodynamic polarization differs from conventional voltammetry in that the potential of the working electrode is swept at a fixed rate by varying current flow, not by varying the potential applied directly. The advantage of the potentiodynamic polarization method is that changes in overpotential effects (activation, concentration polarization, resistance) are ignored.

Metallic corrosion is a combination of oxidation of a metal or alloy and reduction of an oxidizing agent in the corrosive medium (electrolyte solution). The rate of corrosion depends on the kinetics of both anodic (oxidation) and cathodic (reduction) reactions. The value of the corrosion rate can be calculated using Faraday’s law:

\[
Corrosion\ Rate = K \cdot EW \cdot \frac{i_{corr}}{\rho}
\]

where \(K\) is a constant that defines the unit of corrosion rate, \(i_{corr}\) is corrosion current density at the corrosion potential, \(E_{corr}\), \(\rho\) is the density of the corrodible material, and \(EW\) is the equivalent weight of the corrodible material (see Appendix C). The corrosion potential, also called open circuit potential, is the measured potential of any corrodible material in an electrolyte in the absence of external current flow. In other words, the total anodic current and total cathodic current are equal but have opposite sign at the corrosion potential. As a
result, the determination of corrosion current at corrosion potential is impossible due to a zero net current. This problem is solved by application of the Tafel equation that correlates overpotential ($\eta$) and the logarithm of current density ($i$).

$$\eta = a + b \cdot \log i$$

where $a$ and $b$ are Tafel constants accounting for cathodic and anodic transfer coefficients respectively (see Appendix D).

By IUPAC conventions, cathodic current and anodic potential are defined as positive. A graph of $\log i$ versus $\eta$, known as Tafel plot, is constructed to obtain $i_{corr}$. Overpotential is defined as the departure of the potential of the working electrode from its open circuit potential. When the overpotential is large and positive, the anodic reaction dominates over the cathodic reaction. When the overpotential is large and negative, the anodic current becomes negligible and a linear behavior will appear on the cathodic branch of the Tafel plot. These linear behaviors are usually observed for overpotentials of ~59–120 mV away from open circuit potential. When $\eta$ approaches zero, the linear behaviors will fail. The linear sections of both anodic and cathodic regions can be extrapolated back to zero overpotential, and the intersection provides the values of $E_{corr}$ and $i_{corr}$ (Figure 2.2).
In cyclic voltammetry (CV), a triangular potential wave (Figure 2.3) is applied to the working electrode. The potential applied to the working electrode is swept at a linear rate in the anodic (positive) direction from an initial potential to some final potential and then immediately reversed. The technique can be used to assess reversibility and/or kinetics of redox and multiple cycles of potential can be used to assess the stability of the working electrode material. CV can be used to study the reversibility of corrosion reactions, because anodic and cathodic peak currents are approximately identical in absolute value, but opposite in sign for a reversible electrode reaction. A typical cyclic voltammogram is shown in Figure 2.4.
Figure 2.4: Schematic of cyclic voltammogram. $E_{pc}$ and $E_{pa}$ are peak cathodic and anodic potential, $i_{pc}$ and $i_{pa}$ are peak cathodic and anodic current.

2.5.2 Experimental Procedure

Potentiodynamic polarization experiments were performed with an EG&G Princeton Applied Research Potentiostat/Galvanostat Model 273A. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum electrode as the counter electrode. Polished Pd-BMG, stainless steel 316 and Ti-6Al-4V samples as the working electrode were immersed into three different solutions. 1.00 M HCl solutions were prepared using Millipore water and ultrapure concentrated HCl (37%, Aldrich). 1.00 M NaOH solutions were prepared from solid NaOH and Millipore water. Hanks’ solution was purchased from Sigma-Aldrich used without modification. All samples were polished and cleaned by rinsing with Millipore water and isopropanol immediately prior to electrochemical experiments.

The method to calculate corrosion rates (electrochemical measurement) was obtained from ASTM references G1, G5, and G102. All samples, with surface area ~ 0.30 cm$^2$, 24
were submerged in solutions, with the remaining surface areas protected from the electrolyte with Parafilm. Samples were conditioned in the corrosive solutions to achieve stability prior to any potentiodynamic polarization measurements. In potentiodynamic polarization measurements, the potential was swept from -100 mV to +100 mV versus $E_{corr}$ with a 0.5 mV/s sweep rate to obtain the values of $i_{corr}$. In order to study the anodic polarization behavior of samples in 1.00 M HCl solutions, the potential was swept from -250 mV to +1200 mV versus $E_{cor}$ with a 1.0 mV/s sweep rate. Weight loss tests were carried out on Pd-BMG coupons in 1.00 M HCl for 672 hours in order to validate the electrochemically determined corrosion rates. The corrosion rates (weight loss test) were calculated by the method provided in ASTM standard reference G31:$^{44}$

$$Corrosion \ Rate = \frac{(K \cdot W)}{(A \cdot T \cdot D)}$$

where $K$ is a constant (87,600 for a corrosion rate with unit of mm/year), $W$ is mass loss in grams, $A$ is surface area in cm$^2$, $T$ is the time of exposure in hours, and $D$ is the density of material in g/cm$^3$. The masses and surface areas were measured prior to tests. After 672 hours immersion, the samples were weighed to determine mass loss. The surface areas were assumed to remain constant.

Cyclic voltammetry was conducted using a BASi potentiostat and cell stand with a Ag/AgCl reference electrode and Pt counter electrode. A polished Pd-BMG sample (working electrode) was submerged in 1.00 M HCl to condition for 30 minutes to achieve stability prior to measurement. The potential was swept from -200 mV to +800 mV then reversed to
-200 mV relative to \( E_{\text{corr}} \) over a period of 6 minutes. The solution was unstirred and unpurged.

2.6 X-ray Photoelectron Spectroscopy (XPS)

2.6.1 Principle of Operation

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is a spectroscopic technique used to analyze average surface composition. The non-destructive nature and wide scope of information it can provide makes XPS a versatile surface analytical technique. XPS detects all elements on a solid surface (except hydrogen and helium) and offers atomic composition of a sample and, in some cases, the oxidation state of the elements making up the solid being analyzed. XPS is based on the photoelectric effect (Figure 2.5). Core electrons can be ejected into vacuum by incoming photons of sufficient energy. The kinetic energy of expelled electrons (photoelectrons) can be measured by an electron spectrometer. The binding energies (BE) of the electrons can be calculated by:

\[
BE = h\nu - KE - \Phi
\]

where \( h\nu \) is the energy of the incoming photon, \( KE \) is the kinetic energy of the ejected electron, and \( \Phi \) is the work function of the sample/analyzer, a correction factor that can be measured by instrumental calibration. The work function must be obtained experimentally for each instrument to allow accurate measurement of binding energy.
The Auger effect occurs promptly (~$10^{-14}$ seconds) after the initial expulsion of the photoelectron. In the Auger process (Figure 2.5), a valence electron drops into the inner orbital vacancy (hole) that the ejected photoelectron creates, and a second electron in the same subshell is emitted carrying off excess energy. X-ray fluorescence is a competing process, especially in low Z elements, however, the low energy of the soft X-ray source used in XPS favors Auger emission. XPS is especially useful for analyzing the surface properties of a sample since only photoelectrons and Auger electrons originating within 5-10 nm of the solid surface can escape into the vacuum without energy loss.\textsuperscript{45} It is these electrons that form the peaks in the XPS spectra. Auger peaks can provide useful information in analysis but since Auger emission is a three-electron process, peak shapes are intrinsically more complex than photoemission peaks.

Figure 2.5: Schematic of photoelectric process (top) and Auger process (bottom).
The binding energy of a photoelectron is characteristic of the atom and orbital from which the electron is ejected. Consequently, an intensity versus binding energy spectrum can be obtained serving as a “fingerprint” that can be used for the identification of each a Qualitative analysis is achieved by a low-resolution, wide energy XPS spectrum known as a survey spectrum. Typically, a survey spectrum has a binding energy range of 0 to 1200 eV. All the elements present on the sample surface will demonstrate their unique XPS peaks on the survey spectrum. The peaks can be used to identify elements. If overlap occurs between XPS and Auger peaks, Auger peaks can be shifted by varying the X-ray source energy, as the kinetic energy of the Auger electron is independent of the X-ray source energy.

In order to acquire quantitative information, high-resolution XPS spectra (multiplex) for all elements present on sample surface are required. Areas of XPS peaks are determined after background subtraction, as the relative intensities of XPS peaks are proportional to the concentrations of the corresponding element on the sample surface as described by

\[
C_x = \frac{I_x/S_x}{\sum_i I_i/S_i}
\]

where \(C_x\) is the atomic fraction of an element \(x\) in a sample, \(I_x\) is the area of the XPS peak of element \(x\), and \(S_x\) is the atomic sensitivity factor associated with the XPS peak of element \(x\), \(I_i\) and \(S_i\) are the XPS peak area and the associated sensitivity factor of each element in a sample respectively. In some cases, sensitivity factors are provided by the instrument manufacturer otherwise they must be determined experimentally.
Singlet and doublet peaks are observed in XPS spectra. If the photoelectron originates from an s orbital, a singlet XPS peak is present. If the photoelectron originates from a p, d or f orbital, a doublet peak will be generated because of spin-orbit coupling. For an orbital with angular momentum quantum number, \( l \), greater than zero, more than one total angular momentum quantum number, \( j \), becomes possible, due to coupling between the magnetic fields of the electron orbital momentum and its spin, \( s \), according to:

\[
j = |l + s|
\]

For instance, a p orbital has \( l = 1 \) and \( s = \pm 1/2 \), so the two possible \( j \) values are 1/2 and 3/2, giving rise to a doublet peak with a degeneracy given by \( 2 \cdot j + 1 \). In the case of p orbitals, the area ratio of the 2p\(_{3/2}\) and 2p\(_{1/2}\) peaks is \( 2 \cdot \frac{3}{2} + 1 : 2 \cdot \frac{1}{2} + 1 = 2 : 1 \). The spin-orbit area ratio is a characteristic of the angular momentum of the orbital involved, and so this value can be used in XPS for peak identification.

The binding energy of an electron is found to be dependent to a small degree on the chemical environment of atom. Variations in the number of valence electrons and the type of bonds they form impact the binding energies of core electrons. This change in binding energy is called chemical shift. In general, binding energies increase as the oxidation state becomes more positive. Chemical shifts resulting from oxidation state changes can be up to 15 eV. This shift is ascribed to the increase of nuclear attraction to a core electron due to the reduced electron penetration of outer electrons. Therefore, the chemical shift of a XPS peak contains
information on chemical environment of the atom and the oxidation state of elements present on a sample.

The analysis depth of XPS changes if the angle between the plane of the sample surface and the analyzer entrance axis, known as take-off angle, is altered. At normal take-off angle (90°) with respect to the surface plane, the signal from the bulk is maximized. At grazing take-off angle (<90°) with respect to the surface plane, the signal from the surface is enhanced (Figure 2.6). Angle-resolved XPS is a non-destructive technique that can provide information from different sampling depth by varying take-off angle. In order to change take-off angles, the sample must be tilted with respect to the electron analyzer entrance axis. The data obtained by angle-resolved XPS assists in understanding the distributions of elements within a heterogeneous surface film.

Figure 2.6: Variation of analysis depth with take-off angle (d₃₀ < d₄₅ < d₉₀).

The spectral resolution of the XPS technique is partly determined by the analyzer pass energy, the energy to which photoelectrons are retarded before entering the analyzer. When
the pass energy is high, the resolution is poor but the number of electrons collected is high. This setup is useful for survey spectra. On the contrary, when the pass energy is low, the resolution is high but the number of electrons collected is much reduced. Small pass energy is usually applied to acquire multiplex spectra of individual components on a sample surface with high resolution.

2.6.2 Experimental Apparatus

All XPS measurements were carried out using a Perkin Elmer 5200 ESCA system. The system is comprised of a stainless steel main chamber operating at a base pressure of approximately 1×10^{-10} torr. An Edwards RV8 rotary mechanical pump, Edwards EXT 70 turbomolecular pump and Perkin Elmer 270 L/s ion pump were used to reach base pressure. The chamber was equipped with a PHI 04-548 dual anode X-ray source, with Mg (1253.6 eV) and Al (1486.6 eV) anodes, an Omni Focus II semi hemispherical analyzer, and a PHI 04-300 differentially pumped ion gun. The X-ray source was operated at 20 mA emission current and 15 kV anode potential (300 W total power). The angle between the X-ray source and analyzer entrance axis was fixed at 54°. A RBD 147 interface unit was used to control the system electronics. AugerScan 3.22 software was used to generate and analyze XPS spectra. The XPS system was calibrated using the Au 4f_{7/2} (84.0 eV BE) and Cu 2p_{3/2} (932.7 eV BE) photoelectron peaks to ensure the accuracy of XPS data. A 3.00 mm diameter circle of 99.98% Au (Aldrich Chemical Company) surrounded by 0.025 mm thick Cu foil (Aldrich Chemical Company) was used to calibrate the instrument. Sensitivity factors were provided by Physical
Electronics for the Omni Focus lens. A monocular microscope attached to the main chamber provided analysis location on the sample surface. All XPS spectra reported in this thesis were obtained with a take-off angle of 45° unless otherwise stated.

2.6.3 Experimental Procedure

All samples were cleaned by rinsing with Millipore water and isopropanol to remove surface contaminants prior to XPS measurements. 3M™ double-sided carbon tape and aluminum foil were used to mount Pd-BMG samples to the sample holder (puck). Once a sample was placed in the main chamber for analysis, it was positioned at the focal point of the X-ray source and analyzer using the attached optical microscope. The position was then adjusted for maximal electron counts. A high pass-energy survey (143.05 eV) with step size of 1 eV-per-step was conducted for the sample component identification. Once the peak assignments were accomplished, low pass-energy (44.75 eV) region (multiplex) scans with a step size of 0.1 eV-per-step were acquired to quantify the atomic composition. Multiple sweeps of surveys and multiplex spectra were applied to increase signal-to-noise ratios of XPS spectra. Surveys were typically obtained over 10 sweeps. Multiplexes were collected over 10 sweeps, 30 sweeps or 90 sweeps according to the abundance of elements present on the Pd-BMG sample surface. The multiplex regions for Pd-BMG (Table 2.1) were chosen due to their prominence and distinct separation from interfering peaks.

Argon ion sputtering was also carried out to examine the oxidation state of copper in the Pd-BMG. The argon ions (~2 kV) were bombarding on the as-polished Pd-BMG surface for
30 minutes to completely expose the subsurface of the sample. XPS scans were taken prior to and after sputtering.

