



Potential and marketed applications of quasicrystalline alloys at room temperature or above

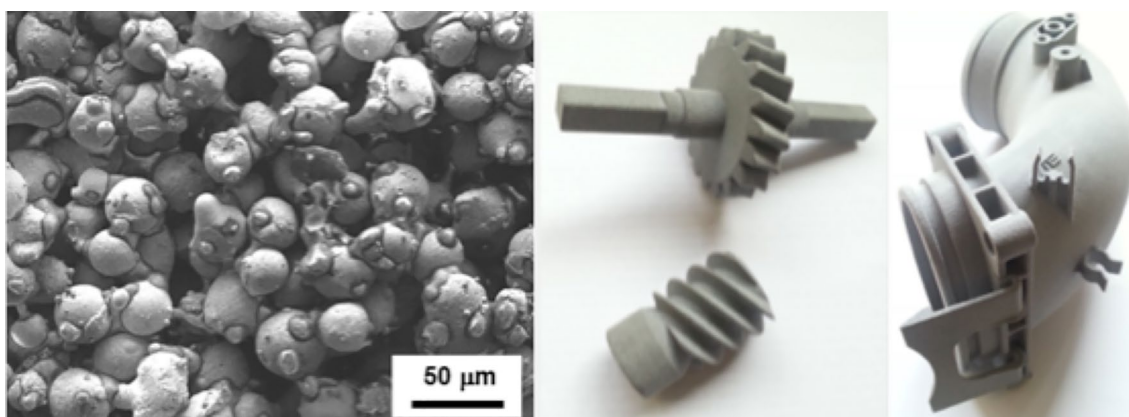
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Abstract

The discovery of quasicrystals by Shechtman et al. in 1982–84 has revolutionised our understanding of crystals and order in solids. Shechtman was awarded a Nobel Prize in Chemistry in 2011 to recognize the importance of this breakthrough. Soon after the initial publication, a patent was filed by the author to secure the potential application of these new materials to the fabrication of low-stick surfaces adapted to the industrial production of cooking utensils. Quite a few more patents followed, covering several areas of technological relevance such as low friction, thermal insulation, solar light absorption, etc. The first application failed, although it reached market. Few others never developed to this stage, but also a (very) small number can now be considered as commercially successful. This is especially the case of polymers reinforced with a quasicrystal powder that are especially adapted to additive manufacturing or 3D printing. Also very advanced is the use of a blend of quasicrystalline and complex intermetallic powders to mark and authenticate an object in a way that cannot be counterfeit. The present article reviews the state of the art and outlines the physics behind few technological breakthroughs that are based on quasicrystalline alloys in the areas of mechanical engineering and solid–solid or solid–liquid adhesion. For the sake of brevity, applications in the areas of catalysis, solar and thermo-electric devices are only shortly evoked.

Graphical abstract



Keywords Quasicrystals · Applied physics · Adhesion · Friction · Applications · Patents

This paper belongs to the topical collection “Quasicrystals: State of the art and outlooks” originated from an international conference organized by the Accademia dei Lincei, held in Rome on November 18, 2022 in the frame of the 2022 International Year of Mineralogy.

Extended author information available on the last page of the article

1 Introduction

Ordered solids were considered to exhibit only translational periodicity until the experimental discovery and first publication about the existence of an icosahedral phase in a melt-spun Al-Mn alloy by Shechtman et al. (Shechtman

et al. 1984). Just a few weeks afterwards, a rationale for the aperiodic structure of this material was published by Levine and Steinhardt (1984) who by the way coined the name “quasicrystals” (QC) to designate this specific and unprecedented type of order in solids. Quasicrystals comprise nowadays quite different types of materials since they were found in metallic alloys, polymers and oxides (Schirber 2007; Cartwright 2013). In this article, I will consider only the family of push–pull alloys (Dubois et al. 2016) that is based on a majority metal mixed with two metals that do not mix together. The most important class of such quasicrystals was pointed out few years after the initial discovery, for the first time in the Al–Cu–Li system (Sainfort and Dubost 1986) and a bit later by Tsai and his co-workers in Al-transition metal alloys, for instance in Al–Cu–Fe (Tsai et al. 1987), Al–Pd–Mn (Tsai et al. 1990) or Al–Co–Ni (Tsai et al. 1989). While the first two examples exhibit true aperiodicity in 3 dimensions (the so-called icosahedral phase), the later yields a periodic stacking of 2D aperiodic atomic layers (the so-called decagonal phase). All three types of quasicrystals are stable in the sense that they can be prepared by slow cooling of the liquid alloy from high temperature down to ambient. Accordingly, the quasicrystalline state can be processed by standard metallurgical techniques, which immediately opens a way to potential applications.

It is along this line that I filed a patent only four years after Shechtman’s early paper to secure the applications of a series of quasicrystalline alloys to potential applications in the areas of surface coatings for mechanical reinforcement of soft metals or for reduced adhesion devices, including frying pans (Dubois and Weinland 1988). I will come back to these areas later in this article. My first paper on this topic (Dubois et al. 1993a) appeared quite a few years after the patent had been (successfully) submitted, due to the confidentiality restrictions imposed by the French patent system. Yet, it was immediately followed by a burst of works and patents that explored the preparation process, coating techniques, applications, and so on (see Dubois 2005 for a review). Slowly, the excitement decayed and almost died out, and only very few applications went to the market. The loss of interest in quasicrystals’ applications was especially boosted when the company in charge of marketing the frying pans withdrew their production, after lots of customers returned their pretty expensive pan that did not resist corrosion in their dishwasher. The reason was that the shell of the pan, initially made of steel that could be heat-treated to eliminate undesired crystalline phases and reach the fully quasicrystalline state, had been replaced by a duplex shell made of stainless steel and an aluminium alloy (Sordelet et al. 2000). Because the heat-treatment temperature was well above the melting point of aluminium alloys, it had been cancelled, thus preventing the quasicrystal to fully grow and leaving in

the coating severe Cu-concentration fluctuations that made it very much prone to corrosion.

