

## SURFACE OXIDATION OF Al-Pd-Mn AND Al-Cu-Fe ALLOYS

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The application of ultrahigh vacuum surface analytical techniques to the study of the oxidation of Al-Pd-Mn and Al-Cu-Fe quasicrystals is presented. Comparisons of the effects of various oxidation environments are made for each material as well as for a cubic phase of Al-Pd-Mn. We find that the oxidation of the two icosahedral alloys is similar. Exposure to oxygen in vacuum, normal air, humid air and immersion in water represent progressively better oxidizing environments, resulting in increasingly deeper oxides. Oxidation of Al occurs most readily, but oxidation of other metals also becomes apparent upon going from oxygen in vacuum to immersion in water; which also attests to the effectiveness of water as an oxidant. Oxide thicknesses for both quasicrystalline alloys are comparable for each oxidation environment. Comparison of quasicrystalline to cubic Al-Pd-Mn shows that the cubic phase is more readily oxidized. In addition, while the surfaces of both quasicrystalline alloys become significantly enriched in Al upon oxidation, such enrichment is not observed for the cubic alloy. This suggests that the structure of quasicrystals plays an important role in their oxidation chemistry.

### 1 Introduction

Potential applications of quasicrystals typically involve their use as surface coatings to exploit properties including their low coefficients of friction, high hardness and low thermal conductivity.<sup>1-6</sup> As such, the surface and interface properties of these materials are extremely important. The use of ultrahigh vacuum (UHV) surface analytical techniques enables one to probe the first few atomic layers of the surface thereby aiding elucidation of structural as well as chemical information about the clean surface. In addition, the effects of various environments such as under atmospheric conditions can be studied on a submonolayer scale with appropriate sample transfer mechanisms. In previous and ongoing work, we examine the structure of the clean surfaces of single grains of icosahedral Al-Pd-Mn oriented perpendicular to the 5-fold and 2-fold axis.<sup>7-11</sup> These studies provide fundamental information about the structure of quasicrystals at the surface and serve as a baseline for understanding the effects of conditions used in industrial applications. Typical environments to which these coatings will be exposed include air and water. In this paper, we examine the effect of oxygen and water on the oxidation of quasicrystalline materials. Specifically, we summarize

and compare recent results for the surfaces of quasicrystalline and cubic Al-Pd-Mn to those for the more industrially viable alloy, quasicrystalline Al-Cu-Fe.

## 2 Experimental

The X-ray photoelectron spectroscopy (XPS) experiments presented here are performed using a Physical Electronics Multitechnique Chamber, Model 5500. This chamber has a base pressure of  $3 \times 10^{-10}$  Torr. Al K $\alpha$  radiation is used to provide monochromatized 250 W X-rays. Binding energies are calibrated using the 4f<sub>7/2</sub> photoelectrons at 84.0 eV for Au and the 2p<sub>3/2</sub> photoelectrons at 932.7 eV for Cu. In this chamber the samples are mounted directly onto a Mo block. This chamber includes sample transfer facilities that allow for rapid introduction of samples from atmosphere into the UHV chamber without breaking vacuum.

Low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) results were gathered in a UHV chamber with a base pressure of  $3 \times 10^{-11}$  Torr. The sample in this chamber is mounted between two Ta plates.

The sample temperature in both chambers is determined using a thermocouple spotwelded to the mount. In the XPS chamber, the sample is heated radiatively with a filament while in the LEED chamber it is heated resistively. Both chambers are equipped with argon ion bombardment capabilities for sample cleaning.

The single grains of quasicrystalline Al-Pd-Mn were grown by T. Lograsso and D. Delaney at the Materials Preparation Center at Ames Laboratory using the Bridgman Method.<sup>12, 13</sup> The sample was oriented with the 5-fold axis perpendicular to the surface. Additional details about Al-Pd-Mn growth and surface preparation for UHV studies are discussed elsewhere.<sup>8</sup>

Because of the difficulty of producing large single phase, single grains of Al-Cu-Fe, we use quasicrystalline powders that are hot isostatically pressed (HIPed) prior to analysis. The HIPing process involves taking the powders, prepared by gas atomization, sealing them in an evacuated stainless steel can and then exposing them to a temperature of 825 °C and an argon pressure of 45,000 psi. HIPing of the quasicrystalline powders yields solid ingots that can be treated and cleaned in vacuum just as the Al-Pd-Mn single-grain is treated. After polishing, analysis by scanning Auger microscopy shows that the surfaces of HIPed powders include both the  $\Psi$  phase, Al<sub>64</sub>Cu<sub>23</sub>Fe<sub>13</sub>, and 6% of a second phase,  $\lambda$ , of composition

$\text{Al}_{71}\text{Cu}_6\text{Fe}_{23}$ . We find that HIPing helps to overcome difficulties encountered while sputtering and annealing the powders and improves our ability to clean the surface.<sup>14</sup>

For both samples, four different oxidizing environments are used. The first we call "exposure in vacuum". For these oxidation studies we first clean and anneal the sample at 600 °C in vacuum and then expose the surface to oxygen (Physical Electronics, 99.9985%) using a dosing tube. We estimate the exposure to be great than 80 Langmuirs.<sup>15</sup> The second environment, we call "oxidation in normal air". Here we either prepare the surface by polishing or cleaning in UHV and then exposing either to room air or storing the sample in a dessicator with  $\text{CaCO}_3$  for 2 - 16 hours. The results, regardless of the exact treatment, are similar and thus we do not distinguish between the treatments. The third environment we call "oxidation in humid air". To perform these experiments, we first clean in UHV and then, for 2 - 16 hours, suspend the sample in air above a beaker containing distilled water. The final environment is termed "immersion in water" and involves cleaning the sample in UHV and then immersing the sample in distilled water.