<table>
<thead>
<tr>
<th>Element</th>
<th>Orbital</th>
<th>Binding Energy Range (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>2p</td>
<td>925-975</td>
</tr>
<tr>
<td>Ni</td>
<td>2p</td>
<td>845-880</td>
</tr>
<tr>
<td>P</td>
<td>2p</td>
<td>123-147</td>
</tr>
<tr>
<td>Pd</td>
<td>3d</td>
<td>330-350</td>
</tr>
<tr>
<td>C</td>
<td>1s</td>
<td>280-300</td>
</tr>
<tr>
<td>O</td>
<td>1s</td>
<td>520-540</td>
</tr>
<tr>
<td>Cl</td>
<td>2p</td>
<td>195-205</td>
</tr>
<tr>
<td>Cu</td>
<td>Auger (LMM)</td>
<td>563-583</td>
</tr>
</tbody>
</table>

Table 2.1: Regions selected for Pd-BMG multiplexes.

The Al anode was selected for the X-ray source for Pd-BMG analysis due to the overlap of Pd MNN Auger and Cu 2p peaks when using the Mg source. Aperture 3 (circular analysis area 1.1 mm diameter) was used. For each multiplex, the area of each selected XPS peak was obtained following Shirley background subtraction. The sample atomic composition was calculated from the peak areas and sensitivity factors. All XPS spectra were referenced to the C 1s peak at 285.0 eV. Angle-resolved XPS with take-off angles of 30° and 90° was also
applied to achieve qualitative depth information. Curve fitting was conducted using XPSPEAK4.1 software.
Chapter 3

Results

The results chapter will be organized into five subsections. The first subsection, section 3.1, will present a surface characterization of as-polished Pd-BMG using XRD, SEM, EDS and XPS. Section 3.2 will present results from corrosion studies of Pd-BMG in 1.00 M HCl solution. For corrosion studies, Tafel plots and weight loss data will be shown together with calculated corrosion rates. XPS and EDS data and SEM images will be presented. For the dealloying studies, section 3.3, potentiodynamic polarization data will be presented, followed by XPS analysis, SEM images and EDS analysis. Cyclic voltammetry and UV-Vis analysis will conclude this section. Section 3.4, will show results from the corrosion studies of Pd-BMG in Hank’s solution and section 3.5 will present results from corrosion studies in a 1.00 M NaOH solution. Tafel plots and corrosion rates will be shown together with XPS, SEM and EDS results will be presented.

3.1 Characterization of Polished Pd-BMG

3.1.1 XRD Measurements

The XRD pattern of the polished Pd-BMG is shown in Figure 3.1. The diffraction pattern displays the characteristic broad scattering feature at $2\theta \sim 41^\circ$ that indicates an amorphous state. It is noteworthy that no sharp features, indicative of crystalline components, are present.
3.1.2 SEM and EDS Measurements

The SEM micrograph in Figure 3.2 demonstrates the as-polished Pd-BMG surface to be uniform and without major defects. Moreover, the composition of the alloy is uniform, as shown in the EDS map in Figure 3.2. The bulk composition determined by EDS agrees well with the nominal alloy composition as shown in Table 3.1. The largest difference is seen for P, which could be a function of the standardless calibration procedure used by the EDS quantitation protocol.

Figure 3.1: XRD pattern of as-polished Pd-BMG.

Figure 3.2: SEM micrograph of as-polished Pd-BMG at 100x magnification.
3.1.3 XPS Measurements

XPS analysis indicates a significant surface composition deviation from the nominal composition and that measured by EDS. The difference between the XPS and EDS-determined compositions can be ascribed to the different surface sensitivities of the two techniques coupled with a heterogeneous distribution of elements. The sampling depth of XPS is ~5-10 nm and EDS ~1000-2000 nm.47 As a result, XPS provides more surface sensitive information. Table 3.2 summarizes the surface compositions of the polished Pd-BMG determined by XPS, EDS together with the nominal composition. The surface composition determined by XPS shows that surface segregation occurs on Pd-BMG, that is, enrichment of surface Pd and P, and surface depletion of Cu. Ni is almost absent from surface. Typical region multiplex scans of Cu, Ni, P and Pd are shown in Figures 3.4-3.7, respectively. The Cu 2p_{3/2} and Pd 3d_{5/2} peak binding energies match closely with those reported in the
literature for elemental copper and palladium (Table 3.1). Angle-resolved XPS spectra of P 2p peak of Pd-BMG (as-polished sample left in air for 1-day) are shown in Figures 3.8-3.10.

<table>
<thead>
<tr>
<th>Element</th>
<th>Measured Binding Energy (eV)</th>
<th>Elemental Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (2p_{3/2})</td>
<td>931.8</td>
<td>932.2^{48}</td>
</tr>
<tr>
<td>Pd (3d_{5/2})</td>
<td>335.0</td>
<td>335.1^{49}</td>
</tr>
</tbody>
</table>

Table 3.1: Binding energies of Cu and Pd (measured versus elemental).

It can be concluded that palladium is present in its unoxidized state. Due to the indistinguishable binding energies of Cu (0) and Cu (I), the oxidation state of copper cannot be assigned by the XPS 2p region data solely. However, the Auger region can be used to clarify the Cu oxidation state. The Auger region of 30-minute Argon ion sputtered Pd-BMG closely matches that of elemental Cu, and the Auger regions of Pd-BMG (prior to and after sputtering) show the same features and no binding energy shift which suggested Cu exists in its elemental state (see Appendix E). The Ni 2p region shows poor signal to noise due to the low concentration of surface Ni and so definitive assignment of the Ni species is difficult. But in addition to metallic (elemental) Ni, indicated by a Ni 2p_{3/2} peak at 852.7 eV binding energy,^{49} there is evidence of an oxidized Ni species, indicated by the broad features to the high binding energy side of the Ni 2p_{3/2} peak. Similarly, P appears to be partially oxidized. The P 2p peak (unresolved doublet) occurring at approximately 129.3 eV binding energy is usually assigned as elemental phosphorus P(0).^{50} However, Elsener^{51} pointed out that a
phosphorus 2p peak at \( \sim 129.2 \) eV was more likely to be \( \text{P}^1 \). Because of the controversies over the assignment of P 2p peak, in this thesis P 2p peak at 129.3 \pm 0.2 \) eV is assigned as P(0). The elemental phosphorus peak is present on the Pd-BMG surface but it is accompanied by another P 2p doublet peak at approximately 132.8 eV binding energy. This shift, to higher binding energy, is indicative of an oxidized form of P and is consistent with a \( \text{P}^{5+} \) type species.\(^{52,53}\) Moreover, Soda\(^{30}\) also found that P is the only element that is partially oxidized on Pd\(_{42.5}\)Ni\(_{7.5}\)Cu\(_{30}\)P\(_{20}\) bulk metallic glass surface.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Fraction Nominal</th>
<th>Atomic Fraction EDS</th>
<th>Atomic Fraction XPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>27%</td>
<td>29%</td>
<td>22%</td>
</tr>
<tr>
<td>Ni</td>
<td>10%</td>
<td>11%</td>
<td>1%</td>
</tr>
<tr>
<td>P</td>
<td>20%</td>
<td>17%</td>
<td>24%</td>
</tr>
<tr>
<td>Pd</td>
<td>43%</td>
<td>43%</td>
<td>53%</td>
</tr>
</tbody>
</table>

Table 3.2: Atomic compositions of as-polished Pd-BMG determined by EDS and XPS. The EDS-determined copper concentration is higher than the nominal value at the expense of the phosphorus concentration. The XPS data show surface segregation, that is, enrichment of surface Pd and P, depletion of Cu (relative to nominal composition) on the sample surface. Ni is almost absent from the polished sample surface.
Figure 3.4: XPS peaks for Cu 2p on as-polished Pd-BMG surface. The presence of two peaks is due to spin-orbit splitting of the 2p orbital. The 2p₀\textsubscript{3/2} peak is at lower BE and the 2p₀\textsubscript{1/2} at higher BE.

Figure 3.5: XPS peaks for Ni 2p on as-polished Pd-BMG surface.

Figure 3.6: XPS peaks for P 2p on as-polished Pd-BMG surface.
Figure 3.7: XPS peaks for Pd 3d on as-polished Pd-BMG surface.

Figure 3.8: Angle resolved P 2p peaks (take-off angle 30°) of as-polished Pd-BMG surface (1 day in air). Peak A at 129.1 eV is assigned as elemental phosphorus, Peak B at 132.8 eV as oxidized phosphorus. Dots indicate the experimental data, solid line indicates the summary of curve fitted data, long dash lines indicate the curve fitted peaks, and square dot dash line indicates the background.

Figure 3.9: Angle resolved P 2p peaks (take-off angle 45°) of as-polished Pd-BMG surface (1 day in air). Peak A at 129.3 eV is assigned as elemental phosphorus, Peak B at 133.0 eV as oxidized phosphorus. Dots indicate the experimental data, solid line indicates the summary of curve fitted data, long dash lines indicate the curve fitted peaks, and square dot dash line indicates the background.
Figure 3.10: Angle resolved P 2p peaks (take-off angle 90°, least surface sensitive) of as-polished Pd-BMG surface (1 day in air). Peak A at 129.2 eV is assigned as elemental phosphorus, Peak B at 133.0 eV as oxidized phosphorus. Dots indicate the experimental data, solid line indicates the summary of curve fitted data, long dash lines indicate the curve fitted peaks, and square dot dash line indicates the background.

The relative intensities of the two P peaks, labeled as A for elemental P(0) and B for oxidized P(V), clearly change as a function of take-off angle. Table 3.3 summarizes the P(V) fraction of total P at 3 different take-off angles of Pd-BMG (as-polished, 1 day in air).

<table>
<thead>
<tr>
<th>Take-off Angle (°)</th>
<th>Surface Sensitivity</th>
<th>P(V)% of Total P</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>Most</td>
<td>57</td>
</tr>
<tr>
<td>45</td>
<td>-</td>
<td>47</td>
</tr>
<tr>
<td>90</td>
<td>Least</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 3.3: P(V) fraction of total P of as-polished Pd-BMG (1 day in air) determined by XPS with different take-off angles.

The intensity of peak B decreases relative to peak A as the surface sensitivity decreases. Consequently, peak B must be associated with P-containing compound existing on the sample surface. In addition, the binding energy of peak B is more positive than that of peak A, thus, peak A is assigned as elemental phosphorus, P(0), and peak B as oxidized phosphorus,
P(V). The assignment of peak B as a P(V)-type compound is consistent with previous measurements of PO$_4^{3-}$ and P$_2$O$_5$.\textsuperscript{52,53,54}

Figures 3.11-3.12 shows curve-fitted XPS spectra for Cu and Pd with 30°, 45° and 90° take-off angles for as-polished Pd-BMG (1 day in air). Table 3.4 lists the atomic ratios Cu:Pd for the angle-resolved XPS analysis of the Pd-BMG. It can be seen that, since there are no binding energy shifts found for either Cu or Pd indicative of phosphates, and Ni is almost absent from sample surface, the P(V) can be assigned as oxidized a P$_2$O$_5$-P$_4$O$_{10}$-like substance.

![Graph](image.png)

Figure 3.11: Cu 2p$_{3/2}$ peaks at 30° (bottom), 45° (middle) and 90° (top) degree take-off angle of as-polished Pd-BMG surface (1 day in air). Dots indicate the experimental data, solid line indicates the summary of curve fitted data, long dash lines indicate the curve fitted peaks, and square dot dash line indicates the background. Note the small peak at around 933.3 eV in the bottom spectrum is assigned as copper hydroxide formed after being exposed in air.
Figure 3.12: Pd 3d peaks at 30° (bottom), 45° (middle) and 90° (top) degree take-off angle of as-polished Pd-BMG surface (1 day in air). Dots indicate the experimental data, solid line indicates the summary of curve fitted data, and square dot dash line indicates the background.

<table>
<thead>
<tr>
<th>Take-off Angle</th>
<th>Surface Sensitivity</th>
<th>Atomic Composition</th>
<th>Cu:Pd ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>Most</td>
<td>Pd$<em>{49}$Cu$</em>{20}$Ni$<em>{19}$P$</em>{30}$</td>
<td>0.41</td>
</tr>
<tr>
<td>45</td>
<td>-</td>
<td>Pd$<em>{56}$Cu$</em>{19}$Ni$<em>{1}$P$</em>{24}$</td>
<td>0.32</td>
</tr>
<tr>
<td>90</td>
<td>Least</td>
<td>Pd$<em>{62}$Cu$</em>{13}$Ni$<em>{4}$P$</em>{23}$</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Table 3.4: Cu:Pd ratio of as-polished Pd-BMG (1 day in air) determined by XPS with different take-off angles.

Taken together, Tables 3.2 and 3.4 suggest surface segregation occurs on the Pd-BMG surface. It can be observed by angle-resolved XPS (Table 3.4) that Cu:Pd ratio increases as the surface sensitivity increases, which underscores that copper accumulates on the very top layer of the Pd-BMG sample, leaving a Pd-rich layer immediately below it.
3.2 Corrosion of Pd-BMG in 1.00 M Hydrochloric Acid

The corrosion behavior of the Pd-BMG was studied in two different states of preparation. In one case, a freshly polished surface was immediately immersed into a corrosive medium/electrolyte solution. In the second case, a freshly polished sample was left in laboratory air for 3 days at room temperature before being immersed into the corrosion medium. Figure 3.13 and Table 3.5 show the effect of laboratory air exposure. Although there is little change in the elemental composition, it is obvious that the air-exposed surface shows less P(0)-type phosphorus and more P(V)-type phosphorus. As such, the polished surface that was immediately corroded was termed the P(V)-poor surface and that which was exposed to laboratory air before experiments was termed the P(V)-rich surface. It should be stressed that polishing, rinsing and inserting the Pd-BMG into the XPS instrument necessitated some air exposure and so it was not possible to perform experiments on a completely P(V)-free surface.

Figure 3.13: Effect of air exposure on atomic fraction of P(V) on as-polished Pd-BMG surface. White column indicates P(0), dark grey column indicates P(V).


<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Fraction (0-day)</th>
<th>Atomic Fraction (3-day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>20%</td>
<td>21%</td>
</tr>
<tr>
<td>Ni</td>
<td>1%</td>
<td>1%</td>
</tr>
<tr>
<td>P</td>
<td>25%</td>
<td>25%</td>
</tr>
<tr>
<td>Pd</td>
<td>54%</td>
<td>53%</td>
</tr>
</tbody>
</table>

Table 3.5: Effect of air exposure on atomic composition of as-polished Pd-BMG.

