

# Comments on quasicrystals and their potential use as catalysts

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## Abstract

Recent findings suggest that quasicrystalline materials may make better catalysts than their crystalline counterparts. On the other hand, detailed surface science studies suggest that the surfaces of Al-based quasicrystals behave as if they are chemically similar to pure Al. In this paper, we discuss these results along with the unique thermodynamic and electronic properties of quasicrystals which could affect their catalytic nature. © 1998 Elsevier Science B.V.

*Keywords:* Quasicrystals; Catalyst; Penrose tiling model

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Quasicrystals were first reported in 1984 by Shechtman et al. [1]. They are materials from which diffraction patterns can be obtained, but the rotational symmetries of the diffraction patterns are ones previously thought to be forbidden (e.g., 5-fold and 10-fold symmetries) [2]. The existence of diffraction patterns demonstrates the presence of long range order, but the forbidden symmetries suggest something unusual. Their discovery led to a flurry of research activity from which it was determined that rather than having a periodic arrangement of atoms as expected in crystalline materials, quasicrystals have an aperiodic atomic motif. They are materials that lack a traditional unit cell. Several models, including the well-known Penrose tiling model, have been used to demonstrate that diffraction patterns can indeed arise from aperiodic atomic arrangements [3–5].

Although one might imagine that the number of alloy systems exhibiting quasicrystalline structures would be low, this is not the case. To date over 100 binary, ternary, and quaternary alloy systems have been found that contain quasicrystalline phases [6]. Typically, quasicrystalline alloys are aluminum-based, although gallium, titanium, and zirconium-based alloys have also been found. The interest in catalytic properties of these materials arises from the fact that the typical constituents, other than aluminum (which comprises 60–70 at.% of the material), are transition metals (TM). Fig. 1 shows some of the known Al-based systems exhibiting quasicrystalline symmetry. As illustrated by the figure, quasicrystals typically find their basis in icosahedral (i) symmetry, either simple- or face-centered. Decagonal (D) structures have also been observed, in which the material is quasicrystalline in two dimensions and periodic in the third direction. Approximant (A) phases to quasicrystals have also been found. These are

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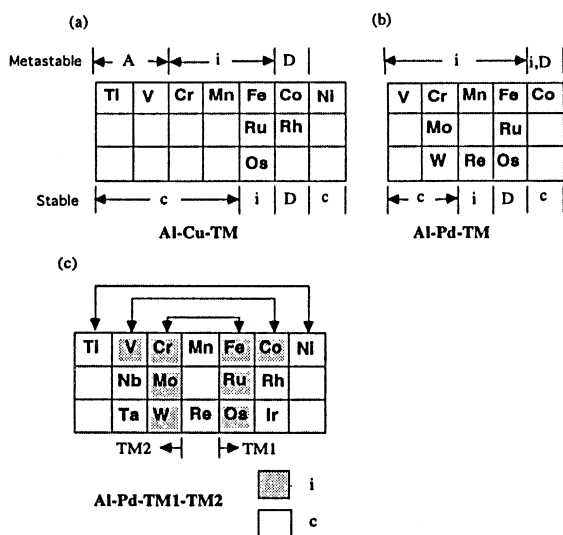


Fig. 1. Phases formed in (a) ternary  $\text{Al}_{65}\text{Cu}_{20}\text{TM}_{15}$ , (b)  $\text{Al}_{70}\text{Pd}_{20}\text{TM}_{10}$  and (c) quaternary  $\text{Al-Pd-TM1-TM2}$  systems. Reprinted from Ref. [6] with permission of World Scientific© 1997 and the author, A.P. Tsai.

materials that are similar in composition to a quasicrystalline phase, but have a finite unit cell, and thus are crystalline (c). Within the unit cell, however, the arrangement of atoms approaches quasicrystalline symmetry, hence, the name approximant [7].

Although quasicrystals form over a narrow composition region, they can, in some cases, be produced using standard metallurgical methods. Large single grains (the term used to describe the analogs to single crystals in periodic materials [8]) of several alloys have been grown using standard crystal growth techniques [6,9–16]. Quasicrystalline powders of the thermodynamically stable materials are made readily by cast and crush methods or gas atomization and, at least in the case of  $\text{Al-Cu-Fe}$ , are available commercially.

No longer mere intellectual curiosities, recent work has focused on trying to exploit the novel properties of these materials for commercial applications. Quasicrystals appear to have a unique set of associated properties. They exhibit low coefficients of friction [17–20], high hardness [21–23], and low thermal and electrical

conductivity [10,24–27]. For  $\text{Al-Cu-Fe}$ , the coefficient of friction using a diamond pin ranges from about 0.02–0.05 which rivals that of diamond itself [28]. Hardness falls in the range 800–1000 Hv [22], which is comparable to silica [29]. The thermal conductivity of  $\text{Al-Cu-Fe}$  is about  $1.1 \text{ W m}^{-1} \text{ K}^{-1}$  at room temperature which is approximately 200 times less than that of pure aluminum [26]. The electrical resistivity of  $\text{Al-Cu-Fe}$  at room temperature is about  $7000 \mu\Omega \text{ cm}$  [24], while for pure aluminum, it is  $2.7 \mu\Omega \text{ cm}$  [25]. A major problem with quasicrystals is that in bulk form they are quite brittle [22,23]. Thus, current interest focuses on uses where brittleness is not a factor.