Oxide thicknesses for the quasicrystalline alloys are calculated using the attenuation method developed by B. Strohmeier.<sup>16</sup> In this method, the oxide thickness is determined by comparing the relative intensities of the metallic and oxidic Al 2p peaks and assuming that the oxide, solely, attenuates the metallic Al signal. An emission angle of 80° is used for the thickest oxides because of the larger probe depth.

### 3.1 Oxidation of Quasicrystalline Al-Pd-Mn<sup>7, 15, 17, 18</sup>

For the clean Al-Pd-Mn surface, no evidence of oxygen or oxide is evident on the surface to within the detection limits of the XPS apparatus (nominally 0.1%). We find by XPS that the clean surface composition is  $\text{Al}_{69}\text{Pd}_{23}\text{Mn}_8$ . This is close to the average quasicrystalline bulk composition of  $\text{Al}_{71}\text{Pd}_{20}\text{Mn}_9$  determined by inductively coupled plasma mass spectrometry (ICP-MS). Oxidation of Al-Pd-Mn in vacuum results in oxidation of Al only. No evidence for the oxidation of either Pd nor Mn is observed in vacuum at saturation. Upon exposure of a clean sample to normal air, we find evidence for additional Al oxidation. The thickness of the oxide in this environment is about 26 Å. Again, no indication of Pd oxidation is found. However, upon exposure to air, evidence of oxidation of Mn is found. Chevrier *et al.* find the thickness of the oxide on the quasicrystal upon exposure to air to be thin and comparable to that for pure Al,<sup>19</sup> consistent with previous results from our laboratory.<sup>17</sup> After

exposure to humid air the presence of oxidized Mn is quite pronounced. It is not readily apparent that Pd is oxidized in this environment. Only upon immersion in water does oxidation of Pd become obvious.

Table 1 summarizes results for the oxidation of Al-Pd-Mn. Two major trends are clear: (1) As the oxide thickness increases, the atomic concentration of Al at the surface increases; and (2) as the amount of water in the oxidation environment increases, so does the thickness of the oxide. This suggests that water is a better oxidant than is O<sub>2</sub>. X-ray reflectivity measurements show the same trends and comparable oxide thicknesses.<sup>20</sup> An increase in the oxide thickness as a function of humidity has also been observed for Al.<sup>16, 21-25</sup> It should be noted that atmospheric gases other than O<sub>2</sub> and water could contribute to the oxidation processes of the quasicrystalline alloys as they do for pure Al and Fe.<sup>26, 27</sup>

It should also be noted that for the Strohmeier method a homogeneous layer of pure aluminum oxide is assumed. Importantly, the fact that both Pd and Mn can be oxidized (under some circumstances) shows that the surface does not always conform to this assumption. However, even at the lowest oxide thickness Al accounts for 74 atomic % (at %) of the metallic elements while for the thickest oxide Al accounts for 94 at %, so this assumption is reasonable.

Table 1: XPS results for the oxidation at room temperature of quasicrystalline Al-Pd-Mn. All results are collected at an emission angle of 45° with the exception of the immersion water data, which is collected at an emission angle of 80°.

Preparation Conditions	Al (at %)	Pd (at %)	Mn (at %)	Oxide (Å)
Clean in UHV	69	23	8	n/a
Saturation with oxygen in vacuum	74	20	6	6
Oxidation in normal air	84	13	3	26
Oxidation in humid air	92	6	2	62
Immersion in water	94	4	2	106

### 3.2 Oxidation of Cubic Al-Pd-Mn

We also studied a cubic phase of Al-Pd-Mn with a composition close to that of the icosahedral phase. The cubic sample we examined is a single crystal with surface composition of Al<sub>56</sub>Pd<sub>33</sub>Mn<sub>11</sub> after cleaning and annealing. This is compared to the icosahedral phase of composition Al<sub>69</sub>Pd<sub>23</sub>Mn<sub>8</sub>.