3.2.1 SEM and EDS Measurements

SEM micrographs, EDS and XPS measurements were used to study the topographical and compositional changes of the freshly polished (P(V)-poor) Pd-BMG after immersion in 1.00 M HCl at room temperature for 0, 3, 7, 10 and 14 days. After each immersion, the Pd-BMG sample was polished to achieve a new surface. Similar measurements were conducted on the P(V)-rich surface.

The SEM micrographs at 100x magnification in Figure 3.14 show the P(V)-poor surface at 0-day (top) and 14-day (bottom) immersion in 1.00 M HCl solution. The surface remained uniform after being soaked into 1.00 M HCl solution. There was no observable pitting and corrosion as observed by SEM. Similar results were obtained for the P(V)-rich surface, shown in Figure 3.15. There was no observable pitting corrosion under the examination of SEM and no apparent changes in the topography of the surfaces.
Figure 3.14: SEM micrographs of P(V)-poor surface: 0-day (top) and 14-day (bottom) immersion in 1.00 M HCl.

Figure 3.15: SEM micrographs of P(V)-rich surface: 0-day (top) and 14-day (bottom) immersion in 1.00 M HCl.
The EDS maps of the P(V)-poor at 0-day (top) and 14-day (bottom) immersion in 1.00 M HCl solution are included in Figure 3.16. All the elements are evenly distributed, and no local compositional changes occur on the two types of surfaces after being immersed in 1.00 M HCl for up to 14 days. P(V)-rich surface showed similar behavior.

Figure 3.16: EDS maps of P(V)-poor surface 0-day (top) and 14-day (bottom) immersion in 1.00 M HCl.

The average surface compositions of the P(V)-poor and P(V)-rich surfaces after 0-, 3-, 7-, 10- and 14-day immersion in 1.00 M HCl solution detected by EDS are listed in Table 3.5 and Table 3.6 respectively. No prominent compositional changes in the upper 1000-2000 nm can be observed by EDS on both P(V)-poor and P(V)-rich surfaces.
<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Fraction (0 day)</th>
<th>Atomic Fraction (3 day)</th>
<th>Atomic Fraction (7 day)</th>
<th>Atomic Fraction (10 day)</th>
<th>Atomic Fraction (14 day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>29.3%</td>
<td>28.5%</td>
<td>29.1%</td>
<td>28.9%</td>
<td>31.4%</td>
</tr>
<tr>
<td>Ni</td>
<td>10.7%</td>
<td>10.7%</td>
<td>10.7%</td>
<td>10.6%</td>
<td>11.7%</td>
</tr>
<tr>
<td>P</td>
<td>17.3%</td>
<td>17.8%</td>
<td>17.5%</td>
<td>18.5%</td>
<td>14.6%</td>
</tr>
<tr>
<td>Pd</td>
<td>42.7%</td>
<td>43.0%</td>
<td>42.7%</td>
<td>42.0%</td>
<td>42.3%</td>
</tr>
</tbody>
</table>

Table 3.6: Atomic compositions of P(V)-poor surface immersed in 1.00 M HCl determined by EDS. No prominent compositional change can be observed by EDS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Fraction (0 day)</th>
<th>Atomic Fraction (3 day)</th>
<th>Atomic Fraction (7 day)</th>
<th>Atomic Fraction (10 day)</th>
<th>Atomic Fraction (14 day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>27.5%</td>
<td>29.7%</td>
<td>27.3%</td>
<td>28.3%</td>
<td>31.0%</td>
</tr>
<tr>
<td>Ni</td>
<td>10.5%</td>
<td>10.9%</td>
<td>10.1%</td>
<td>10.6%</td>
<td>11.3%</td>
</tr>
<tr>
<td>P</td>
<td>19.0%</td>
<td>15.9%</td>
<td>18.7%</td>
<td>18.0%</td>
<td>14.1%</td>
</tr>
<tr>
<td>Pd</td>
<td>43.0%</td>
<td>43.5%</td>
<td>43.9%</td>
<td>43.1%</td>
<td>43.6%</td>
</tr>
</tbody>
</table>

Table 3.7: Atomic compositions of P(V)-rich surface immersed in 1.00 M HCl determined by EDS. No prominent compositional change can be observed by EDS.

The absence of topographical and compositional changes both P(V)-poor and P(V)-rich surfaces indicates that if corrosion occurs on Pd-BMG in 1.00 M HCl, it occurs on the very top surface of the Pd-BMG sample.
3.2.2 XPS Measurements

In contrast to the EDS measurements above, XPS analysis reveals significant compositional changes that occur on both P(V)-poor and P(V)-rich surfaces during the immersion experiments in 1.00 M HCl solution. Tables 3.7 and 3.8 detail the surface compositions of P(V)-poor and P(V)-rich surfaces at 0-, 3-, 7-, 10- and 14-day immersion in 1.00 M HCl solution determined by XPS, respectively. In addition, Figures 3.17-24 show the typical region multiplex scans of Cu, Ni, P and Pd as a function of immersion duration.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Fraction (0 day)</th>
<th>Atomic Fraction (3 day)</th>
<th>Atomic Fraction (7 day)</th>
<th>Atomic Fraction (10 day)</th>
<th>Atomic Fraction (14 day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>20%</td>
<td>7%</td>
<td>8%</td>
<td>7%</td>
<td>7%</td>
</tr>
<tr>
<td>Ni</td>
<td>1%</td>
<td>2%</td>
<td>2%</td>
<td>2%</td>
<td>2%</td>
</tr>
<tr>
<td>P</td>
<td>25%</td>
<td>30%</td>
<td>28%</td>
<td>23%</td>
<td>24%</td>
</tr>
<tr>
<td>Pd</td>
<td>54%</td>
<td>61%</td>
<td>62%</td>
<td>68%</td>
<td>67%</td>
</tr>
</tbody>
</table>

Table 3.8: Atomic compositions of P(V)-poor surface immersed in 1.00 M HCl determined by XPS. Cu concentration dropped 13% after being soaked for 3 days, and then the concentration remained constant. Pd increased 8% after 3 days, and eventually came to 67%. P increased 5% after 3 days due to the formation of P(V), then P(V) disappeared and the concentration of P dropped back to its original concentration after 10-day immersion and remained constant. Ni remained almost absent from the surface.
Figure 3.17: XPS peaks of Cu 2p$_{3/2}$ 0-day (bottom), 3-day (middle) and 14-day (top) immersion in 1.00 M HCl on P(V)-poor surface. Dots indicate the experimental data, solid line indicates the summary of curve fitted data, and square dot dash line indicates the background. Note no binding energy shift can be observed meaning Cu was not oxidized on surface.

Figure 3.18: XPS peaks of Ni 2p 0-day (bottom), 3-day (middle) and 14-day (top) immersion in 1.00 M HCl on P(V)-poor surface. The low signal to noise ratio and the absence of any discernible feature suggests the near-absence of Ni on the sample surface.
Figure 3.19: XPS peaks of P 2p 0-day (bottom), 3-day (middle) and 14-day (top) immersion in 1.00 M HCl on P(V)-poor surface. Dots indicate the experimental data, solid line indicates the summary of curve fitted data, long dash lines indicate the curve fitted peaks and square dot dash line indicates the background. Note that P(V) (at ~133 eV) was almost absent from the surface at 0-day, increased at 3-day immersion, and disappeared at 14-day immersion.

Figure 3.20: XPS peaks of Pd 3d 0-day (bottom), 3-day (middle) and 14-day (top) immersion in 1.00 M HCl on P(V)-poor surface. Dots indicate the experimental data, solid line indicates the summary of curve fitted data, and square dot dash line indicates the background. Note that no binding energy shift can be observed meaning Pd was not oxidized on surface.
Table 3.9: Atomic compositions of P(V)-rich surface immersed in 1.00 M HCl determined by XPS. Cu concentration dropped 9% after being soaked for 3 days, and then the concentration remained constantly. Pd (53%) increased 8% after 3 days, and eventually came to 65%. P concentration remained constantly during the immersion tests in 1.00 M HCl, however P(V) disappeared after 3 days and never observed again. Ni remained absence from the surface.

Figure 3.21: XPS peaks of Cu 2p\textsubscript{3/2} 0-day (bottom), 3-day (middle) and 14-day (top) immersion in 1.00 M HCl on P(V)-rich surface. Dots indicate the experimental data, solid line indicates the summary of curve fitted data, long dash lines indicate the curve fitted peaks and square dot dash line indicates the background. Note the small peak at around 933.3 eV at 0-day is assigned as copper hydroxide formed after being exposed in air. There was no binding energy shift during the immersion test meaning Cu was not oxidized on surface.
Figure 3.22: XPS peaks of Ni 2p 0-day (bottom), 3-day (middle) and 14-day (top) immersion in 1.00 M HCl on P(V)-rich surface. The low signal to noise ratio and the absence of any discernible feature suggests the near absence of Ni on the sample surface.

Figure 3.23: XPS peaks of P 2p 0-day (bottom), 3-day (middle) and 14-day (top) immersion in 1.00 M HCl on P(V)-rich surface. Dots indicate the experimental data, solid line indicates the summary of curve fitted data, long dash lines indicate the curve fitted peaks and square dot dash line indicates the background. Note that P(V) (at ~133 eV) present on the surface at 0 days (left in air for 3 days after polishing), diminished greatly at 3-day immersion and disappeared afterwards.
3.2.3 **Electrochemical Measurements**

Potentiodynamic polarization measurements were conducted on freshly-polished samples to determine the average corrosion rate of Pd-BMG in 1.00 M HCl solution. In order to compare, the same measurements were performed on stainless steel 316 (S.S 316), and Ti-6Al-4V and also on the Pd-BMG sample after 14 days of immersion in 1.00 M HCl. A typical voltammogram is shown in Figure 3.25. The curve demonstrates the typical characteristics of a Tafel plot, displaying a linear decrease in current density in both cathodic
(negative) and anodic (positive) regions near \( E_{corr} \) (at \( \approx +0.30 \) V vs. SCE), followed by a precipitous current density drop as \( E_{corr} \) is approached. The Tafel extrapolation was performed to estimate \( i_{corr} \).

Figure 3.25: Tafel plot of as-polished Pd-BMG in 1.00 M HCl (versus SCE reference electrode). \( E_{corr} \) is observed at 300 mV vs. SCE. Tafel extrapolation yields an approximate \( i_{corr} \) of 1.02 \( \mu \)A/cm\(^2\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_{corr} ) (mV)</th>
<th>( i_{corr} ) (( \mu )A/cm(^2))</th>
<th>Corrosion Rate (mm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-BMG (as-polished)</td>
<td>280</td>
<td>1.02</td>
<td>0.016</td>
</tr>
<tr>
<td>Pd-BMG (14-day immersion in 1.00 M HCl)</td>
<td>-34.0</td>
<td>0.20</td>
<td>0.0020</td>
</tr>
<tr>
<td>S.S 316 (as-polished)</td>
<td>-320</td>
<td>34.4</td>
<td>0.35</td>
</tr>
<tr>
<td>Ti-6Al-4V (as-polished)</td>
<td>-330</td>
<td>2.72</td>
<td>0.032</td>
</tr>
</tbody>
</table>
The results derived from the Tafel plots and calculated corrosion rates are listed in Table 3.9. The corrosion rate in 1.00 M HCl of the as-polished Pd-BMG is approximately half that of Ti-6Al-4V, and 30 times lower than that of stainless steel 316. Moreover, the corrosion rate in 1.00 M HCl of the Pd-BMG after 14-day immersion in 1.00 M HCl is approximately 5 times lower than the as-polished one. To confirm the validity of these values, weight loss experiments yield a corrosion rate of 0.010 mm/yr for the freshly-polished Pd-BMG in 1.00 M HCl solution, in good agreement with the 0.016 mm/year deduced from the Tafel plot. Similarly, literature values for the corrosion rate of stainless steel 316 and Ti-6Al-4V in 1.00 M HCl are 0.70 mm/yr\textsuperscript{55} and 0.0234 mm/yr\textsuperscript{56}, respectively.

3.3 Dealloying of Pd-BMG in 1.00 M Hydrochloric Acid

Anodic polarization was conducted on an as-polished Pd-BMG coupon to study the delloying behavior of Pd-BMG in 1.00 M HCl. Sweeping the potential to much more anodic potentials than a typical Tafel region results in more severe oxidation of the surface.

3.3.1 Electrochemical Measurements

Figure 3.26 shows the anodic polarization curve of an as-polished Pd-BMG coupon in 1.00 M HCl solution. A current density plateau can be observed on the polarization curve near +0.6 V potential as outlined by the dotted line box, which suggests the existence of a passivation film, perhaps due to the formation of oxidized phosphorus. As the potential is
swept to more anodic (positive) potentials, the passive film appears to lose its effectiveness and the current density increases again. Eventually, the curve reaches another current density plateau due to the diffusion limit, at potentials above about +1.0 V. The 1.00 M HCl solution turned yellow after polarization at this potential and a porous black film was formed on the coupon surface. The black film was not firmly attached to the coupon surface, and could be removed with rinsing.

![Anodic polarization curve of as-polished Pd-BMG in 1.00 M HCl (versus SCE reference electrode). Passive region is indicated using dotted line box. No sharp increase after the breakdown of passive film indicates low tendency to pit. Cyclic voltammetry (Figure 3.27) was used to examine a possible reversible redox reaction occurring at the as-polished Pd-BMG surface in 1.00 M HCl. The result indicates the occurrence of a partially reversible reaction on the Pd-BMG surface due to both oxidation and reduction peaks/waves can be observed on the cyclic voltammogram. The partially reversible reaction is assigned to $Cu - 2e^- \rightleftharpoons Cu^{2+}$ on the basis of the half-wave potential, $E_{1/2}$, of ~230 mV (versus Ag/AgCl electrode). This agrees well with literature values of 229.5 mV (versus Ag/AgCl electrode by assuming concentration of Cu$^{2+}$ is $10^{-3}$ M). It was notable that at no time was a second wave visible due to redox reactions.](image-url)
reactions of Pd, which would appear near 752 mV (versus Ag/AgCl electrode). As revealed by the cyclic voltammogram, it appears that only copper took part in the redox reaction on the surface. Consequently, the black film was formed was likely due to the delloying of BMG, and preferential removal of copper from the surface. The dissolution of copper left behind a Pd-rich surface slowing down the corrosion further, as indicated by the data of Table 3.10, and/or lack of pitting in 1.00 M HCl.

Figure 3.27: Cyclic voltammogram of as-polished Pd-BMG in 1.00 M HCl (versus Ag/AgCl reference electrode relative to open circuit potential).