Today, I see three, at most four, applications that can be considered successful because they reached market and are commercialised under different trademarks. I will summarize my understanding of those applications in the following sections, namely the use of quasicrystalline precipitates to produce a steel of outstanding mechanical strength that is employed in surgical tools and razor blades, the use of an atomised quasicrystalline powder to prepare complex-shape parts made of a polymer-matrix composite by additive manufacturing, the use of a blend of quasicrystalline and so-called approximants to authenticate an object, and last but not least, a lubricant oil that shows improved performance when it contains quasicrystalline grains. Nevertheless, many so far unsuccessful attempts are worth to consider, either because they are linked to the way the science of quasicrystals has evolved over the years, or because—like my frying pan—they went close enough to the market, but failed for a reason or another. They may trigger innovation in a different area and I will select few of them in the body of the paper, e.g. thermal barriers for car or aircraft engines, and thermal absorbers that may complement thermoelectric energy harvesters adapted to the internet of things. Yet, room is too scarce in this review to write even few words about important areas of potential innovation carried by quasicrystals such as hydrogen storage (Kelton and Gibbons 1997), catalysis (Tanabe et al. 2010; Armbrüster et al. 2014), thermoelectricity (Tritt et al. 1997; Takeuchi 2014), infra-red absorption (Eisenhamer et al. 1997; Dubois and Machizaud 2003), and photonics, although this is not in the area of metallic alloys (Steurer and Sutter-Widmer 2007). The Reader may grab more data about these topics in the literature (Dubois 2005; Macia-Barber 2021). But let’s start with the fundamental property of quasicrystals made of metals that underpins all applications I will come to in the following sections, I mean the formation of a deep pseudo-gap at the Fermi energy in quasicrystals and their approximants.

2 The pseudo-gap at the Fermi level in quasicrystals and approximants

Approximants are periodic crystals of chemical composition similar to that of the quasicrystal, which furthermore exhibit a (periodic) crystalline structure that resembles that of the quasicrystal because it can be derived from the same high-dimensional space but through a rationale cut and projection scheme, see the literature already cited (Dubois 2005; Macia-Barber 2021) and Steurer and Deloudi (2008). Chemical properties (e.g. corrosion resistance) are therefore very much the same for both types of complex compounds and physical properties (e.g. electronic and thermal

conductivities) differ by an amount that can be related to the complexity index of the compound (Dubois 2012). This complexity index β_C is a measure of the number of independent information required to define the structure. A simplified approach is to consider only the number N_{UC} of atoms in the unit cell, i.e. $\beta_C = \text{Ln } N_{UC}$, which up to a small number, is proportional to the true index and is directly related to the Shannon entropy carried by the unit cell at 0 K. It is worth noticing that no sample or object is of infinite size. Therefore, a sizeable quasicrystalline sample is characterized by a finite (although very large compared to periodic crystals) value of β_C . For instance, an atom-gram of aperiodic material yields a β_C index in the range of $\beta_C = 54\text{--}55$ whereas a fcc cell has $\beta_C = \text{Ln}4 = 1.4$.

The existence of a deep pseudo-gap at the Fermi energy E_F in quasicrystalline alloys was first pointed out by Belin-Ferré and her co-workers (Traverse et al. 1988) and confirmed a bit later on the basis of computer simulations by Fujiwara (1989). Belin-Ferré (2002) performed a throughout analysis of many quasiperiodic as well as periodic metallic compounds based on soft X-ray spectroscopy (SXRS) experiments. A summary of her findings in Al-based compounds is shown in Fig. 1a. It turns out that the depth of the pseudo-gap increases with increasing complexity of the compound until it saturates to a value about an order of magnitude below that of pure fcc aluminium for the most complex periodic crystals available in this alloy system. Then, it keeps almost constant for the few true quasicrystals known in these Al-based alloys (Fig. 1b).

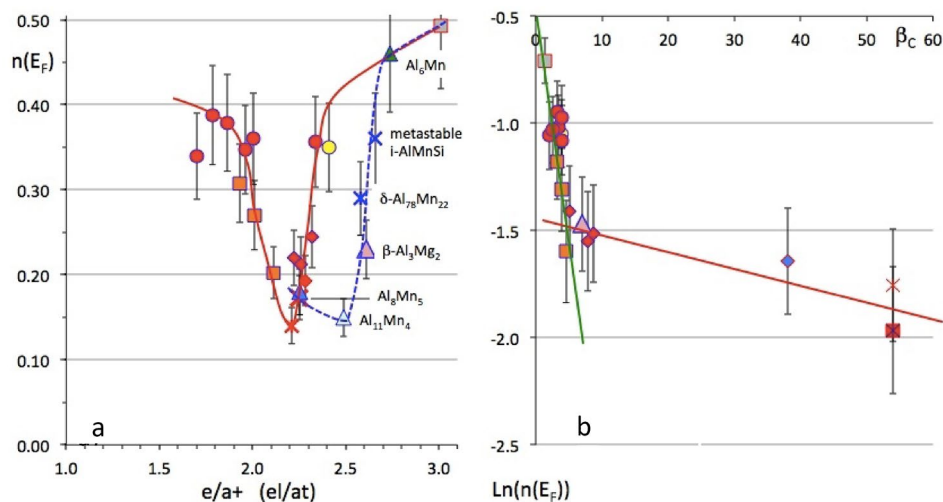


Fig. 1 **a** Partial density of Al3p states measured by SXRS in a series of Al-based compounds as a function of the number of itinerant electrons $e/a+$ defined by Mizutani and Sato (2017). The solid curve guides the eye through a series of stable compounds whereas the dashed curve is for metastable compounds (with the exception of the triangle that represents the data for the stable $\beta\text{-Al}_3\text{Mg}_2$ Samson phase). The upper right square stands for pure fcc Al, the dots for various Al–Cu–Fe crystals, the solid squares for CsCl β -phases, dia-

According to Mizutani (1998), the electronic conductivity is expected to vary in proportion to the square of the density of states (DOS) at the Fermi energy. It is therefore not a surprise to find that the low temperature conductivity of a quasicrystal is roughly two orders of magnitude below that of fcc Al, its parent major constituent metal, which is indeed what is observed experimentally (Belin-Ferré et al. 2005). Thermal conductivity at and above room temperature is essentially due to electrons and accordingly behaves the same way. Hence, experimental evidence is found that the thermal conductivity at 300 K of an Al–Cu–Fe quasicrystal is $\kappa=1$ (Dubois et al. 1993b), quite comparable to that of zirconia, a typical heat insulator utilised in the aeronautic industry to protect the turbine blades of the engine (Fig. 2). In comparison, $\kappa=240$ W/mK for metallic aluminium at the same temperature. The applications we will deal with in the following of this article exploit—in a way or the other—this specificity of all quasicrystals based on metals.