Table 2 shows results of oxidation studies of the cubic sample. Note that significant enrichment of Al at the surface is not observed as the oxidation environment is changed. Based on XPS results, saturation of the surface with oxygen in vacuum leads to not only Al oxidation but also some Mn oxidation. In this respect, the cubic phase oxidizes more readily than the icosahedral phase. XPS after oxidation in normal air shows that the surface contains 69 at % Al, 21 at % Pd, and 10 at % Mn. This is in contrast to the icosahedral phase which shows a surface composition of  $\text{Al}_{84}\text{Pd}_{13}\text{Mn}_3$  after oxidation in normal air. In addition, we find that the Mn at the surface of the cubic phase is almost completely oxidized, much of the Pd is also oxidized, and, relatively speaking, more of the Al at the surface is oxidized compared to the icosahedral phase. After immersion in water, the Al, Pd and Mn at the surface are almost completely oxidized. Because of the significant amount of Pd at the surface for all of the oxidizing environments studied, the assumption of a homogeneous oxide layer at the surface clearly breaks down. Thus, using the attenuation method of Strohmeier is not valid for the cubic alloy oxidation studies. Because of this, the oxide thicknesses are not tabulated in Table 2.

Table 2: XPS results for the oxidation at room temperature of cubic Al-Pd-Mn. All results are collected at an emission angle of  $45^\circ$ . Oxide thicknesses are not provided because of a breakdown in the assumptions for the Strohmeier method of calculating oxide thicknesses.<sup>18</sup>

Preparation Conditions	Al (at %)	Pd (at %)	Mn (at %)
Clean in UHV	56	33	11
Saturation with oxygen in vacuum	57	33	10
Oxidation in normal air	69	21	10
Immersion in water	61	30	9

### 3.3 Oxidation of Al-Cu-Fe<sup>14</sup>

The HIPed Al-Cu-Fe sample used has a bulk composition of  $\text{Al}_{65}\text{Cu}_{23}\text{Fe}_{12}$  as determined by ICP-MS. Oxidation of the HIPed sample in vacuum results in oxidation of Al only; we find no evidence for the oxidation of either Cu or Fe. Likewise, oxidation in air results only in oxidation of Al, although the extent of Al oxidation increases. The same cannot be said upon oxidation in humid air. While XPS shows additional oxidation of the Al relative to that for oxidation in air, oxidation of Cu is

evident also. Because of the low signal to noise, it is unclear if the Fe also oxidizes. Table 3 summarizes the thickness of the oxide as a function of preparation conditions along with the atomic percentages of the elements. As one can see from this table, the oxide thickness increases as a function of humidity. Kang *et al.* have studied oxidation in a dry atmosphere of Al-Cu-Fe powders and also find a relatively thin oxide layer, about 30 Å.<sup>28</sup> In addition they also determined that diffusion of oxygen into the bulk of the powders can occur; this has not been observed for other Al-based alloys.<sup>28</sup>

Table 3: XPS results for the oxidation at room temperature of HIPed quasicrystalline Al-Cu-Fe powders. All results are collected at an emission angle of 45° with the exception of the immersion in water data which is collected at an emission angle of 80°.

Preparation Conditions	Al (at %)	Cu (at %)	Fe (at %)	Oxide (Å)
Clean in UHV	58	30	12	n/a
Saturation with oxygen in vacuum	61	27	12	13
Oxidation in normal air	78	13	9	25
Oxidation in humid air	92	7	1	60
Immersion in water	97	2	1	75

### 3.4 Comparison of Oxidation of Al-Pd-Mn to Al-Cu-Fe

The oxidation of Al-Cu-Fe and Al-Pd-Mn icosahedral alloys is very similar. In both cases, the only metal which oxidizes in vacuum, at room temperature, is Al. The passivating oxide layer is very thin, 6-13 Å. Formation of this layer is accompanied by enrichment in the surface Al content. Our results suggest that an almost pure layer of aluminum oxide forms in both cases.

Normal air, humid air, and liquid water are progressively better oxidants, in that they produce increasingly deeper oxides, and oxidize metals other than Al. However, these trends are accompanied by progressively higher levels of Al enrichment at the surface, suggesting that the oxide layer at the quasicrystal surface, under typical atmospheric conditions, is still primarily aluminum oxide. The same cannot be said of the cubic phase of Al-Pd-Mn for which significant enrichment of Al at the surface is not observed. The surface composition of icosahedral Al-Pd-Mn goes from Al<sub>69</sub>Pd<sub>23</sub>Mn<sub>8</sub> to Al<sub>94</sub>Pd<sub>4</sub>Mn<sub>2</sub> upon immersion in water, whereas, the surface composition of cubic Al-Pd-Mn goes from Al<sub>56</sub>Pd<sub>33</sub>Mn<sub>11</sub> to Al<sub>61</sub>Pd<sub>30</sub>Mn<sub>9</sub>.

## 4 Conclusions

The similarities between the two quasicrystalline alloys suggest that the oxidation chemistry of one may be used to predict the oxidation chemistry of the other. However, related crystalline alloys can behave much differently as shown by comparing the icosahedral phase of Al-Pd-Mn to a cubic phase of similar composition. We find that the cubic phase more readily oxidizes than the quasicrystalline alloy and forms an oxide layer dissimilar in composition to that of icosahedral Al-Pd-Mn. Our findings suggest that the structure of these alloy materials may play an important role in determining their physical properties.

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