Anodic polarization (-0.25 V to +0.6V versus $E_{corr}$) of the P(V)-poor and P(V)-rich surfaces in 1.00 M HCl were carried out to examine the role the of oxidized phosphorus in the dealloying behavior in 1.00 M HCl solution (Figure 3.28).
Figure 3.28: Anodic polarization curves of P(V)-poor and P(V)-rich Pd-BMG in 1.00 M HCl (versus SCE reference electrode).

Figure 3.28 reveals a more prominent current density plateau near +0.4 V on the anodic branch of the polarization curve for the P(V)-rich surface compared with the P(V)-poor surface. The more prominent current density plateau on P(V)-rich surface indicates that oxidized phosphorus serves as a protective layer in 1.00 M HCl solution.

3.3.2 SEM and EDS Measurements

The SEM micrographs at 150x magnification of as-polished Pd-BMG surface, black film and surface after the removal of black films (Figures 3.29-3.31) show significant topographical change of the Pd-BMG surface after the anodic polarization to +1.4 V. The as-polished surface was uniform and featureless. The surface after anodic polarization
showed rough texture and porous features characteristic of the black film formed. After removing the black film by rinsing with milipore water, the surface showed a rough topography but without the presence of pits.

Figure 3.29: SEM micrograph of as-polished Pd-BMG at 150x magnification.

Figure 3.30: SEM micrograph of as-polished Pd-BMG after anodic polarization (black film) at 150x magnification. A porous and rough texture can be observed.
EDS analysis was conducted on the black film to examine the compositional changes. Figure 3.33 shows the EDS maps of the black film and the surface after the removal of the black film. The distribution of elements on the black film was no longer uniform, and palladium was highly localized in the black film, with the very significant decrease of the other components. After removing the black film, the surface remained a uniform distribution of all components, similar to the polished surface.
Figure 3.32: EDS maps of the black film (top) and the surface after removing the black film (bottom). Pd was heavily accumulated on the black film region.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Fraction (as-polished)</th>
<th>Atomic Fraction (black film)</th>
<th>Atomic Fraction (after removal of black film)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>29%</td>
<td>2%</td>
<td>33%</td>
</tr>
<tr>
<td>Ni</td>
<td>11%</td>
<td>1%</td>
<td>12%</td>
</tr>
<tr>
<td>P</td>
<td>17%</td>
<td>10%</td>
<td>15%</td>
</tr>
<tr>
<td>Pd</td>
<td>43%</td>
<td>83%</td>
<td>40%</td>
</tr>
<tr>
<td>Cl</td>
<td>-</td>
<td>4%</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.11: Summary of EDS data (Anodic polarization in 1.00 M HCl). Note that chlorine was detected on the black film, however, the EDS signals of Cl and Pd are overlapped.
Table 3.8 lists the surface compositions of Pd-BMG determined by EDS during dealloying studies. The Pd concentration increased greatly on the black film to the point where the surface was almost 90% Pd, the remainder being mostly P. After the removal of the black film, the surface composition agreed well with the as-polished one.

3.3.3 XPS Measurements

XPS was conducted to examine the surface compositional change after the anodic polarization in 1.00 M HCl. Table 3.11 includes the surface compositions of Pd-BMG determined by XPS.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Fraction (as-polished)</th>
<th>Atomic Fraction (black film)*</th>
<th>Atomic Fraction (black film)</th>
<th>Atomic Fraction (after removal of black film)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>20%</td>
<td>8%</td>
<td>6%</td>
<td>5%</td>
</tr>
<tr>
<td>Ni</td>
<td>1%</td>
<td>0%</td>
<td>0%</td>
<td>2%</td>
</tr>
<tr>
<td>P</td>
<td>25%</td>
<td>26%</td>
<td>21%</td>
<td>26%</td>
</tr>
<tr>
<td>Pd</td>
<td>54%</td>
<td>66%</td>
<td>60%</td>
<td>67%</td>
</tr>
<tr>
<td>Cl</td>
<td>-</td>
<td>-</td>
<td>13%</td>
<td>-</td>
</tr>
</tbody>
</table>

* Atomic composition with chlorine excluded

Table 3.12: Summary of XPS data (Anodic polarization in 1.00 M HCl). Chlorine was detected on the black film.

The chlorine observed on the black film might be chlorine residue from the HCl and an improperly-rinsed surface. No XPS binding energy shifts can be observed for any element.
suggesting that a persistent surface chloride is not formed. The large decrease in copper concentration indicated that copper was lost during the anodic polarization. As EDS suggested, the film was dominated by Pd and P. The palladium concentration increased up to 65% after anodic polarization in 1.00 M HCl. The phosphorus concentration remained unaffected, and P(V) fraction increased on the black film. After removing the black film, the surface composition was similar to that of the original black film. Figures 3.34-3.40 show the typical region scans of Cu, Ni, P and Pd of the as-polished surfaces (control, black film and after removal of black film). The concentration oxidized phosphorus P(V) was low on the initial surface, almost absent after removing the film but increased on the black film.

Figure 3.33: XPS peaks of Cu 2p3/2 control (bottom), black film (middle) and after removal of black film (top) on Pd-BMG surface in anodic polarization in 1.00 M HCl. Dots indicate the experimental data, solid line indicates the summary of curve fitted data and square dot dash line indicates the background. Note that no binding energy shift can be observed meaning Cu was not oxidized on surface.
Figure 3.34: XPS peaks of Ni control (bottom), black film (middle) and after removing black film (top) on Pd-BMG surface in anodic polarization in 1.00 M HCl. The low signal to noise ratio and the absence of any discernible feature suggests the absence of Ni on the sample surface.

Figure 3.35: XPS peaks of P 2p control (bottom), black film (middle) and after removing black film (top) on Pd-BMG surface in anodic polarization in 1.00 M HCl. Dots indicate the experimental data, solid line indicates the summary of curve fitted data, long dash lines indicate the curve fitted peaks and square dot dash line indicates the background. Note that no distinct P(V) peaks can be observed on the surface after removal of black film.
Figure 3.36: XPS peaks of Pd 3d control (bottom), black film (middle) and after removing black film (top) on Pd-BMG surface in anodic polarization in 1.00 M HCl. Dots indicate the experimental data, solid line indicates the summary of curve fitted data and square dot dash line indicates the background. Note that no binding energy shift can be observed meaning Pd was not oxidized on surface.

Figure 3.37: XPS peaks of Cl 2p control (bottom), black film (middle) and after removing black film (top) on Pd-BMG surface in anodic polarization in 1.00 M HCl. The chlorine peak was not observed on the as-polished surface and the surface after removing black film. Note that the chlorine detected on the black film is probably Cl\(^-\) residue from 1.00 M HCl.
The selective dealloying of copper of Pd-BMG in 1.00 M HCl resulted in a black film that contained a high fraction of palladium, and this Pd-rich black film might serve as weak protective film that reduced further attack of aggressive ions and inhibited the formation of pits.

3.3.4 UV-Vis Measurements

UV-Vis spectroscopy was carried out to study the composition of the yellow solution that resulted from anodic polarization of Pd-BMG in 1.00 M HCl. A second portion of this solution was diluted 1:20 with deionized water. A 0.05 M HCl solution was used as blank, and a mixture of 0.05 M CuCl$_2$ and 0.05 M HCl solution used as a standard. Typical UV-Vis spectra of the standard and the neat and diluted yellow solutions (See Appendix A) are shown Figures 3.38-3.40.

![UV-Vis spectrum](image)

Figure 3.38: UV-vis spectrum of standard solution (0.05 M CuCl$_2$ and 0.05 M HCl).
Figure 3.39: UV-vis spectrum of the yellow solution. The broad feature around 220 nm contains unresolved overlapped peaks. The peak at 280 nm is [PdCl$_4$-n(H$_2$O)]$^{(2-n)^-}$. 

Figure 3.40: UV-vis spectrum of the yellow solution (1:20 diluted). The peak around 209 nm is HCl, around 236 nm is a Cu complex. The [PdCl$_4$-n(H$_2$O)]$^{(2-n)^-}$ peak is missing due to low concentration.

It can be concluded from the UV-Vis spectra that a Cu complex$^{59}$ (probably CuCl$_2$) and a Pd-based complex [PdCl$_4$-n(H$_2$O)]$^{(2-n)^-}$ are formed after the anodic polarization of Pd-BMG in 1.00 M HCl solution. The presence of chloride facilitated the dissolution of copper in 1.00 M HCl, and assisted minor dissolution of palladium in 1.00 M HCl.
3.4 Corrosion of Pd-BMG in Hanks’ Solution

The polished Pd-BMG, the surface containing a minimum amount of P(V) and designated as P(V)-poor, was studied for topographical and compositional changes after 3-day and 7-day immersion in Hanks’ solution. SEM micrographs, EDS and XPS measurements were acquired. After the immersion tests were complete, the Pd-BMG sample was repolished and then left in laboratory air for three days to form a P(V)-rich surface. The same measurements were conducted on P(V)-rich surface.

3.4.1 SEM and EDS Measurements

The SEM micrographs at 100x magnification in Figure 3.41 and Figure 3.42 show the P(V)-poor and P(V)-rich surface after 0-day (top) and 7-day (bottom) immersion in Hanks’ solution. The surface remained uniform and undamaged after being soaked into Hanks’ solution. There was no observable pitting and corrosion under the examination of SEM.
Figure 3.41: SEM micrographs of P(V)-poor surface 0-day (top) and 7-day (bottom) immersion in Hanks’ solution.

Figure 3.42: SEM micrographs of P(V)-rich surface 0-day (top) and 7-day (bottom) immersion in Hanks’ solution.
The EDS maps of the P(V)-poor surface at 0-day (top) and 7-day (bottom) immersion in Hanks’ solution are included in Figure 3.43. All the elements are evenly distributed, and no localized compositional changes occur on the two kinds of surfaces after being immersed in Hanks’ solution. P(V)-rich surface showed similar behavior.

The average surface compositions of the P(V)-poor and P(V)-rich surfaces at 0-day, 3-day and 7-day immersion in Hanks’ solution detected by EDS are listed in Table 3.13 and Table 3.14 respectively. No prominent compositional changes can be observed by EDS on both P(V)-poor and P(V)-rich surfaces.
<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Fraction (0 day)</th>
<th>Atomic Fraction (3 day)</th>
<th>Atomic Fraction (7 day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>31.6%</td>
<td>30.9%</td>
<td>31.0%</td>
</tr>
<tr>
<td>Ni</td>
<td>11.6%</td>
<td>11.4%</td>
<td>11.4%</td>
</tr>
<tr>
<td>P</td>
<td>14.5%</td>
<td>15.0%</td>
<td>15.4%</td>
</tr>
<tr>
<td>Pd</td>
<td>42.3%</td>
<td>42.7%</td>
<td>42.2%</td>
</tr>
</tbody>
</table>

Table 3.13: Atomic compositions of P(V)-poor surface immersed in Hanks’ solution determined by EDS. No prominent compositional change can be observed by EDS indicating the corrosion occurs on the top surface of the Pd-BMG sample if it occurs.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Fraction (0 day)</th>
<th>Atomic Fraction (3 day)</th>
<th>Atomic Fraction (7 day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>28.7%</td>
<td>29.0%</td>
<td>29.4%</td>
</tr>
<tr>
<td>Ni</td>
<td>10.8%</td>
<td>10.9%</td>
<td>11.1%</td>
</tr>
<tr>
<td>P</td>
<td>18.5%</td>
<td>17.7%</td>
<td>17.7%</td>
</tr>
<tr>
<td>Pd</td>
<td>42.0%</td>
<td>42.4%</td>
<td>41.8%</td>
</tr>
</tbody>
</table>

Table 3.14: Atomic compositions of P(V)-rich surface immersed in Hanks’ solution determined by EDS. No prominent compositional change can be observed by EDS indicating the corrosion occurs on the top surface of the Pd-BMG sample if it occurs.

The absence of topographical and compositional changes for both P(V)-poor and P(V)-rich surfaces indicates that if corrosion occurs on Pd-BMG in Hanks’ solution, it occurs on the very top surface of the Pd-BMG sample. The more surface-sensitive technique of XPS
was used to assess compositional changes occurring in the uppermost 5-10 nm of the surface, as discussed in the next subsection.

3.4.2 XPS Measurements

In contrast to EDS, XPS analysis demonstrated significant compositional changes occurred on both P(V)-poor and P(V)-rich surfaces during the immersion tests in Hanks’ solution. Tables 3.15 and 3.16 list the surface composition of P(V)-poor and P(V)-rich surfaces, respectively, at 0-day, 3-day and 7-day immersion in Hanks’ solution as determined by XPS. In addition, Figures 3.44-3.51 show the typical region multiplex scans of Cu, Ni, P and Pd at the 0-day, 3-day, and 7-day immersion in Hanks’ solution for P(V)-poor and P(V)-rich surfaces respectively.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Fraction (0 day)</th>
<th>Atomic Fraction (3 day)</th>
<th>Atomic Fraction (7 day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>19%</td>
<td>7%</td>
<td>6%</td>
</tr>
<tr>
<td>Ni</td>
<td>2%</td>
<td>1%</td>
<td>0%</td>
</tr>
<tr>
<td>P</td>
<td>26%</td>
<td>19%</td>
<td>11%</td>
</tr>
<tr>
<td>Pd</td>
<td>53%</td>
<td>73%</td>
<td>83%</td>
</tr>
</tbody>
</table>

Table 3.15: Atomic compositions of P(V)-poor surface immersed in Hanks’ solution determined by XPS. Cu concentration dropped significantly after being soaked for 3 days with little change thereafter. The Pd increased rapidly after 3 days and eventually reached to 83% after 7 days soaking. There was a gradual decrease in P and Ni remained almost absent from the surface.
Figure 3.44: XPS peaks of Cu $2p_{3/2}$ 0-day (bottom), 3-day (middle) and 7-day (top) immersion in Hanks’ solution on P(V)-poor surface. There was no binding energy shift during the immersion test meaning Cu was not oxidized on surface.

Figure 3.45: XPS peaks of Ni 2p 0-day (bottom), 3-day (middle) and 7-day (top) immersion in Hanks’ solution on P(V)-poor surface. The low signal to noise ratio and the absence of any discernible feature suggests the absence of Ni on the sample surface.
Figure 3.46: XPS peaks of P 2p 0-day (bottom), 3-day (middle) and 7-day (top) immersion in Hanks’ solution on P(V)-poor surface. Note that P(V) (at ~133 eV) concentration is low on the surface at 0-day, and almost absent at 3-day and 7-day.