Potential applications, aside from the catalytic ones as discussed below, involve using these materials as hard, abrasion resistant coatings on softer metals [30], using them as selective solar absorbers [31], encouraging their formation in the processing of stainless steels and alloy production to increase strength [32–36] or exploiting the Ti-rich quasicrystals as hydrogen storage materials [37,38]. The only real commercial application to date is the maraging steel, which is fashioned into high-strength surgical tools [34].

Recently, it has been reported that quasicrystalline materials may be better catalysts than their crystalline counterparts. In 1994, Masumoto et al. [39], described the catalytic behavior of quasicrystalline  $\text{Al-Pd}$ , relative to crystalline  $\text{Al-Pd}$ , pure Pd, and pure Cu. Ultrafine particles (particle size less than 200 nm) of each material were mixed with MgO and calcined at 775 K for 5 h to form the catalysts. They reported that for the methanol decomposition reaction, the amount of hydrogen gas generated is highest and the reaction initiation temperature lowest for the quasicrystalline catalyst. In addition, for the quasicrystalline catalyst, the catalytic behavior and quasicrystallinity appeared to be retained over an extended period of operation and the catalyst was stable to high temperature (870–940 K). It should be noted that the thermal stability of quasicrystals depends upon

the exact constituents and composition. Generally speaking, the thermodynamically-stable quasicrystalline materials will maintain their quasicrystallinity to at least 800 K. Several other quasicrystalline systems containing Pd were tested and all found to be highly active toward methanol decomposition. Methanol decomposition probably has limited industrial demand, but a notable potential use is for on-board hydrogen production in hydrogen fueled cars [40]. It should also be noted that quasicrystalline Al–Ni–Co has been mentioned as an effective catalyst in hydrogenation reactions, but details have not been provided [39]. In general, the work of Masumoto et al. served to demonstrate the possibility of superior catalytic performance using quasicrystalline materials.

Understanding potential catalytic differences between crystalline and quasicrystalline alloys relies on understanding differences in surface characteristics. However, it was not until recently (circa 1992) that simple questions about the surfaces of quasicrystals, such as whether the surface is quasicrystalline or reconstructs to an approximant or crystalline phase, began to be addressed. Surface-related studies since that date have focused on the structure of clean surfaces, the electronic nature of the surface, and the low surface energies reported for these materials. In the following paragraphs, the results of some studies in these areas are reviewed briefly—with emphasis on the work originating in our own laboratory.

A basic prerequisite to surface studies is the ability to obtain large, perfect samples. For characterizing the structure of the clean surface, it is also necessary to be able to clean the samples in ultrahigh vacuum with the standard techniques of ion bombardment and annealing. Elsewhere, we have described our methodology for overcoming these problems [14,15,41]. Structural studies on clean surfaces of Al-based quasicrystals prepared in this way indicate that quasicrystallinity is maintained at the surface, so long as the surface composition is close to that required for phase stability in the bulk.

Furthermore, the data suggest that the surface termination after sputtering and annealing is Al-rich [42,43].

Since the chemical nature of a catalyst is greatly affected by its electronic properties, the electronic characteristics of quasicrystals are notable. Bulk studies of quasicrystals have elucidated some very interesting electronic properties associated with these materials [44]. As mentioned earlier, the electrical conductivity of quasicrystals is quite low. In fact, not only is the conductivity of quasicrystals low, it also depends on defects and temperature differently than do normal metals. As the number of defects within the sample increases, the conductivity increases; for Al–Cu–Fe, it has been shown that this is due to an increase in the density of Al states at the Fermi level [45]. Additionally, above 50 K, conductivity decreases as a function of temperature for quasicrystalline materials, whereas for crystalline materials conductivity increases [24].

The low electrical conductivity is ascribed in part to a suppression of the density of states at the Fermi level of a quasicrystal, the so-called pseudogap [45,46]. A pseudogap is also observed for crystalline materials of similar composition. However, this gap is larger for the quasicrystals [46]. Recent theoretical work by Janssen and Fasolino [47] and Rivier [48] indicates that this pseudogap is present not only in the bulk but also at the surface.

Taken together with the electronic properties mentioned above, recent surface energy determinations suggest that quasicrystalline materials could have unique catalytic properties. Wetting experiments [49] show that the surface of a quasicrystal behaves more like a covalently bound material than a metallic one. Surface energies can be divided into two components, a polar component and a dispersive component. Surface energies of icosahedral Al<sub>70</sub>Pd<sub>21</sub>Mn<sub>9</sub> and Al<sub>65</sub>Cu<sub>23</sub>Fe<sub>12</sub> are similar to Teflon, which has a low surface energy with almost no polar component, and quite different from related crystalline materials and pure Al. Crystalline

alloys, including an approximant phase, made from the same elements as a group of quasicrystalline samples exhibited much higher polar components than the quasicrystalline samples. Furthermore, these studies also showed that surface energy decreases as quasicrystalline structural perfection increases.