3 Quasicrystals used as reinforcement precipitates

3.1 Maraging steels

Maraging (for martensitic ageing) steels are sufficiently ductile steels that present outstanding mechanical performance due to intergranular precipitation on top of carbon saturation

monds for Al–Cu–Fe approximants of diverse complexities and the crosses for the Al–Cu–Fe and Al–Pd–Mn icosahedral quasicrystals. Fig. 1b shows the same partial DOS, but according to the complexity index of each compound (the solid diamond shown at $\beta_C = 39$ is for a decagonal quasicrystal, see Dubois (2012) for details). The straight lines are only to guide the eye. The slope change of the lines occurs for compounds containing few thousands atoms per unit cell

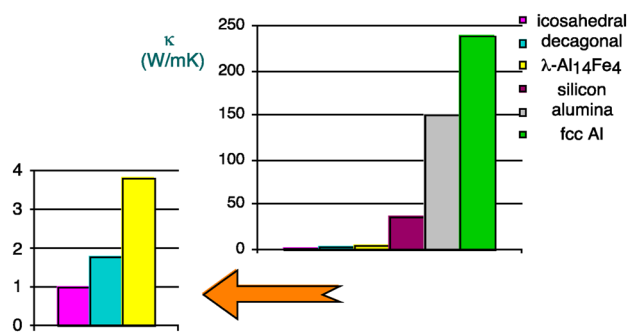


Fig. 2 Comparative display of the thermal conductivity measured at room temperature in the materials listed in the right hand side inset (Dubois et al. 1993b). For better clarity, the lowest values are shown blown up in the left side part of the figure. Zirconia exhibits a thermal conductivity comparable to that of the icosahedral material (the data shown most left in the figure). Based on this comparison, Dubois et al. (1996) designed a range of thermal barrier applications for aircraft turbines. Unfortunately, the melting point of Al-based quasicrystals is too low to fulfil the demanding constraints of modern aircrafts, although the plasticity of quasicrystals at high temperature offers a favourable solution to limit the interfacial strain towards the substrate upon temperature cycling of the blade

of the martensite cell. Such steels are used for demanding applications such as surgery tools or dental wires, for which failure is not an option. Sandvik, a company based in Sweden, has secured such an alloy under trademark “Nanoflex” soon after Shechtman’s discovery with a claim that the precipitates can be clearly identified as icosahedral by transmission electron microscopy (Hultin-Stigenberg et al. 1994; Nilsson 1994). To the best of my knowledge, this is the most successful application of quasicrystals so far, with a yearly production of around 100 tons of steel per year. Razor blades, surgery tools, and dentistry cables are produced thereof (Fig. 3).

3.2 Light alloys

The attempts to use quasicrystalline precipitates to reinforce light alloys (Al- and Mg-based) are too numerous to be quoted all in this review. The topic was pioneered by Inoue and his students at Tohoku University in Japan (Inoue and Kimura 1999). Singh (2014) developed a whole range of studies to better understand the in-situ precipitation of quasicrystalline particles within a metallic matrix and assess the performance improvement brought by this process in comparison to standard metallurgical routes. An alternative process is to introduce the quasicrystals in the form of an atomized powder added to the liquid alloy. Attractive results were obtained this way in different laboratories, hence leading to a variety of patents such as e.g. Binner et al. (1998). A broad-scope study of the formation and stability of icosahedral as well as decagonal quasicrystals in Al-based alloys containing additions of transition metals (essentially Mn,



Fig. 3 Electric razor and surgery tools that make use of a maraging steel exhibiting outstanding yield strength thanks to quasicrystal precipitation hardening (reproduced after Sandvik 2012)

but also Cu or Fe) and Be or Si was designed at the Metallurgical Institute of Ljubljana, Slovenia by Markoli (Markoli et al. 2012, 2023; Leskovar et al. 2020). This study included significant progress on the metallographic tools required to analyse the shape and crystallography of the quasicrystalline inclusions (Bončina 2008). The most favourable conditions for the formation of those precipitates were related to the electron to atom ratio (see Fig. 1) and to the atomic sizes (Nalič et al. 2017). Significant improvement was made on the mechanical performance in relation with the cooling rate imposed on the sample by use of a cooled copper mould (Fig. 4).

4 Additive manufacturing of composites reinforced with quasicrystal powder grains

The group of Valerie Sheares, when she was a member of Iowa State University (my American University), showed (Bloom et al. 2000) that addition of a fraction of a fine grained quasicrystalline powder to various polymers increases the mechanical performance of the composite compared to the neat polymer as well as its resistance to wear (Fig. 5). After verifying that QC-containing composites present no cytotoxicity risk, this discovery has led to the claim by the same group that ultra-high molecular weight polyethylene (UHMWPE) composites reinforced by a fraction of Al–Cu–Fe quasicrystalline particles are good candidates to prepare a new performing kind of hip prosthesis (Andersson et al. 2002). So far, I have no information that this invention ever went to the hospital, but the concept is quite attractive in view of the results reported in Fig. 5.

Definite success in this area of potential application of quasicrystalline alloys was made few years later thanks to additive manufacturing (Kenzari and Fournée 2009).

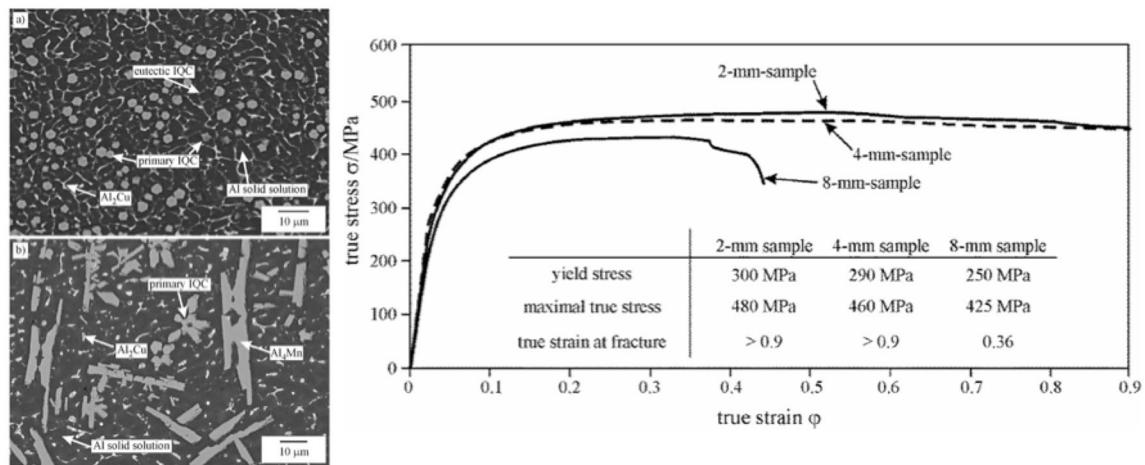


Fig. 4 Left: SEM micrographs of the microstructure observed for two samples of 2 mm in diameter (upper part) and 8 mm (lower part), which experienced high and low cooling rates, respectively. Right: true stress-true strain deformation curves measured in compression

for the same specimens and another of 4 mm diameter. The resulting strain at rupture exceeds by far the performance of conventional Al-based alloys (reproduced after Markoli et al. 2012)