Figure 3.47: XPS peaks of Pd 3d 0-day (bottom), 3-day (middle) and 7-day (top) immersion in Hanks’ solution on P(V)-poor surface. Note that no binding energy shift can be observed meaning Pd was not oxidized on surface.
Table 3.16: Atomic compositions of P(V)-rich surface immersed in Hanks’ solution determined by XPS. A similar behavior to the P(V) poor surface was observed. P dropped from 26% to 12% at 3-day immersion and remained constant. Ni remained nearly absent from the surface.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Fraction (0 day)</th>
<th>Atomic Fraction (3 day)</th>
<th>Atomic Fraction (7 day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>21%</td>
<td>7%</td>
<td>5%</td>
</tr>
<tr>
<td>Ni</td>
<td>2%</td>
<td>1%</td>
<td>1%</td>
</tr>
<tr>
<td>P</td>
<td>26%</td>
<td>12%</td>
<td>10%</td>
</tr>
<tr>
<td>Pd</td>
<td>51%</td>
<td>80%</td>
<td>84%</td>
</tr>
</tbody>
</table>

Figure 3.48: XPS peaks of Cu 2p$_{3/2}$ 0-day (bottom), 3-day (middle) and 7-day (top) immersion in Hanks’ solution on P(V)-rich surface. Dots indicate the experimental data, solid line indicates the summary of curve fitted data, long dash lines indicate the curve fitted peaks and square dot dash line indicates the background. Note the small peak at around 933.3 eV at 0-day is assigned as copper hydroxide formed after being exposed in air. There was no binding energy shift during the immersion test meaning Cu was not oxidized on surface.
Figure 3.49: XPS peaks of Ni 2p 0-day (bottom), 3-day (middle) and 7-day (top) immersion in Hanks’ solution on P(V)-rich surface. The low signal to noise ratio and the absence of any discernible feature suggests the absence of Ni on the sample surface.

Figure 3.50: XPS peaks of P 2p 0-day (bottom), 3-day (middle) and 7-day (top) immersion in Hanks’ solution on P(V)-rich surface. Dots indicate the experimental data, solid line indicates the summary of curve fitted data, long dash lines indicate the curve fitted peaks and square dot dash line indicates the background. Note that P(V) (at ~133 eV) almost disappeared after 7 days immersion.
Figure 3.51: XPS peaks of Pd 3d 0-day (bottom), 3-day (middle) and 7-day (top) immersion in Hanks’ solution on P(V)-rich surface. Dots indicate the experimental data, solid line indicates the summary of curve fitted data and square dot dash line indicates the background. Note that no binding energy shift can be observed meaning Pd was not oxidized on surface.

In summary, noticeable surface compositional changes can be observed in XPS measurements of the P(V)-poor and P(V)-rich surfaces in Hanks’ solution. The changes are similar in both cases with the difference of P behavior, that is, P lost more rapidly on P(V)-rich surface at 3-day immersion in Hanks’ solution compared with the P(V)-poor surface.

3.4.3 Electrochemical Measurements

Potentiodynamic polarization measurements were conducted on the freshly-polished sample to determine the corrosion rate of Pd-BMG in Hanks’ solution. In order to compare, the same measurements were performed on stainless steel 316, and Ti-6Al-4V and the sample
after 7-day immersion in Hanks’ solution. A typical Tafel is shown in Figure 3.52. The curve demonstrates the typical characteristics of a Tafel plot. The Tafel extrapolation was done to estimate $i_{corr}$.

Figure 3.52: Tafel plot of as-polished Pd-BMG in Hanks’ solution (versus SCE reference). $E_{corr}$ is observed at -35.2 mV vs. SCE. Tafel extrapolation yields an approximate $i_{corr}$ of 0.84 µA/cm².

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{corr}$ (mV)</th>
<th>$i_{corr}$ (µA/cm²)</th>
<th>Corrosion Rate (mm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-BMG (as-polished)</td>
<td>-35.2</td>
<td>0.84</td>
<td>0.013</td>
</tr>
<tr>
<td>Pd-BMG (7-day immersion in Hanks’ solution)</td>
<td>-108</td>
<td>0.15</td>
<td>0.0024</td>
</tr>
<tr>
<td>S.S 316 (as-polished)</td>
<td>-209</td>
<td>0.12</td>
<td>0.0012</td>
</tr>
<tr>
<td>Ti-6Al-4V (as-polished)</td>
<td>-365</td>
<td>0.032</td>
<td>0.00030</td>
</tr>
</tbody>
</table>

Table 3.17: Summary of Tafel plots data (Hanks’ solution)
The results derived from the Tafel plots and calculated corrosion rates are listed in Table 3.14. The corrosion rate in Hanks’ solution of the as-polished Pd-BMG is 6 times higher than that of stainless steel 316, and 24 times higher than that of Ti-6Al-4V. However, the corrosion rate in Hanks’ solution of the Pd-BMG after 7-day immersion in Hanks’ solution is approximately 6 times lower than the as-polished one, making it comparable to stainless steel 316.

3.5 Corrosion of Pd-BMG in 1.00 M Sodium Hydroxide

3.5.1 SEM and EDS Measurements

The SEM micrographs at 100x magnification in Figure 3.53 and Figure 3.54 show the P(V)-poor and P(V)-rich surfaces after 0 days (top) and 7 days (bottom) immersion in 1.00 M NaOH solution. As judged by SEM, the surface remained uniform and undamaged after being soaked in 1.00 M NaOH solution. There was no observable pitting or corrosion.
Figure 3.53: SEM micrographs of P(V)-poor surface 0-day (top) and 7-day (bottom) immersion in 1.00 M NaOH.

Figure 3.54: SEM micrographs of P(V)-rich surface 0-day (top) and 7-day (bottom) in 1.00 M NaOH.
The EDS maps of the P(V)-poor surface at 0-day (top) and 7-day (bottom) immersion in 1.00 M NaOH solution are included in Figure 3.55. P(V)-rich surface shows similar behavior.

Figure 3.55: EDS maps of P(V)-poor surface 0-day (top) and 7-day (bottom) immersion in 1.00 M NaOH.

The average surface compositions of the P(V)-poor and P(V)-rich surfaces at 0-day, 3-day and 7-day immersion in 1.00 M NaOH solution detected by EDS are listed in Table 3.18 and Table 3.19 respectively. Taken together Figure 3.55, Table 3.18 and Table 3.19, a conclusion can be drawn that no prominent compositional and topographical changes can be observed by EDS on both P(V)-poor and P(V)-rich surfaces. Consequently, it is safe to state that the corrosion might only occur on the top surface of Pd-BMG in 1.00 M NaOH.
<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Fraction (0 day)</th>
<th>Atomic Fraction (3 day)</th>
<th>Atomic Fraction (7 day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>31.0%</td>
<td>29.7%</td>
<td>32.1%</td>
</tr>
<tr>
<td>Ni</td>
<td>11.4%</td>
<td>11.2%</td>
<td>11.9%</td>
</tr>
<tr>
<td>P</td>
<td>15.4%</td>
<td>14.8%</td>
<td>14.6%</td>
</tr>
<tr>
<td>Pd</td>
<td>42.2%</td>
<td>44.3%</td>
<td>41.4%</td>
</tr>
</tbody>
</table>

Table 3.18: Atomic compositions of P(V)-poor surface immersed in 1.00 M NaOH determined by EDS. No prominent compositional change can be observed by EDS indicating the corrosion occurs on the top surface of the Pd-BMG sample if it occurs.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Fraction (0 day)</th>
<th>Atomic Fraction (3 day)</th>
<th>Atomic Fraction (7 day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>28.2%</td>
<td>29.1%</td>
<td>30.2%</td>
</tr>
<tr>
<td>Ni</td>
<td>10.4%</td>
<td>10.8%</td>
<td>11.2%</td>
</tr>
<tr>
<td>P</td>
<td>18.8%</td>
<td>17.6%</td>
<td>16.8%</td>
</tr>
<tr>
<td>Pd</td>
<td>42.6%</td>
<td>42.5%</td>
<td>41.8%</td>
</tr>
</tbody>
</table>

Table 3.19: Atomic compositions of P(V)-rich surface immersed in 1.00 M NaOH determined by EDS. No prominent compositional change can be observed by EDS indicating the corrosion occurs on the top surface of the Pd-BMG sample if it occurs.
3.5.2 XPS Measurements

Table 3.20 and Table 3.21 list the surface composition of P(V)-poor and P(V)-rich surfaces, respectively, at 0-day, 3-day and 7-day immersion in NaOH determined by XPS respectively. In contrast to the results determined by EDS, XPS measurements revealed significant compositional changes in 1.00 M NaOH. Moreover, the XPS data of Pd-BMG in 1.00 M NaOH renders an unique corrosion behavior that highlights the emergence of Ni, decrease of Pd and heavy depletion of Cu and P. Typical multiplex scans of Cu, Ni, P and Pd at the 0-day, 3-day, and 7-day immersion in 1.00 M NaOH for P(V)-poor and P(V)-rich surfaces respectively are shown in Figures 3.57-3.64.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Fraction (0 day)</th>
<th>Atomic Fraction (3 day)</th>
<th>Atomic Fraction (7 day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>23%</td>
<td>3%</td>
<td>4%</td>
</tr>
<tr>
<td>Ni</td>
<td>2%</td>
<td>65%</td>
<td>64%</td>
</tr>
<tr>
<td>P</td>
<td>23%</td>
<td>2%</td>
<td>3%</td>
</tr>
<tr>
<td>Pd</td>
<td>52%</td>
<td>30%</td>
<td>29%</td>
</tr>
</tbody>
</table>

Table 3.20: Atomic compositions of P(V)-poor surface immersed in 1.00 M NaOH determined by XPS.
Figure 3.56: XPS peaks of Cu 2p$_{3/2}$ 0-day (bottom), 3-day (middle) and 7-day (top) immersion in 1.00 M NaOH on P(V)-poor surface. Dots indicate the experimental data, solid line indicates the summary of curve fitted data and square dot dash line indicates the background. Note Cu signal was almost lost after 3-day immersion indicating the heavy loss of Cu in 1.00 M NaOH.

Figure 3.57: XPS peaks of Ni 2p 0-day (bottom), 3-day (middle) and 7-day (top) immersion in 1.00 M NaOH on P(V)-poor surface. Dots indicate the experimental data, solid line indicates the summary of curve fitted data, and long dash lines indicate the curve fitted peaks, and square dot dash line indicates the background. Note that Ni is almost absent on 0-day and the Ni species appeared on the 3-day and 7-day immersion are assigned as Ni(OH)$_2$. 

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Figure 3.58: XPS peaks of P 2p 0-day (bottom), 3-day (middle) and 7-day (top) immersion in 1.00 M NaOH on P(V)-poor surface. Dots indicate the experimental data, solid line indicates the summary of curve fitted data, and long dash lines indicate the curve fitted peaks and square dot dash line indicates the background. Note that concentration of P(V) (at ~133 eV) was low at 0-day, and P signal became undistinguishable after 3-day immersion indicating the heavy diminishment of P.

Figure 3.59: XPS peaks of Pd 3d 0-day (bottom), 3-day (middle) and 7-day (top) immersion in 1.00 M NaOH on P(V)-poor surface. Dots indicate the experimental data, solid line indicates the summary of curve fitted data, and square dot dash line indicates the background. Note that there is no binding energy shift of Pd 3d peaks demonstrating that Pd was not oxidized in the immersion in 1.00 M NaOH.
<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Fraction (0 day)</th>
<th>Atomic Fraction (3 day)</th>
<th>Atomic Fraction (7 day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>21%</td>
<td>2%</td>
<td>5%</td>
</tr>
<tr>
<td>Ni</td>
<td>2%</td>
<td>60%</td>
<td>61%</td>
</tr>
<tr>
<td>P</td>
<td>23%</td>
<td>3%</td>
<td>2%</td>
</tr>
<tr>
<td>Pd</td>
<td>54%</td>
<td>35%</td>
<td>32%</td>
</tr>
</tbody>
</table>

Table 3.21: Atomic compositions of P(V)-rich surface immersed in 1.00 M NaOH determined by XPS.

Figure 3.60: XPS peaks of Cu 2p3/2 0-day (bottom), 3-day (middle) and 7-day (top) immersion in 1.00 M NaOH on P(V)-rich surface. Dots indicate the experimental data, solid line indicates the summary of curve fitted data, long dash lines indicate the curve fitted peaks and square dot dash line indicates the background. The small peak at around 933.3 eV at 0-day is assigned as copper hydroxide formed after being exposed in air. Note that Cu signal was almost lost after 3-day immersion indicating the heavy loss of Cu in 1.00 M NaOH.
Figure 3.61: XPS peaks of Ni 2p 0-day (bottom), 3-day (middle) and 7-day (top) immersion in 1.00 M NaOH on P(V)-rich surface. Dots indicate the experimental data, solid line indicates the summary of curve fitted data, and long dash lines indicate the curve fitted peaks, and square dot dash line indicates the background. Note that Ni is almost absent on 0-day, the Ni species appeared on the 3-day and 7-day immersion are assigned as Ni(OH)$_2$.

Figure 3.62: XPS peaks of P 2p 0-day (bottom), 3-day (middle) and 7-day (top) immersion in 1.00 M NaOH on P(V)-rich surface. Dots indicate the experimental data, solid line indicates the summary of curve fitted data, and long dash lines indicate the curve fitted peaks and square dot dash line indicates the background. Note that P signal became undistinguishable after 3-day immersion indicating the heavy diminishment of P.
3.5.3 Electrochemical Measurements

Potentiodynamic polarization measurements were conducted on a freshly-polished sample to determine the corrosion rate of Pd-BMG in 1.00 M NaOH solution. In order to compare, the same measurements were performed on stainless steel 316, Ti-6Al-4V and the Pd-BMG sample after 7-day immersion in 1.00 M NaOH solution. Additionally, air-saturated 1.00 M NaOH, nitrogen-purged 1.00 M NaOH, and oxygen-purged NaOH solutions were used to examine the effect of presence of oxygen in 1.00 M NaOH solution on the corrosion rate of freshly-polished Pd-BMG. The typical Tafel regions are shown in Figures 3.64-3.66.

Figure 3.63: XPS peaks of Pd 3d 0-day (bottom), 3-day (middle) and 7-day (top) immersion in 1.00 M NaOH on P(V)-rich surface. Dots indicate the experimental data, solid line indicates the summary of curve fitted data, and square dot dash line indicates the background. Note that there is no binding energy shift of Pd 3d peaks demonstrating that Pd was not oxidized in the immersion in 1.00 M NaOH.
Figure 3.64: Tafel plot of as-polished Pd-BMG in unpurged 1.00 M NaOH (versus SCE reference electrode). \( E_{\text{corr}} \) is observed at -282 mV vs. SCE. Tafel extrapolation yields an approximate \( i_{\text{corr}} \) of 11.8 \( \mu \text{A/cm}^2 \).