Oxidation of these alloys is also important to catalysis. We have examined the oxidation of a clean surface of icosahedral Al–Pd–Mn oriented perpendicular to the 5-fold axis, both in vacuum and under atmospheric conditions. X-ray photoelectron spectroscopy results show that a sputtered-and-annealed Al–Pd–Mn surface forms an Al oxide layer, varying in thickness from 5–10 Å in vacuum up to about 100 Å after immersion in water [50–54]; i.e., an aluminum oxide passivation layer is formed at the surfaces of these materials. For the quasicrystalline phase of Al–Pd–Mn, the thickness of the Al oxide is comparable to that formed on pure Al under similar conditions. Furthermore, just as Al is more susceptible to oxidation by water so is quasicrystalline Al–Pd–Mn [51]. For a crystalline phase of Al–Pd–Mn, with a composition close to that of the quasicrystal, all of its constituent metals are more vulnerable to oxidation, so that a mixed metal oxide forms rather than a pure Al oxide [54].

In short, the thermodynamic and electronic properties of quasicrystals suggest that their surface properties may be unusual by the standards of most metals. However, studies of the clean and oxidized surfaces suggest that these materials may be structurally and chemically similar to Al. In terms of catalytic properties, it is not yet clear which will be the determining factor, the similarities to Al, or the dissimilarities to usual metals. Recently, we have begun to investigate this issue by examining the chemical reactivity of clean surfaces in ultrahigh vacuum. For the specific case of methanol, we find that adsorption and reaction on the 5-fold surface of quasicrystalline Al–Pd–Mn proceed much as on pure Al. In these studies, temperature programmed desorption experiments are performed

following adsorption of methanol at 100 K. For pure aluminum, similar experiments under similar conditions by other authors [55] have shown that methanol dissociates, leading to the evolution of H<sub>2</sub> at about 145 K, coincident with molecular desorption. In addition, methane desorbs at 445 K. An increase in methane signal is observed at 600 K which increases until 625 K, the maximum temperature presented. As shown in Fig. 2, for clean Al–Pd–Mn, we also observe H<sub>2</sub> evolution coincident with molecular desorption in this case at 155 K and methane evolution at 435 K and 600 K for large exposures. Evidence that methane evolves is provided by the ratio of  $m/e = 16$  to  $m/e = 15$ , shown in Fig. 2, which is consistent with the cracking pattern of methane [56]. Residual carbon and oxygen are evident by Auger electron spectroscopy after the thermal desorption studies. For low exposures, methane desorption is not detected on the clean surface, but subsequent exposures, without recleaning, do result in methane formation. On pure Pd, methanol is also known to dissoci-

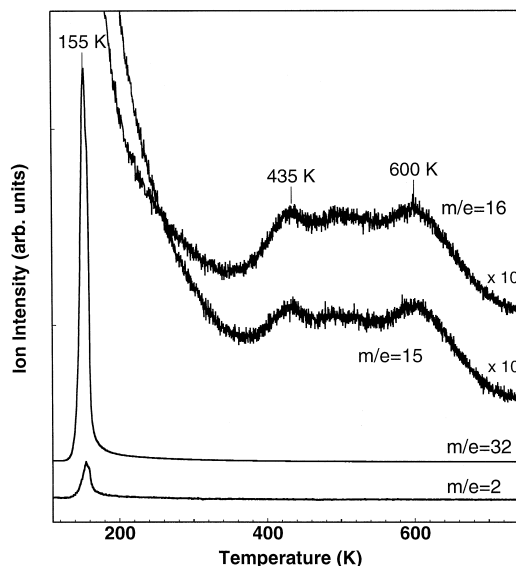


Fig. 2. Temperature programmed desorption spectra of the indicated ions following the adsorption of 200 Torr s of methanol onto a clean 5-fold surface of icosahedral Al–Pd–Mn at 100 K. The peaks at 155 K are indicative of H<sub>2</sub> ( $m/e = 2$ ) and methanol ( $m/e = 32$ ) evolution, while those at higher temperatures are attributed to methane evolution.

ate. However, Pd is characterized by evolution of H<sub>2</sub> at 350 K and CO at 450 K. In none of our studies have we detected CO evolution.

In summary, studies of methanol reactions with the clean quasicrystalline surface, do not yet elucidate why the quasicrystals might be superior catalysts for methanol decomposition. In any case, the unique electronic and thermodynamic surface properties of these materials, plus the fact that several of the quasicrystals alloys discovered to date contain catalytically important constituents, suggest that additional exploration of the catalytic properties of quasicrystals is warranted.

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