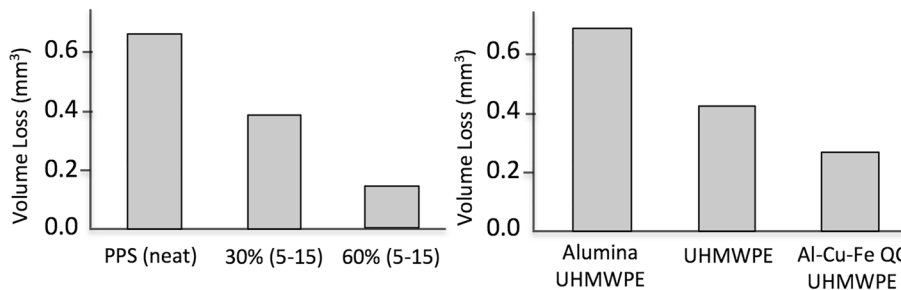


Fig. 5 Left: Volume loss measured using a pin-on-disk test against hard-Cr steel for the neat poly-phenylene sulphide (PPS) polymer and 2 composites containing 30% and 60% volume fractions of QC powder sieved in the 5–15 m range (Redrawn from Bloom et al. 2000).

Right: Pin-on-disk volume loss against stainless steel for the unloaded UHMWPE material and composites loaded with alumina and QC particles, indicating a possible application to the fabrication of hip prosthesis (Redrawn from Andersson et al. 2002)

Additive manufacturing (AM), also referred to as 3D-printing, like many great ideas, arose almost simultaneously in different places (Wikipedia 2018). Stereo-lithography is one such technique that is well adapted to 3D-printing of polymers. It was invented in my (French) university by a friend of mine and his co-workers (André et al. 1984). AM and 3D-printing have developed since to a fantastic level that re-invents most of the manufacturing industry for it is being used to produce all kinds of goods made of polymers as well as of metals. Often, the yield strength offered by the polymer alone is insufficient, but better mechanical performance can be given to the polymer when it is loaded with a reinforcing powder: steel, aluminium alloy, fibres, glass, etc.

The starting material is a blend of two powders, a polymer, for instance nylon polyamide PA12 (PA), and a quasicrystal, for instance Al–Cu–Fe–B produced by Saint Gobain Coating Solutions based on my patent (Dubois and Weiland 1988). The powder is produced by gas atomisation and

later, sieved in a 25–75 m range to feed a batch placed in a horizontal tank after mixing with the polymer powder. The flat surface of this batch of powder is irradiated by an infrared laser beam, which produces melting of the polymer and therefore local solidification of the top part of the powder batch. A solid part is manufactured layer by layer and any shape can be produced as long as a hole remains to withdraw un-melted powder from the interior of the part. This manufacturing technique is now widely used by a SME located in the vicinity of Nancy, France, which proudly exhibits on its web site an automotive part made this way (Fig. 6). Its undisputable commercial breakthrough thanks to this technology is the second success on the market of a product derived from a quasicrystalline alloy.

The advantage of using a quasicrystal powder in additive manufacturing is due to its electronic properties, I mean the absence of any Drude peak in the infrared range, in strong contrast to metals (Demange et al. 2002). As a consequence,

IR light is highly absorbed, with a reflection coefficient as low as $R=0.6$ to be compared to $R \geq 0.99$ for a piece of aluminium metal. This characteristic has opened the way to secure light absorbers in view of green energy harvesting (Eisenhammer et al. 1997; Dubois and Machizaud 2003). We will come back to this topic later in this paper. An analysis of the balance of the heat flux brought in a powder grain by the beam and lost by the grain in its environment (Kenzari et al. 2014a) shows that the temperature increment ΔT of the grain is inversely proportional to its diameter and proportional to the time it is irradiated by the laser beam (or equivalently, is in inverse proportion to the velocity with which the beam scans the bed surface). Using typical data for a metal gives ΔT is the range of a few kelvins whereas the physical properties of a standard quasicrystal such as icosahedral Al–Cu–Fe lead to $\Delta T \geq 40$ K. The process to elaborate a composite by additive manufacturing using an IR laser beam is therefore made considerably easier since the polymer powder surrounding each QC grain will be fully melted. Hence, porosity is absent and the part is directly tight to gases (case of exhaust pipes shown in Fig. 7) or liquids, an advantage that is missed by standard fabrication systems, which require supplementary steps to achieve the same performance (Kenzari et al. 2014b). The patents (Kenzari and Fournée 2009; Kenzari et al. 2013) that secure this invention are now currently used in industry, see above, which represents in my opinion the second successful breakthrough of QCs on the market.

On top of the fabrication process made easier, the composites made of a polymer reinforced by quasicrystalline particles show definitely higher performance compared to both the neat polymer or the ones reinforced by a classical filler such as glass, fibres, metallic spherical particles, etc.



Fig. 7 Ensemble of exhaust pipes made by additive manufacturing of a polyamide powder loaded with atomised quasicrystalline grains (see Graphical Abstract) for a race car. The part is fabricated in one single step, in spite of its high complexity. No further surface treatment is required to make it tight to the exhaust gases (taken from Kenzari et al. 2012)

Fig. 6 Screen copy of the welcome page of the web site (<https://cini.fr/#>) of Ateliers Cini, a small and medium enterprise based near Nancy in France and which makes use of an Al–Cu–Fe quasicrystal-

line powder to manufacture complex-shaped parts (photography in the middle) for its automotive partner industries (listed above)

This result is already illustrated in Fig. 5 and once more in Fig. 8 that was produced by the team of Kenzari et al. (2014a). Space is too limited in this review to give a full account of the large number of works that were dedicated to different composites reinforced by QC particles, but the Reader may have a look at the excellent review given on the subject of aluminium-matrix composites by Wolf et al. (2021).