Figure 3.65: Tafel plot of as-polished Pd-BMG in nitrogen-purged 1.00 M NaOH (versus SCE reference electrode). \( E_{\text{corr}} \) is observed at -237 mV vs. SCE. Tafel extrapolation yields an approximate \( i_{\text{corr}} \) of 10.7 \( \mu \text{A/cm}^2 \).
Figure 3.66: Tafel plot of as-polished Pd-BMG in oxygen-saturated 1.00 M NaOH (versus SCE reference electrode). $E_{corr}$ is observed at -356 mV vs. SCE. Tafel extrapolation yields an approximate $i_{corr}$ of 21.7 µA/cm$^2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{corr}$ (mV)</th>
<th>$i_{corr}$ (µA/cm$^2$)</th>
<th>Corrosion Rate (mm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-BMG (as-polished)</td>
<td>-282</td>
<td>11.8</td>
<td>0.12</td>
</tr>
<tr>
<td>Pd-BMG (7-day immersion in 1.00 M NaOH)</td>
<td>-265</td>
<td>8.35</td>
<td>0.086</td>
</tr>
<tr>
<td>S.S 316 (as-polished)</td>
<td>-304</td>
<td>0.47</td>
<td>0.040</td>
</tr>
<tr>
<td>Ti-6Al-4V (as-polished)</td>
<td>-108</td>
<td>0.15</td>
<td>0.020</td>
</tr>
</tbody>
</table>

Table 3.22: Summary of Tafel plots data (1.00 M NaOH unpurged).

The results derived from the Tafel plots and calculated corrosion rates are listed in Table 3.22. It will be recalled that the corrosion rate of the Pd-BMG in Hanks’ solution is 6 times higher than that of stainless steel 316 and 24 times higher than that of Ti-6Al-4V for the
freshly-polished surface. However, the corrosion rate in 1.00 M NaOH of the Pd-BMG after 7-day immersion is approximately 2 times lower than the polished one.

The importance of the cathodic reaction that occurs in parallel with the anodic dissolution of the alloy components is illustrated by considering the corrosion rates for Pd-BMG in purged NaOH solution. In the N₂-purged 1.00 M NaOH solution $i_{corr}$ is only slightly lower than that in unpurged (air-saturated) NaOH, whereas, in the O₂-saturated 1.00 M NaOH solution $i_{corr}$ is approximately twice that in the air-saturated NaOH, suggesting O₂ is an important reactant in the corrosion reduction reaction.
Chapter 4

Discussion

4.1 Characterization of Pd-BMG

The surface composition of as-polished Pd-BMG measured by XPS differed from the nominal and the EDS-determined compositions. The surface compositions of the Pd-BMG determined by XPS and EDS were $\text{Pd}_{53}\text{Cu}_{22}\text{Ni}_{1}\text{P}_{24}$ and $\text{Pd}_{42}\text{Cu}_{31}\text{Ni}_{12}\text{P}_{15}$, respectively (Table 3.2). The difference in these compositions is due to the different sampling depths of the two techniques. EDS samples further into the bulk than XPS and so the composition determined by this technique is much closer to the nominal composition, $\text{Pd}_{43}\text{Cu}_{27}\text{Ni}_{10}\text{P}_{20}$. The minor differences between the EDS-measured and nominal compositions are likely due to the use of the standardless quantitation method used by the SEM-EDS software.

Taken together, the EDS and XPS data indicates that surface segregation results in a Pd- and P-enriched, Cu-depleted and Ni-absent near-surface region (top ~ 5-10 nm). This surface segregation has crucial impacts on the corrosion behavior of the Pd-BMG as discussed below. At first sight, segregation is an unexpected occurrence for glassy alloys. As was noted in the introduction, metallic glasses exist in metastable states at room temperature, effectively forming undercooled frozen-liquid states. If atomic diffusion occurred to any great degree, crystalline nuclei would form and the material would convert to the crystalline state. As such, atomic diffusion at room temperature in metallic glasses is extremely low. Of course, the phenomenon of segregation, where the near-surface composition is different than the bulk,
must be the result of diffusion, that is, the movement of atoms to or from the bulk to the near-surface region.

It will be recalled that the average composition measured by EDS is very similar to the nominal composition and that repolishing the surface always produces approximately the same near-surface composition, measured by XPS. This means that the near-surface composition cannot be the result of the heterogeneities within the alloy due to manufacture of the alloy, for example while the material was still in the molten state. It seems plausible that the altered surface composition is a result of the polishing process. A small amount of friction-generated heat develops during polishing but the temperature rises are modest (<50 °C estimated) and not sufficient to approach the alloy $T_g$, when diffusion becomes significant. Therefore, it seems likely that the action of the polishing particles is enough to mechanically scramble atoms in the top few atomic layers and cause the segregation (the polishing particles are on the order of 500 nm in diameter and so this scrambling effect could penetrate up to ~500 nm into the surface). It is speculated that the mechanical polishing creates dislocations and some other defects that also serve as diffusion paths for segregating elements.  

The XPS and EDS measurements permit a tentative explanation of the observed compositional variations. It is common for a binary metallic alloys to have a surface composition that is significantly different from the nominal composition. As a result, the surface segregation on the Pd-BMG surface might be rationalized by thermodynamic
considerations. The driving force for surface segregation is to minimize the total surface free energy (surface tension) by promoting the constituent with the lowest surface free energy from bulk to surface through diffusion. Surface segregation is a strong function of bulk and surface composition.\textsuperscript{62} P is known as a surface-active element that lowers the surface energy of an alloy.\textsuperscript{63} In addition, the small atomic radius and large negative enthalpy of oxide formation of P facilitates segregation\textsuperscript{64} and the enrichment of P on the as-polished Pd-BMG surface, as shown in Table 4.1.

<table>
<thead>
<tr>
<th>Element</th>
<th>$\Delta H_f$\textsuperscript{65} (kJ·mol$^{-1}$)</th>
<th>Atomic Radius\textsuperscript{65} (pm)</th>
<th>Surface Free Energy\textsuperscript{66} ($\gamma$ (J·m$^{-2}$))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>-159 (Cu$_2$O)</td>
<td>140</td>
<td>1.83</td>
</tr>
<tr>
<td>Ni</td>
<td>-240 (NiO)</td>
<td>135</td>
<td>2.40</td>
</tr>
<tr>
<td>P</td>
<td>-1504 (P$_2$O$_5$)</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>Pd</td>
<td>-85 (PdO)</td>
<td>135</td>
<td>2.05</td>
</tr>
</tbody>
</table>

Table 4.1: Surface segregation data summary of all constituents of Pd-BMG.

Of the metal components of the Pd-BMG alloy, Cu possesses the lowest surface free energy while Ni possesses the highest surface free energy (Table 4.1). As a result, Cu and Pd should be promoted to the surface and Ni reduced to minimize surface free energy of the Pd-BMG, as verified experimentally by XPS measurements; it will be recalled that Ni is almost absent from the uppermost 5-10 nm. However, Cu should be more enriched than
Pd due to the lower surface free energy it possesses. Both Cu and Pd remain as metallic (unoxidized) components so the enthalpy of oxide formation should not be important in driving segregation in this case. In fact, it appears that P oxidizes preferentially and perhaps prevents oxidation of Cu or Pd. Angle-resolved XPS data (Figures 3.8-3.10, Table 3.4) reveals that, indeed, the Cu concentration increases at the uppermost layer of the as-polished Pd-BMG surface. Similar segregation was observed by Miller on a Pd$_{70}$Cu$_{30}$ alloy showing a Cu monolayer overlays the uppermost surface by LEISS measurements.$^{67}$ The promotion of Cu and P to the surface will create a region below the surface that is relatively deficient in these elements, in other words, a subsurface in which Pd is enriched.

It should be remembered that the XPS results indicated that, overall, the near-surface region was Pd rich. This seems at odds with the information that Cu is concentrated near the uppermost part of the surface. However, this structure can be rationalized assuming that the polishing process preferentially removes Cu atoms. In this hypothesis, Cu would segregate to the surface during polishing and so would be preferentially removed, which leaves a near-surface region that is depleted of Cu on average. Cu segregation during the final polishing process, or perhaps immediately following it, would create a layered structure in which the near-surface region is depleted of Cu but the extreme surface is Cu rich.

Based on the XPS and EDS measurements, a sandwich-like structure of Pd-BMG can be proposed as shown in Figure 4.1, that is, a Cu-rich, Pd-poor layer as the topmost layer,
a Cu-poor, Pd-rich sublayer underneath, and a bulk with the nominal alloy composition beneath.

**Figure 4.1: Sandwich-structure of Pd-BMG.**

It may be worthwhile to explore the surface composition using a more surface-sensitive analytical method or through sputter depth profiling to give a detailed examination of the topmost surface of Pd-BMG to understand the surface segregation in this bulk metallic glass.

### 4.2 Corrosion of Pd-BMG in 1.00 M HCl

The corrosion resistance of freshly-polished Pd-BMG in 1.00 M HCl is higher than the two corrosion resistant commercial available alloys; the corrosion rate was 0.016 mm/yr compared with 0.35 mm/yr and 0.032 mm/yr for stainless steel 316 and Ti-6Al-4V, respectively (Table 3.10). The EDS determination (Table 3.6-3.7) of both P(V)-poor and P(V)-rich surfaces showed no prominent compositional change during the soaking experiment in 1.00 M HCl. All the elements are uniformly distributed on the Pd-BMG
surface indicating the corrosion only occurred on the 5-10 nm uppermost surface of the Pd-BMG. Figure 4.2-4.3 summarize the compositional changes on Pd-BMG surfaces during the soaking experiments in 1.00 M HCl determined by XPS.

Figure 4.2: Compositional changes of Pd-BMG in 1.00 M HCl on P(V)-poor surface. Hatched column indicates Cu, light grey column indicates Ni, dark grey column indicates P(V), white column indicates P(0) and black column indicates Pd.

Figure 4.3: Compositional changes of Pd-BMG in 1.00 M HCl on P(V)-rich surface. Hatched column indicates Cu, light grey column indicates Ni, dark grey column indicates P(V), white column indicates P(0) and black column indicates Pd.
After being soaked for 14 days in 1.00 M HCl, regardless of whether the surface initially contained a small or large proportion of P(V)-type phosphorus, the Pd-BMG surface reached a surface composition of Pd_{65}Cu_{7}Ni_{2}P_{26} compared to the as-polished surface composition of Pd_{53}Cu_{21}Ni_{1}P_{25}. Cu was lost primarily during the immersion experiment on P(V)-rich and P(V)-poor surfaces.

According to the Pourbaix diagram\(^{68}\), Pd stays intact and Cu forms soluble CuCl\(_{2}\) in HCl solution at open circuit potential. The soluble CuCl\(_{2}\) then leaves the Pd-BMG surface and enters the HCl solution. This mechanism appears to be also active for this Pd-BMG. Regardless, the rate of Cu depletion is higher for the P(V)-poor surface, suggesting that P(V) plays a protective role in corrosion in 1.00 M HCl.

It has been reported that phosphorus can significantly increase the corrosion resistance of bulk metallic glasses by forming metal phosphates on the alloy surface.\(^{28,69}\) The metal phosphate serves as a passive film that inhibits the charge transfer between the alloy surface and solution which therefore reduces the corrosion rate.\(^{69}\) However, this mechanism fails to explain the corrosion behavior of Pd-BMG in 1.00 M HCl due to the absence of metal phosphate(s). As mentioned in Chapter 3, all metal constituents remained in their elemental state indicating the absence of any form of metal phosphate, thus, the oxidized phosphorus can only be assigned to a P\(_{2}\)O\(_{5}\)-like oxidized phosphorus. It should be noted that the form of the oxidized phosphorus cannot be the molecular compound P\(_{2}\)O\(_{5}\)/P\(_{4}\)O\(_{10}\) itself. The Pourbaix diagram for P\(^{68}\) suggests that P will form H\(_{3}\)PO\(_{4}\) under the...
conditions of pH = 0 and the measured corrosion potential in 1.00 M HCl. In other words, the concentration of P on Pd-BMG surface should decrease drastically in 1.00 M HCl. However, the P concentration remained constant (around 24%) in the 1.00 M HCl solution on both P(V)-rich and P(V)-poor surfaces.

![Figure 4.4: Relative compositional changes of P(0)/P(V) in 1.00 M HCl on P(V)-poor surface. White column indicates P(0), dark grey column indicates P(V).](image)

![Figure 4.5: Relative compositional changes of P(0)/P(V) in 1.00 M HCl on P(V)-rich surface. White column indicates P(0), dark grey column indicates P(V).](image)

Figures 4.4-4.5 include the relative compositional change of P(V) on both P(V)-poor and P(V)-rich surfaces. Whereas the total amount of P on the surface remained constant
approximately constant throughout the immersion experiments, the proportions of P(0) and P(V) changed remarkably. The proportion of oxidized phosphorus increased after 3-day soaking on the P(V)-poor surface and decreased rapidly thereafter, remaining approximately constant from 7 to 14 days. On the other hand, the amount of oxidized phosphorus decreased smoothly over the entire 14-day period on the P(V)-rich surface. The different behaviors of oxidized phosphorus of the two types of surfaces may be ascribed to different corrosion mechanisms.

On the P(V)-poor surface, one noteworthy aspect is the reproducible increase in P(V) over the first 3 days of immersion in 1.00 M HCl. Of course, this different behavior of oxidized phosphorus on P(V)-poor surface is likely tied up to different P(0):P(V) ratio on the two types of surfaces. It seems reasonable that when the P(V)-poor surface was immersed in the 1.00 M HCl solution, dissolved O₂ in the solution reacted with P(0) to form P(V). The reduction of P(V) to P(0) from 7-day to 14-day in 1.00 M HCl on the P(V)-poor surface might be rationalized by the unique atomic structure of the Pd-BMG (Figure 4.6). Guan and his co-workers have reported the existence of P-centered clusters that are covalently bonded to Pd in a Pd-Ni-P BMG.70 Hosokawa and his co-workers discovered a covalently bonded Pd-P-Pd structure in Pd₄₂.₅Ni₇.₅Cu₃₀P₂₀ BMG using an anomalous x-ray scattering (AXS) experiment.71 Additionally, it has been known that Pd can trigger the reduction of protons72 and alloying P to Pd can significantly increase hydrogen adsorption/absorption of Pd on an amorphous Pd-P alloy.73 Moreover, Shibata74
stated that H$_2$ can reduce the oxidized phosphorus on the amorphous Ni$_{81}$P$_{19}$ alloy, and Song$^{75}$ pointed out in his research on the synthesis of Ni$_2$P/MCM-41 catalysts that the H atoms dissociated from molecular hydrogen can reduce oxidized phosphorus to phosphorus or phosphine. Thus, it is reasonable to speculate that the covalent bond between Pd and P might have significant impact on the behavior of P in the 1.00 M HCl. It can be speculated that when the Pd-BMG surface was immersed in the 1.00 M HCl solution, the protons in the solution adsorb on the alloy surface, the absorbed H atoms or H$_2$ (recombination of absorbed H atoms) that diffuses into the Pd-P clusters and reacts with P(V) to reduce it to P(0).