Going a step further may lead to metal-matrix composites when a polymer-matrix composite is prepared first and then, the polymer is replaced by a metallic alloy that is injected in the porosity left open after the polymer has been withdrawn (by evaporation for instance at elevated temperature). Metallic-matrix parts of high shape-complexity may be produced this way (Fig. 9), yet at some economic cost (Kenzari et al. 2014b).

5 Anti-fraud labels

A third successful breakthrough to the market was derived by Kenzari and Fournée (2018) from the invention of composites containing QC particles. It comprises a mixture of a

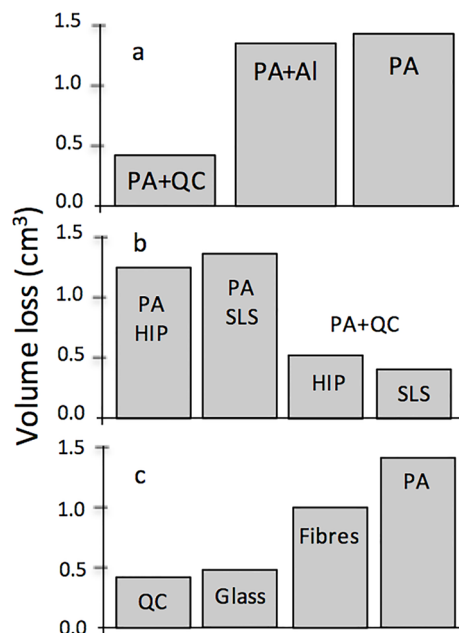
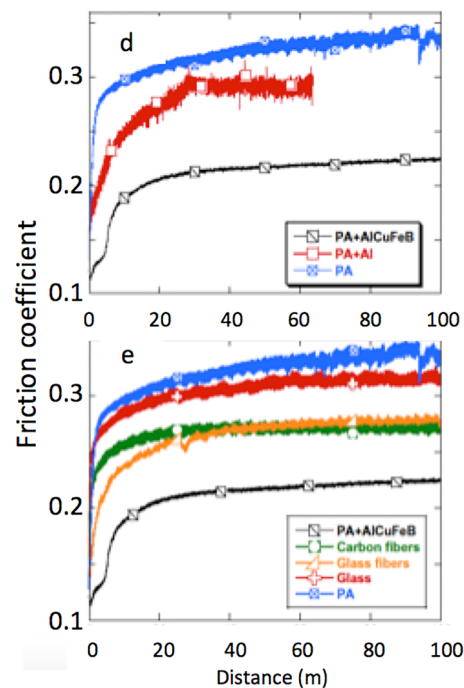


Fig. 8 Assessment of the performance of a polyamide (PA) matrix composite reinforced by a commercial icosahedral AlCuFeB quasicrystalline powder (QC) sold by Saint Gobain Coating Solutions in comparison to other fillers (glass and fibres). All samples were prepared by additive manufacturing (or selective laser sintering SLS) as explained in text except those marked “HIP” which were prepared by conventional hot pressing. Figures **a**), **b**) and **c**) are for the volume

variety of complex metallic compounds, including quasicrystals and their approximants (Quiquandon et al. 1996) that are incorporated in a polymer by additive manufacturing to produce a QR code (Fig. 10, left). The code is readily readable and contains the information that identifies the object carrying it. The point is that the X-ray diffraction pattern is made unique by an appropriate choice of the compounds added to the polymer, and it is impossible to counterfeit it without knowing exactly the composition and the phase content of the complex compounds mixture. A start-up company has been created recently to promote the production of such labels, which will be used during the coming Olympic Games in Paris to trace the art pieces that will be exposed to the public. An example is shown in Fig. 10, right.

6 Applications based on adhesion properties

One application exploiting the reduced adhesion of quasicrystalline surfaces that went to the market, but failed, was already introduced in Sect. 1 above. I am not aware of any other attempt that turned into a commercial success in this



loss measured during standard wear tests against abrasive paper, **d**) and **e**) are for the friction coefficient measured in ambient conditions during non-lubricated pin-on-disk experiments against a hard Cr-steel indenter. The observed performance is improved by a factor larger than 2 in favour of the QC-reinforced composite (redrawn after Kenzari et al. 2012)

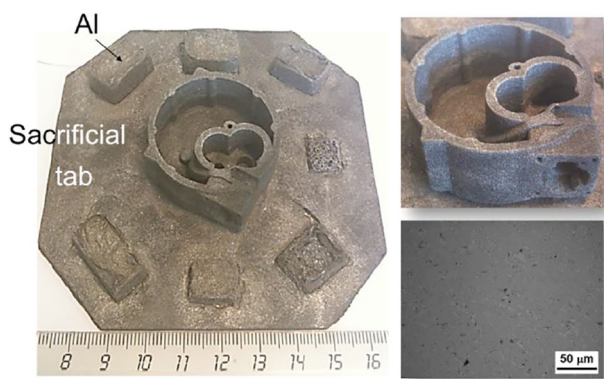


Fig. 9 Complex-shape part made of an aluminium alloy reinforced by QC particles (redrawn after Kenzari et al. 2014b). The part is first fabricated by additive manufacturing of a nylon-QC composite (not shown). The polymer is then evaporated to leave the QC frame the porosity of which is infiltrated by the alloy (left). The resulting solid part is shown on the right hand side. The bottom right image is an enlargement of the final porosity state of the part

area. Interestingly, a Chinese company sells lubricant oil that contains very thin quasicrystal particles with the claim that a decrease by a few per cents of the diesel consumption is obtained (Zhang et al. 2009). I could not get evidence that this is actually true, but I imagine that the presence of the particles decreases the friction losses in the liquid and therefore improves the efficiency of the engine. I must confess, however, that this is more a guess than a serious scientific explanation.

Fig. 10 Left: Anti-fraud label prepared by additive manufacturing of a polymer-matrix composite added with a blend of complex metallic alloy powders. The fingers show the approximate size of the device. It can be read directly with visible light, but its X-ray diffraction pattern is unique and therefore cannot be counterfeited. Right: Example of a piece of art entitled “In memory of us, la beauté du geste” by Stéphane Simon that will be on exhibition in Paris during the Olympic Games in 2024 and is labelled using a QR code as shown on the left (Courtesy of Samuel Kenzari, Institut Jean Lamour, Nancy, France)



As shown elsewhere (Dubois 2004), the reduced adhesion of a quasicrystal such as icosahedral AlCuFe or AlPdMn (Fig. 11) is observed only against polar liquids due to the possibility to prepare the surface in a way that it exhibits a very small, or even no polar contribution. This behaviour is surprising because the quasicrystal is always terminated by a layer of its native alumina oxide in ambient conditions, and alumina is a well-known polar solid. In turn, the Lifshitz-van der Waals contribution is determined by the chemistry of the outer most layers and is more or less the same as on alumina or aluminium in ambient air. This layer of oxide is usually thin on a quasicrystal of high lattice perfection, below 0.5 nm, and its growth during ageing at room temperature or annealing above it is found pretty slow due to passivation effects (Weisbecker et al. 2005). As a consequence, the dipolar charges on the liquid molecules (such as water) do not couple to the ionic impurities that form on oxides and do not produce acid–base interactions at the interface. Instead, they induce dipole images in the Fermi sea of electrons found below the QC/liquid interface. The force that applies to the triple line (vapour/liquid/solid) varies in proportion to the square of the density of itinerant electrons well under the surface, which according to Fig. 1 is at least an order of magnitude lower on a quasicrystal compared to the pure Al metal. This situation is observed on a high purity quasicrystal as long as the surface remains flat and that no impurity formed by atomic diffusion protrudes through the oxide layer (Bonhomme et al. 2004). The upper limit of the temperature

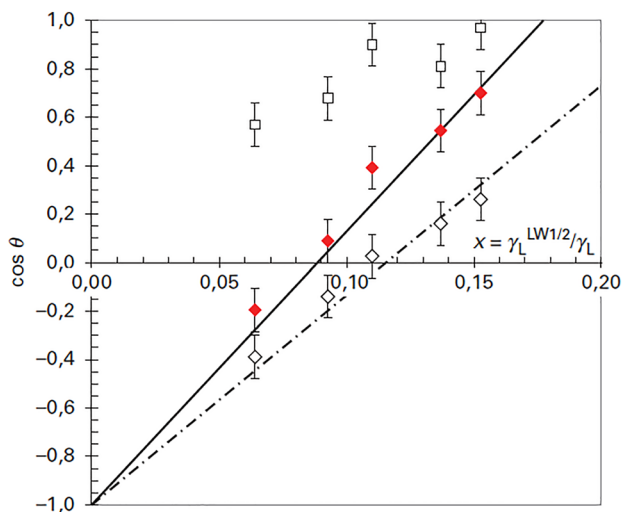


Fig. 11 Contact angle θ measurements performed on PTFE (Teflon[®]) (solid diamonds), alumina (open squares) and an icosahedral Al–Pd–Mn single grain quasicrystal (open diamonds) using five liquids of varying Lifshits-van der Walls and polar components of the surface energy. The variation of $\cos \theta$ with the ratio $x = \sqrt{\gamma_L^{LW} / \gamma_L}$ (where γ_L stands for the total surface energy and γ_L^{LW} for its Lifshitz-van der Walls component) is linear as expected for PTFE, which is a highly apolar solid, whereas it departs clearly from linear for ionic alumina. Surprisingly, it is also linear for the quasicrystal, in spite of the presence of a surface layer of alumina in ambient conditions, thus indicating the absence of polar contributions to the surface energy of the quasicrystal. More details are given by Dubois and Belin-Ferré (2015)

range within which the QC layer may be used for cookware is found around 300 °C, approximately (Kušter et al. 2023).

The absence of any polar (or acid–base) contribution to the energy of the surface equipped with its native oxide is in line with the low surface energy assessed for the naked surface: γ_{QC} 0.6–0.8 Jm⁻² (Dubois et al. 2004). This result, as well, is a surprise since the constitutive metals show significantly higher values: γ_{Al} = 1.2, γ_{Cu} = 1.8, γ_{Fe} = 2.2 Jm⁻² (Vitos et al. 1998). It points out to applications in the domain of contact mechanics and tribology. Solid contact is indeed a source of wear and energy waste, which consumes a significant fraction of the national gross product in developed nations. The absence of adhesion is an *ab initio* condition for the successful use of metallic parts in many devices such as satellites or ultra-high vacuum ancillary equipment. Fretting experiments performed in a vacuum chamber that mimics the conditions found in space have indeed shown that quasicrystalline materials are good candidates to produce adhesion-less coatings against hard metals that are used on satellite parts placed in strong contact during launch and travel of the vessel, and which must separate later on (Fig. 12).

The reduced surface energy of quasicrystalline alloys compared to standard alloys also points toward applications in tribology either as surface coatings made by spray techniques or as thin films made by magnetron sputtering. A lot of effort was dedicated to this topic by the author (Dubois 2005), or by several groups in the USA or Asia (see for instance Park and Thiel 2008). The friction coefficient against e.g. a hard steel indenter was found very significantly below that of hard indenters, especially under vacuum when tribo-oxidation plays no role (Dubois and Belin-Ferré 2014). In ambient atmosphere unfortunately, abrasive wear at the oxide/quasicrystal interface produces cracks that easily propagate to the (brittle) bulk material and destroy it. Lubrication of the contact area is therefore mandatory, which can be achieved using a solid lubricant incorporated in the coating. This goal was obtained using high velocity oxygen fuel (HVOF) spraying (Guedes de Lima et al. 2016): graphite particles generated from the kerosene propellant are deposited together with the QC material and produce such an efficient lubrication that the friction is reduced to its ploughing component (approx. 5–6% against hard steel) and the test may last for hours without showing any sign of failure of the coating (Fig. 13). Other attempts, using for example soft metals like tin, were far less successful (Shao et al. 2004).