![Diagram](image)

Figure 4.6: Illustration of proposed mechanism of the behavior of P on P(V)-poor surface in 1.00 M HCl. H$_{ad}$ is the adsorbed H atoms on the Pd-BMG surface.

On the P(V)-rich surface, when the P(V) to P(0) reduction is slow (7-14 day immersion), the loss of Cu is slow. On the other hand, the loss of Cu is more rapid when P(V) to P(0)
reduction is fast (3-day immersion). Hence, the oxidation of Cu and reduction of P in 1.00 M HCl could be tied together.

**Oxidation:**  \[ \text{Cu (s)} \rightarrow \text{Cu}^{2+} (\text{aq}) + 2 \text{e}^- \]

**Reduction:**  \[ \text{P}^{5+} (\text{s}) + 5 \text{e}^- \rightarrow \text{P} (\text{s}) \]

Over the initial 3 days on the P(V)-rich surface, the Cu component drops from 21% to 12%, providing electrons to reduce \((2/5) \times 9\%\) P(V) on the surface, or \(~4\%\) of the total surface atoms. In fact, the proportion of P(V) on the P(V)-rich surface drops from \(~56\%\) of the total P to \(~26\%\) of the total P; in other words about 30% of the total P is reduced in 3 days, amounting to about 7.5% of the total surface atoms. A similar calculation for 7-, 10- and 14-day immersion period yield similar result. In other words, the electrons generated from copper oxidation can only reduce approximately 50% of total P(V) to P(0) on P(V)-rich surface. The rest of P(V) is possibly reduced by absorbed H atoms or H\(_2\) as on P(V)-poor surface. Moreover, the oxidized phosphorus on P(V)-rich surface has reached a saturation level that retards, or at least slows the reaction between dissolved O\(_2\) and P(0). The proposed mechanism of P behavior on P(V)-rich is illustrated in Figure 4.7.
Figure 4.7: Illustration of proposed mechanism of the behavior of P on P(V)-rich surface in 1.00 M HCl. H_{ad} is the adsorbed H atoms on the Pd-BMG surface. Note that it is also plausible that the majority of P(V) is reduced by absorbed H atoms or H_{2}.

The unique covalent bonding between Pd and P might assist the reduction of P(V), and retard or inhibit the dissolution of P into HCl. The dissolution of Cu in 1.00 M HCl formed a Pd-dominated surface that inhibited further corrosion on Pd-BMG surface.

4.3 Corrosion of Pd-BMG in Hanks’ Solution

The corrosion resistance of Pd-BMG in Hanks’ solution (see Appendix A for composition) is slightly worse than that of stainless steel 316 and Ti-6Al-4V (Table 3.17). There was no distinct compositional or topological change under the examination of SEM-EDS demonstrating that the corrosion of Pd-BMG only occurred on the top 5-10 nm of the surface. Figure 4.8-4.9 summarize the compositional changes on Pd-BMG surfaces during the immersion experiments in Hanks’ solution determined by XPS. In many ways, the
compositional changes are similar to those observed in 1.00 HCl; loss of Cu and enrichment of Pd. However, a significant difference is that on both the P(V)-poor and P(V)-rich surfaces there was a significant decrease in the total P.

Figure 4.8: Compositional changes of Pd-BMG in Hanks’ solution on P(V)-poor surface. Hatched column indicates Cu, light grey column indicates Ni, dark grey column indicates P(V), white column indicates P(0) and black column indicates Pd.

Figure 4.9: Compositional changes of Pd-BMG in Hanks’ solution on P(V)-rich surface. Hatched column indicates Cu, light grey column indicates Ni, dark grey column indicates P(V), white column indicates P(0) and black column indicates Pd.
As indicated by the Pourbaix diagram\textsuperscript{68}, Pd is immune to corrosion and Cu dissolves in the form of Cu\textsuperscript{2+} in neutral solution under the corrosion potential in Hanks’ solution. Unlike in 1.00 M HCl, the P concentration dropped in Hanks’ solution on both P(V)-poor and P(V)-rich surfaces. Figures 4.10-4.11 show the relative compositional change of P(V) on both P(V)-poor and P(V)-free surfaces. It is notable that the decrease in total P in this solution is attributable almost entirely to loss of the P(V) type of P, rather than its conversion to P(0) possibly due to the low concentration of H\textsuperscript{+} in Hanks’ solution that limits the reduction of P(V) by H\textsubscript{2}. Moreover, the loss rate of P is higher in P(V)-rich surface during the 3-day immersion period. Consequently, it can be speculated that P(0) needs to be oxidized into P(V) in order to remove P from Pd-BMG surface. According to the Pourbaix diagram, P(0) is oxidized and dissolves in the form of P(V) in both neutral and acidic solutions. A high concentration of H\textsuperscript{+} in acidic solution facilitates the effective absorption of H atoms and/or the formation of H\textsubscript{2} on Pd-BMG surface that might reduce P(V) to P(0) rapidly and prevents the loss of P during the initial immersion period. The rapid loss of copper at the same time meant the Pd-BMG surface became Pd-dominated and remained inactive to corrosion afterwards. Since H atoms and/or H\textsubscript{2} cannot be effectively formed on the Pd-BMG in neutral solution, P is quickly oxidized to P(V) and leached out of Pd-BMG surface during the initial immersion period until the formation of a Pd-dominated surface.
Regardless of the initial fraction of P(V) presented on alloy surface, the Pd-BMG quickly formed a surface with Pd concentration around 84% by dissolution of P and Cu, the Pd-dominated surface inhibited further corrosion and demonstrated good corrosion resistance in Hanks’ solution (Table 3.17).
4.4 Corrosion of Pd-BMG in 1.00 M NaOH

The corrosion resistance of Pd-BMG in 1.00 M NaOH solution is worse than that of stainless steel 316 and Ti-6Al-4V (Table 3.22). Figures 4.12-4.13 summarize the compositional changes on the Pd-BMG surfaces during the immersion experiments in 1.00 M NaOH solution determined by XPS.

![Figure 4.12: Compositional changes of Pd-BMG in 1.00 M NaOH on P(V)-poor surface. Hatched column indicates Cu, light grey column indicates Ni, dark grey column indicates P(V), white column indicates P(0) and black column indicates Pd.](image1)

![Figure 4.13: Compositional changes of Pd-BMG in 1.00 M NaOH on P(V)-rich surface. Hatched column indicates Cu, light grey column indicates Ni, dark grey column indicates P(V), white column indicates P(0) and black column indicates Pd.](image2)
The corrosion behavior of Pd-BMG in NaOH differed significantly from 1.00 M HCl and Hanks’ solution. The amount of Pd, Cu and P decreased significantly after 3-day immersion in 1.00 M NaOH on both P(V)-poor and P(V)-rich surfaces. The amount of Cu and P were reduced to <5% of the total surface atoms and Pd concentration decreased from about 50% of the surface to about 30% of the surface. The remainder of the surface was dominated by Ni, mostly in the form of Ni(OH)₂.

The electrochemical measurements in N₂, O₂ and air-saturated solutions also revealed that as the concentration of oxygen present in the 1.00 M NaOH increased, the corrosion rate of Pd-BMG increased. This might be rationalized by the additional cathodic reduction of oxygen (O₂ +2H₂O+4e⁻ → 4OH⁻) accelerated the counter anodic dissolution since corrosion is not only determined by anodic dissolution. The Pourbaix diagram indicates that at pH=14 and open circuit potential in 1.00 M NaOH, Cu reacts with OH⁻ to form soluble CuO₂⁻. That might account for the loss of Cu in 1.00 M NaOH. The corrosion behavior of Pd in basic solution is uncertain according to Pourbaix. It is possible that Pd forms Pd(OH)₂ in basic solution that dissolves to give PdO₂²⁻ (palladites). The solubility of Pd(OH)₂ depends highly on its degree of hydration, however, no substantial research has been conducted on it. In addition, it has been reported by Wood that the dissolution of Pd occurred in NaOH solution. With the dissolution of Pd, the covalent bond between Pd and P will be damaged and P can be leached out of the alloy surface in the form of soluble ions. With the dissolution of Cu, P and Pd, Ni was exposed to the 1.00 M NaOH solution and quickly formed Ni(OH)₂. The Ni(OH)₂
presented on the alloy surface served as a partially-protective film that prohibited further reaction (Table 3.22). Similarly, Pd$_{79}$Ag$_{3.5}$Si$_{9.5}$P$_6$Ge$_2$ BMG showed a higher corrosion rate in 1.00 M NaOH than in 1.00 M HCl by electrochemical measurements. It might be worthwhile carrying out surface studies of Pd$_{79}$Ag$_{3.5}$Si$_{9.5}$P$_6$Ge$_2$ BMG in 1.00 M NaOH to understand the corrosion mechanism of Pd-based P-containing BMG in basic media.

4.5 Anodic dealloying of Pd-BMG in 1.00 M HCl

A porous black film was formed after anodic polarization of Pd-BMG in 1.00 M HCl. The XPS and EDS data showed different compositions of the black film (Figure 4.14).

![Figure 4.14: Compositional changes of as-polished Pd-BMG after anodic polarization in 1.00 M HCl by XPS and EDS. Hatched column indicates Cu, light grey column indicates Ni, dark grey column indicates P(V), white column indicates P(0), black column indicates Pd, and vertical hatched column indicates Cl.](image)

The Cu concentration decreased after anodic polarization with XPS and EDS measurements. Nonetheless, the concentration of Cu determined by XPS was higher than that
determined by EDS. P remained unchanged after anodic polarization by XPS determination, but dropped as determined by EDS measurement. Consequently, a more Pd-dominated black film was obtained by EDS measurement. Based on the fact that XPS is more surface-sensitive than EDS, the difference between XPS and EDS-determined black film surface composition might be rationalized by the redeposition of Cu and P on the topmost surface. A possible structure of the black film is illustrated in Figure 4.15. The cyclic voltammogram also indicated the possibility of redeposition of Cu on the topmost surface.

![Redeposition of Cu and P](image.png)

Figure 4.15: Illustration of the structure of the black film. *Choline is excluded.

![Composition changes](image.png)

Figure 4.16: Compositional changes of as-polished Pd-BMG after removal of black film by XPS and EDS. Hatched column indicates Cu, light grey column indicates Ni, dark grey column indicates P(V), white column indicates P(0) and black column indicates Pd.
The presence of Cl⁻ is known to facilitate the dissolution of Pd in HCl solution by complexing.⁷⁶ The UV-vis spectra of the yellow solution that resulted from anodic polarization in 1.00 M HCl also suggested the presence of Pd complexes based on the comparison to Xiong’s⁵⁸ work. After removing the black film, EDS measurement showed a composition similar to the as-polished counterpart, however, XPS data showed a composition similar to the black film counterpart (Figure 4.16). The porous film formed after anodic polarization in 1.00 M HCl was not firmly attached on the alloy surface. The removal of the black film resulted in a rough surface without any presence of pits. Hence, the black film might also resist the initiation of pits by forming a Pd-dominated surface. Dealloying experiments conducted on Pd-BMG in 1.00 M H₂SO₄ solution yielded a similar behavior. In addition, the porous black film formed by selective dealloying of Cu on Pd-BMG surface might be categorized as a nano-porous surface that possesses potential catalytic property.⁷⁸

The presence of a current plateau of Pd-BMG (Figure 3.26) in the anodic polarization curve in 1.00 M HCl might be the result of the occurrence of reduction of P(V) (either formed during air exposure or electrochemically formed) to P(0) on the sample surface consuming electrons generated from the oxidation of Cu and/or Pd during the anodic polarization. Moreover, the more prominent current plateau of P(V)-rich surface shown in Figure 3.28 indicates that the presence oxidized phosphorus serves as a passive or protective film in 1.00 M HCl solution.
Chapter 5

Conclusion

1. Surface segregation occurs on Pd-BMG surface creating a Pd, P-enriched, Cu-depleted and Ni-absent near surface composition. P is partially oxidized to a $\text{P}_2\text{O}_5$-like species, while all the other elements remain unoxidized. The phenomenon can be explained by simple thermodynamic arguments. Future studies using more surface sensitive technique are necessary to fully understand the nature of surface segregation on Pd-BMG surface.

2. Pd-BMG possesses higher corrosion resistance in 1.00 M HCl solutions than the commercially available stainless steel 316 and Ti-6Al-4V, but slightly worse corrosion resistance in Hanks’ solution and 1.00 M NaOH solution. A speculative reason for the corrosion resistance in 1.00 M HCl is the stability of the Pd and P to oxidation at this pH while, at high pH, Cu, Pd and P are effectively dissolved.

3. In order to leach P out of Pd-BMG surface, P needs to be oxidized to P(V) first. pH can dictate the dissolution of phosphorus. In the acidic solution, the presence of $\text{H}^+$ and the special local atomic structure of Pd-BMG might assist the reduction of P(V) to P(0) by H$_2$ that prevents overall loss of P. The low concentration of $\text{H}^+$ present in the neutral solution disables the reduction of P(V) and leads to the loss of P. In basic solution, the loss of Pd might damage the special binding between Pd and P that accelerates the loss of P. It is worthwhile to carry out more experiments to develop a detailed corrosion mechanism of Pd-BMG in basic solution in the future.
4. Corrosion in all three corrosive media falls into one pattern, that is, the corrosion mechanism consists of two stages. The first stage is the initiation stage, in which quick dissolution of the electrochemically active component, Cu, or Cu & P, occurs. In the second stage, the formation of a stable surface, either Pd-dominated or Ni(OH)$_2$-dominated, slows or prohibits the further corrosion.