7 Energy insulation and harvesting

The low thermal conductivity of quasicrystalline alloys (Perrot et al. 1995), especially at low temperatures (i.e. typically below 100 K) immediately points towards their application in heat insulating devices. To the best of my knowledge, this has never been used in a low-temperature device of technological relevance. Far above room temperature, the situation is more critical because electron conduction becomes the main mechanism for heat transport and heat conductivity raises few times that of zirconia around 1000 K. Yet, ductility enters the game since no work hardening is observed above 70–80% of the melting temperature (Kang and Dubois 1992; Urban et al. 2002), which provides a definite advantage compared to brittle insulating oxides because it anneals the interfacial stresses that form during heat cycling (Dubois and Pianelli 1992). A vast programme of tests was based on this observation and applied to a real aircraft engine (Sanchez-Pascual et al. 1999). Unfortunately, the demand for better fuel efficiency of modern aircrafts imposes to increase the functioning temperature significantly above 1300 K, which rules out quasicrystals and their approximants that show too low melting points. Helicopter turbines work, however, at much lower temperatures and a turbine blade adapted to such an engine was equipped with a thermal barrier produced by magnetron sputtering of an

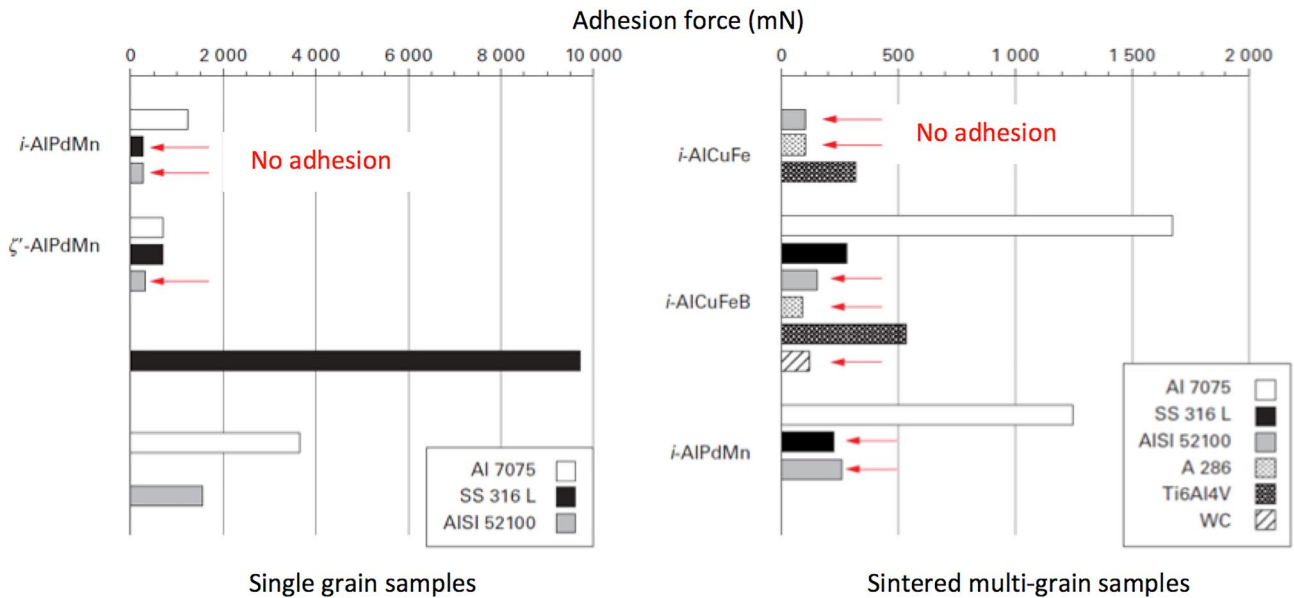


Fig. 12 Data obtained from fretting tests managed in a secondary vacuum chamber by placing various samples against hard materials as shown in the inset of each figure. The long bars in the bottom part of the left hand side figure show the adhesion force observed against reference materials, using the hard materials placed in contact with themselves: strong adhesion is found for the SS316L hard steel in contact with a sample of the same steel. Adhesion is less important

but still significant against the two other steels, but no adhesion at all is observed against the quasicrystalline samples, whether used as single grains (left side figure) or sintered and multigrained (right side part). An approximant (marked ξ -AIPdMn) of the AIPdMn quasicrystal was tested and shows no adhesion as well (Reproduced from Sales et al. 2006)

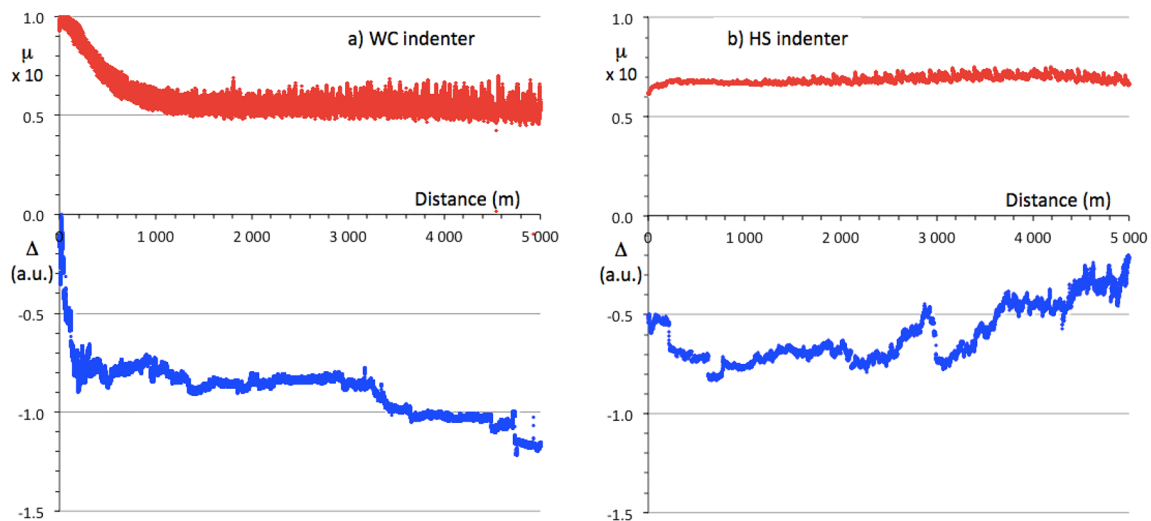


Fig. 13 Friction coefficient μ and wear Δ measured during pin-on-disk tests in air on an Al–Cu–Fe quasicrystalline coating produced by the HVOF technique. A sintered WC indenter was used for the left hand side figure and hard steel for the right side one. The bottom part of the figures shows the distance Δ between sample surface and indenter holder as a function of the distance ran by the indenter on the sample, hence the sum of the wear experienced by both solids in contact. The value of Δ is essentially constant with time, except for

the first moments of the test, when the initial roughness of the sample is worn out. Friction is found around 5%, which is the value expected for the ploughing contribution, considering the load, shape and hardness of the solids (see Guedes de Lima et al. 2016 for details). The test was stopped after the indenter had ran 5 km on the sample, a distance by far large enough to guarantee that no failure of the coating may occur (Redrawn from Guedes de Lima et al. 2016)

approximant of the decagonal quasicrystal of composition $\text{Al}_{71}\text{Co}_{13}\text{Fe}_8\text{Cr}_8$ (at %) (Fig. 14).

The absence of a Drude peak in the optical conductivity of quasicrystals and high order approximants (Demange et al. 2002) make them very suitable for energy harvesting equipment such as solar absorbers or miniaturised collectors for the Internet of Things (IoT). The industrial production of solar absorbers was set up by an industrial company based in Munich, Germany, but was finally abandoned because this line of production was in competition (and possibly more expensive) with another product of the same company (Eisenhammer et al. 1997). Figure 15 illustrates how miniature solar light collectors may be designed to feed the small devices found in the IoT with the little amount of energy they request (Silva Oliveira et al. 2021).

The low thermal conductivity of quasicrystals also promoted hopes that they could be used as thermo-electricity generators (Tritt et al. 1997), but the reduced electronic conductivity soon turned at their disadvantage while other conventionally crystalline materials made their way to much



Fig. 14 Helicopter turbine blade equipped with a thermal barrier made of a hexagonal approximant of the decagonal quasicrystal that was deposited on top of the metallic substrate by PVD magnetron sputtering (Courtesy of S. Drawing, ONERA)

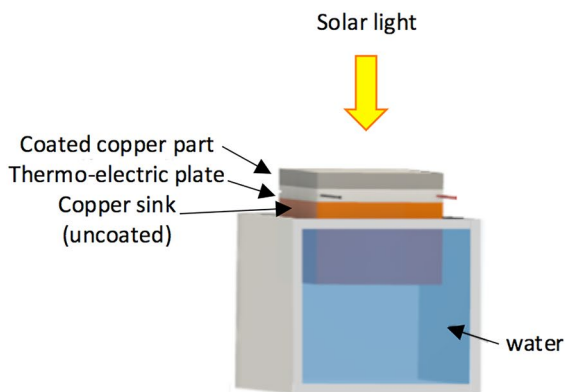
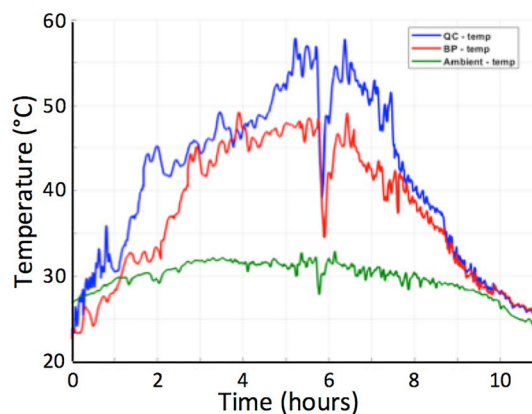


Fig. 15 Example of a miniature energy harvester designed by Silva Oliveira et al. (2021) to power an element in the Internet of Things. Left: solar light is directed towards a heat collector comprising a copper block coated with a layer of quasicrystal (not shown) placed on top of it. The collected heat actuates a thermoelectric component placed below. On the opposite side is a heat sink (here, a small amount of water), which ensures a thermal gradient through the ther-

mo-electrics and generates the electric power required by the IoT. Right: plot of the temperature versus illumination time observed when the upper copper block is coated with a layer of quasicrystal (QC, upper curve) or with black paint (BP, middle curve). The lower curve is the ambient temperature (Redrawn from Silva Oliveira et al. 2021)

8 Conclusion

Regrettably, due to shortage of space, I could not address all the potential applications that were studied so far. I selected preferably topics with which I am familiar enough, because I had some contribution published or patented, and I deliberately ignored important areas such as catalysis. The Reader may find relevant information in the articles already cited and in Kameoka et al. (2014). Despite their enhanced performance, quasicrystals and approximants did not reach so far an outstanding level of performance that would justify their substitution to conventional catalysts that are in use in chemistry plants. In my opinion, the same holds true for precipitation-hardened alloys, with the major exception of maraging steels produced by Sandvik in Sweden. To the best of my knowledge, it is still too early to know if the discovery of long range ferromagnetism in Au-Ga-Dy quasicrystals (Takeuchi et al. 2023) will lead to magnets with very low coercivity as can be expected from the high symmetry of the lattice. As well, the occurrence of superconductivity in icosahedral AlZnMg quasicrystals (Kamiya et al. 2018) opens an avenue for another type of potential high-tech applications. Also, I did not mention few side-effect applications that have accompanied the development of the ones listed in the lines above. One typical example is the invention by a major toilet paper producer of a toilet tissue



moelectrics and generates the electric power required by the IoT. Right: plot of the temperature versus illumination time observed when the upper copper block is coated with a layer of quasicrystal (QC, upper curve) or with black paint (BP, middle curve). The lower curve is the ambient temperature (Redrawn from Silva Oliveira et al. 2021)

that was supposed to be (mechanically) reinforced by a Penrose tiling embossed in it (Criton 2021). Although this invention did not deal with an alloy, the story is interesting from the point of view of intellectual property rights. The pattern imprinted in the paper tissue was a simple copy-paste of a pattern that appeared in an article by Sir Roger Penrose, showing details that could be easily related to the original work. Penrose, who did not like the concept, could then argue in court that the regulations on copyright were not obeyed and in the end obtained that the blasphemous invention was withdrawn.

Forty years (almost) after the initial publication by Shechtman and his colleagues, and a Nobel Prize bestowed on him, it turns out that quasicrystals made a huge impact on fundamental science, but not yet in technology. They not only forced the scientific community to revise its paradigm about order in condensed matter, but also shed new light on many aspects of metal physics: this is where their real usefulness has to be looked upon (Dubois 2005, 2011). Regarding practical applications, only three, at most four, inventions using them came successfully to the market. All of them are in the area of composites or in association with other materials: steels, polymers and oil. *Per se*, quasicrystals made of metals have not yet demonstrated economic usefulness because they form in a very narrow composition range and they are brittle (except in the nanometre range (Zou et al. 2016)). Yet, once associated with another material, or if (at least one of) the dimensions is sufficiently reduced, they may prove some utility. Therefore, as an incurable optimist, I would bet that the story is not over ...

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Declarations

Conflict of interest The author declares that there is no conflict of interest.

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