5. Oxidized phosphorus presented on the Pd-BMG can serve as a protective film in acidic solution.

6. The presence of the Cl$^-$ can facilitate the dissolution of Cu and Pd, as indicated by Cu and Pd complexes in the electrolyte medium, in 1.00 M HCl creating a nano-porous structure that might hold potential catalytic properties. In-depth studies in the future are required to obtain a more comprehensive understanding of the dealloying behavior of Pd-BMG in HCl solution.
References:


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Appendix A

Composition of Hanks’ Solution

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl$_2$.2H$_2$O</td>
<td>-</td>
</tr>
<tr>
<td>MgSO$_4$ (anhyd)</td>
<td>-</td>
</tr>
<tr>
<td>KCl</td>
<td>0.4</td>
</tr>
<tr>
<td>KH$_2$PO$_4$ (anhyd)</td>
<td>0.06</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>0.35</td>
</tr>
<tr>
<td>NaCl</td>
<td>8.0</td>
</tr>
<tr>
<td>Na$_2$HPO$_4$ (anhydrous)</td>
<td>0.04788</td>
</tr>
<tr>
<td>D-Glucose</td>
<td>1.0</td>
</tr>
<tr>
<td>Phenol Red∙Na</td>
<td>-</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>-</td>
</tr>
</tbody>
</table>

Table A.1: Composition of Hanks’ solution (Aldrich-Sigma).
Appendix B

Photographs of as-polished Pd-BMG and the yellow solution resulted after anodic polarization

Figure B.1: Photograph of as-polished Pd-BMG.
Figure B.2: Photograph of the yellow solution resulted after anodic polarization.
Appendix C

Determination of Pd_{43}Cu_{27}Ni_{10}P_{20} Equivalence Weight

The equivalence weight of an alloy can be determined by using the equation as follows:  
\[
EW = \frac{100}{Q}, \text{where } Q = \sum n_i \cdot f_i / W_i
\]

where \( n_i \) is the valence of the \( i^{th} \) element of the alloy, \( f_i \) is the mass fraction of the \( i^{th} \) element of the alloy, and \( W_i \) is the atomic weight of the \( i^{th} \) element of the alloy. The valence state of each element in the alloy can be retrieved from the Pourbaix diagrams.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Weight (g/mol)</th>
<th>Mass Fraction (%)</th>
<th>Valence ( (1.00 \text{ M HCl}) )</th>
<th>Valence ( (\text{Hanks' Solution}) )</th>
<th>Valence ( (1.00 \text{ M NaOH}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>106.4</td>
<td>65</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Cu</td>
<td>63.55</td>
<td>19</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Ni</td>
<td>58.69</td>
<td>8</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>P</td>
<td>30.97</td>
<td>8</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

Table C.1: Valence states of alloying components of Pd_{43}Cu_{27}Ni_{10}P_{20} BMG in different media (obtained from Figures C.1-C.4)

Using the valence states obtained from the Pourbaix diagrams:

\[
Q = \frac{65}{106.4} \cdot 0 + \frac{19}{63.55} \cdot 2 + \frac{8}{58.69} \cdot 2 + \frac{8}{30.97} \cdot 5 = 2.2
\]

\[\therefore EW = \frac{100}{2.2} = 45 \text{ g equivalents in 1.00 M HCl and Hanks' solution}\]

\[
Q = \frac{65}{106.4} \cdot 2 + \frac{19}{63.55} \cdot 2 + \frac{8}{58.69} \cdot 2 + \frac{8}{30.97} \cdot 5 = 3.4
\]

\[\therefore EW = \frac{100}{3.4} = 30 \text{ g equivalents in 1.00 M NaOH solution}\]
Figure C.1: Potential-pH equilibrium diagram (Pourbaix diagram) for copper-water system at 25°C. 68
Figure C.2: Potential-pH equilibrium diagram (Pourbaix diagram) for nickel-water system at 25°C. \(^\text{68}\)
Figure C.3: Potential-pH equilibrium diagram (Pourbaix diagram) for phosphorus-water system at 25°C.\textsuperscript{68}
Figure C.4: Potential-pH equilibrium diagram (Pourbaix diagram) for palladium-water system at 25° C.68
Appendix D

Deduction of Tafel Equation

Bulter-Volmer equation provides a relationship between the potential and current density. The electrochemical reaction can be generalized as:\(^{38}\)

\[ O + n e \overset{\text{Vol}}{\underset{\text{B}} \rightarrow} R \quad (D.1) \]

where \( O \) is the dissolved oxidized species, \( R \) is the reduced form of \( O \), \( v_a \) and \( v_c \) are the rates of anodic (oxidation) and cathodic (reduction) reactions respectively.

According to Faraday’s law, the current density at the electrode, \( i \), is proportional to the rate of reaction, \( v \). With charge \( n = 1 \), the relationship below can be obtained: \(^{80}\)

\[ i = F \cdot v = F \cdot (v_a - v_c) \quad (D.2) \]

where \( F \) is the Faraday’s constant. The rate \( v_a \) and \( v_c \) are proportional to the concentrations of \( O \) and \( R \) at the electrode surface respectively, and they obey Arrhenius’ law. \(^{80}\)

\[ v_a = k_a \cdot C_{O,s} \cdot \exp\left(-\frac{\Delta G_a^\#}{RT}\right) \quad (D.3) \]

\[ v_c = k_c \cdot C_{R,s} \cdot \exp\left(-\frac{\Delta G_c^\#}{RT}\right) \quad (D.4) \]

where \( k_a \) and \( k_c \) are constants, \( C_{O,s} \) and \( C_{R,s} \) are the concentrations of \( O \) and \( R \) at electrode surface, \( \Delta G_a^\# \) and \( \Delta G_c^\# \) are the Gibbs energies of activation of anodic and cathodic partial reactions. According to transition state theory: \(^{80}\)

\[ k_a = k_c = \nu \cdot \frac{k \cdot T}{h} \quad (D.5) \]
where $v$ refers to the statistical frequency factor ($0 < v < 1$), $k$ is the Boltzmann constant and $h$ is the Planck’s constant. For an electrochemical reaction, the Gibbs energy of activation depends on the potential difference $\Delta \Phi$. If the equilibrium potential (open circuit potential), $E_0$, is changed by $\Delta \Phi$ to a new value, $E$, the relative energy of the electrons on the electrode changes by $F \cdot \Delta \Phi$. Thus,$^{38}$

\[
\Delta G^a_\# = \Delta G^a_{\#0} - \alpha \cdot F \cdot \Delta \Phi \quad (D. 6)
\]

\[
\Delta G^c_\# = \Delta G^c_{\#0} + (1 - \alpha) \cdot F \cdot \Delta \Phi \quad (D. 7)
\]

where and $\Delta G^a_{\#0}$, $\Delta G^c_{\#0}$ are Gibbs energies of activation of anodic and cathodic partial reactions at $E_0$, $\alpha$ refers the charge transfer coefficient ($0 < \alpha < 1$).

By grouping all the potential independent terms into the constants $k_a'$ and $k_c'$, and substituting them into equation $(D.2)$ and $(D.3-4)$, equation $(D.8)$ can be obtained.$^{80}$

\[
v = k_a' \cdot C_{O,S} \cdot \exp\left(\frac{\alpha \cdot F}{R \cdot T} \cdot \Delta \Phi\right) - k_c' \cdot C_{R,S} \cdot \exp\left(-\frac{(1 - \alpha) \cdot F}{R \cdot T} \cdot \Delta \Phi\right) \quad (D. 8)
\]

where $k_a' = k_a \cdot \exp\left(-\frac{\Delta G^a_{\#0}}{R \cdot T}\right)$ and $k_c' = k_c \cdot \exp\left(-\frac{\Delta G^c_{\#0}}{R \cdot T}\right)$. The potential of the working electrode, $E$, is measured with respect to a reference electrode, thus$^{80}$

\[
E = \Delta \Phi + \text{Constnat} \quad (D. 9)
\]

By introducing $(D.9)$ into $(D.8)$, and group all the constant terms into $k_a$ and $k_c$, the equation $(D.10)$ can be obtained:$^{80}$

\[
v = k_a \cdot C_{O,S} \cdot \exp\left(\frac{\alpha \cdot F}{R \cdot T} \cdot E\right) - k_c \cdot C_{R,S} \cdot \exp\left(-\frac{(1 - \alpha) \cdot F}{R \cdot T} \cdot E\right) \quad (D. 10)
\]
The values of $k_a$ and $k_c$ vary as a function of the reference electrode selected. The current density, $i$, is the sum of the partial anodic density $i_a$ and the partial cathodic current density $i_c$:

$$i = i_a + i_c \quad (D.11)$$

By combining equation (D.2), (D.10) and (D.11), one form of Butler-Volmer equation for a given electrode reaction with charge $n=1$ can be obtained:

$$i = F \cdot \left[ k_a \cdot C_{O,S} \cdot \exp \left( \frac{\alpha \cdot F}{R \cdot T} \cdot E \right) - k_c \cdot C_{R,S} \cdot \exp \left( -\frac{(1 - \alpha) \cdot F}{R \cdot T} \cdot E \right) \right] \quad (D.12)$$

Analogous reasoning can be applied to obtain the electrode reaction with charge $n$,

$$i = n \cdot F \cdot \left[ k_a \cdot C_{O,S} \cdot \exp \left( \frac{\alpha \cdot n \cdot F}{R \cdot T} \cdot E \right) - k_c \cdot C_{R,S} \cdot \exp \left( -\frac{(1 - \alpha) \cdot n \cdot F}{R \cdot T} \cdot E \right) \right] \quad (D.13)$$

At equilibrium (open circuit potential, $E_0$), the net current is zero but the charger transfer still undergoes. As a result, at zero current:

$$i_a = -i_c = i_0 \quad (D.14)$$

where $i_0$ is defined as exchange current density of an electrode reaction that represents the rate of charge transfer at equilibrium. Under equilibrium circumstances, the concentrations of species $O$ and $R$ in the bulk solution (subscript b) and on the electrode surface are the same as shown in equation (D.15), (D.16).

$$C_{O,S} = C_{O,b} \quad (D.15)$$

$$C_{R,S} = C_{R,b} \quad (D.16)$$

By combining equation (D.13) to (D.16), equation (D.17) can be obtained.
\[ i_0 = n \cdot F \cdot k_a \cdot C_{O,b} \cdot \exp\left(\frac{\alpha \cdot n \cdot F}{R \cdot T} \cdot E_0\right) \]
\[ = n \cdot F \cdot k_c \cdot C_{R,b} \cdot \exp\left(-\frac{(1 - \alpha) \cdot n \cdot F}{R \cdot T} \cdot E_0\right) \quad \text{(D.17)} \]

Dividing \((D.13)\) by \((D.17)\) yields another form of Butler-Volmer equation:

\[ i = i_0 \cdot \frac{C_{O,s}}{C_{O,b}} \cdot \exp\left(\frac{\alpha \cdot n \cdot F}{R \cdot T} \cdot (E - E_0)\right) - i_0 \cdot \frac{C_{R,s}}{C_{R,b}} \cdot \exp\left(-\frac{(1 - \alpha) \cdot n \cdot F}{R \cdot T} \cdot (E - E_0)\right) \quad \text{(D.18)} \]

If overpotential \((\eta = E - E_0)\) is large (either negative or positive), one of the exponential term in equation \((D.18)\) becomes negligible. At large positive potential \(\exp\left(\frac{\alpha \cdot n \cdot F}{R \cdot T} \cdot \eta\right) \gg \exp\left(-\frac{(1 - \alpha) \cdot n \cdot F}{R \cdot T} \cdot \eta\right)\) and equation \((D.18)\) becomes:

\[ i = i_a = i_0 \cdot \frac{C_{O,s}}{C_{O,b}} \cdot \exp\left(\frac{\alpha \cdot n \cdot F}{R \cdot T} \cdot \eta\right) \quad \text{(D.19)} \]

By assuming species \(O\) and \(R\) concentrations at equilibrium are uniform in the bulk solution \((C_{O,s} = C_{O,b} \text{ and } C_{R,s} = C_{R,b})\), equation \((D.19)\) becomes:

\[ i = i_a = i_0 \cdot \exp\left(\frac{\alpha \cdot n \cdot F}{R \cdot T} \cdot \eta\right) \quad \text{(D.20)} \]

By further defining anodic Tafel coefficient \(\beta_a = \frac{R \cdot T}{\alpha \cdot n \cdot F}\) and cathodic Tafel coefficient \(\beta_c = \frac{R \cdot T}{(1 - \alpha) \cdot n \cdot F}\), the equation \((D.20)\) becomes:

\[ i = i_a = i_0 \cdot \exp\left(\frac{\eta}{\beta_a}\right) \quad \text{(D.21)} \]

Similarly, at large negative potential:

\[ i = i_c = -i_0 \cdot \exp\left(-\frac{\eta}{\beta_c}\right) \quad \text{(D.22)} \]

Combination of equation \((D.21)\) and \((D.22)\) yields most common form of Bulter-Volmer equation:

\[ i = i_0 \cdot \exp\left(\frac{\eta}{\beta_a}\right) - i_0 \cdot \exp\left(-\frac{\eta}{\beta_c}\right) \quad \text{(D.23)} \]
By taking the logarithm of both ends of equation \((D.21)\) yields: 

\[
\eta = a_a + b_a \cdot \log i \quad (D.24)
\]

where \(a_a = -2.303 \cdot \beta_a \cdot \log i\) and \(b_a = 2.303 \cdot \beta_a\) are anodic Tafel constants.

In analogous manner, equation \((D.22)\) can be transformed into:

\[
\eta = a_c - b_c \cdot \log|i| \quad (D.25)
\]

where \(a_c = 2.303 \cdot \beta_c \cdot \log i\) and \(b_c = 2.303 \cdot \beta_c\) are anodic Tafel constants.

The generalization of equation \((D.24)\) and \((D.25)\) produces the Tafel equation appears in Chapter 2.

\[
\eta = a + b \cdot \log i
\]

Equation \((D.24)\) and \((D.25)\) are the Tafel equations that describe the anodic and cathodic limits of the Bulter-Volmer equation. The slopes of the extrapolated lines are the Tafel constants, and the reciprocal of them yields the Tafel coefficients \(\beta_a\) and \(\beta_c\). The Tafel constants account for the charge transfer and number of electrons involved in the electrochemical reactions, and can be used to calculate the polarization resistance.
Appendix E

Auger Spectra of Copper (LMM)

Figure E.1: Cu (LLM) Auger peaks of P(V)-poor surface before (bottom) and after sputtering (top). The binding energies of the major peak of the control and after-sputtering sample are at 567.37 eV and 567.36 eV respectively. Note that there is no binding energy shift of Cu (LLM) Auger peak prior to and after sputtering on the P(V)-poor surface indicating Cu exists in its elemental state.
Figure E.2: Cu (LLM) Auger peaks of P(V)-rich surface before (bottom) and after sputtering (top). The binding energies of the major peak of the control and after-sputtering sample are at 567.46 eV and 567.39 eV respectively. Note that there is no distinct binding energy shift of Cu (LLM) Auger peak prior to and after sputtering on the P(V)-rich surface indicating Cu exists in its elemental state.