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New prospects from potential applications of quasicrystalline materials

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Abstract

Since 1984, several quasicrystalline materials were selected for possible technological applications as coatings and composites. A few examples of products derived from such materials are now on the market. The aim of this review is along several key points raised by the technological prospects of quasicrystals, namely composition tailoring and industrial processing of thick coatings, surface preparation and properties, and new potential applications. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nowadays, a small number of the potential applications that were dreamt of in the years shortly following Shechtman's discovery [1] have been commercialized. Hence, quasicrystalline materials offer a new challenge to materials scientists and to production engineers [2]. Processing these materials as thin films, thick coatings, sinters, fillers for composites, etc. with reproducible characteristics, reliable lifetime and low cost has become an issue of interest for several private companies. Hence, the stream of the paper will be along a few questions that arise now from the premises of technological use of quasicrystals, both from the point of fundamentals in physics and chemistry and in view of improving their performance in devices, or equivalently narrowing the scatter of their characteristics. In this respect, the control of the manufacturing process of quasicrystalline materials in very large quantities should become soon a new frontier in quasicrystal sciences.

2. Tailoring compositions

Quasicrystals are rather easy to obtain in the laboratory [3]. Most of these alloys form metastable quasicrystals which turn irreversibly into regular crystals upon heating. A number however are stable: they belong to an equilibrium phase diagram and may be grown out of the liquid by slow casting techniques. They are of special interest since thermodynamic equilibrium and reversibility of the formation conditions also implies that they may be prepared by conventional metallurgy techniques, hence lower cost. In a few systems addition, or partial substitution, of new chemical species allows to enhance some property of the quasicrystal or a better match of its performance with the environment. This is the case for instance when a few atomic percent of boron (less than 7 at.%) are substituted to Al atoms in i-Al–Cu–Fe. The yield stress of $Al_{59}B_3Cu_{25.5}Fe_{12.5}$, a pure icosahedral compound, is found up to three times larger than that of i-$Al_{62}Cu_{25.5}Fe_{12.5}$, with no boron substitution for Al atoms [4]. The hardness H_v also increases slightly from 700 to 800 (Vickers units). Meanwhile, the friction coefficient with respect to diamond keeps identical, but more importantly the normal load which the material surface is able to sustain goes in proportion to the yield stress. Hence, the quaternary Al–B–Cu–Fe is a better choice for tribological applications than the more classical Al–Cu–Fe [5]. The Al–Co–Fe–Cr system was considered in the same spirit in view of designing thermal barrier coatings [6]. Again, an approximant of the decagonal phase isotypic with hexagonal Al_5Co_2 forms in the $Al_{71}Co_{13}Fe_8Cr_8$ region. It turns out that it shows appreciably low thermal conductivity, good corrosion resistance to sulphur, low oxidation rate and a thermal expansion coefficient comparable to that of metallic substrates. Furthermore, melting is nearly congruent close to 1170°C so that it may be used in several applications of combustion engines and power generators.

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In terms of a competition with doped zirconia, this alloy clearly suffers from melting at a too low temperature but wins on the side of plasticity and thermal expansion.

It is clear that a precise design of quasicrystalline material compositions will become a key task in view of applications. So far, this was mostly focused at Al-based alloys, including the adequate definition of precursors for PVD or laser abrasion targets, but attempts were also done to tailor hydrogen-storing quasicrystals [7,8]. I would rank in this category the formation of quasicrystalline precipitates in Mn-implanted Ga substrates [9] and, of course, the precipitation-hardened maraging steels [10] and Al-based alloys [11].

The most common route for preparing samples in the laboratory is casting ingots after melting the pure constituents under vacuum or inert atmosphere. For most compositions, quasicrystals form by peritectic solidification of high temperature crystalline phases reacting with residual liquid. This process is necessarily slow, and most often some crystalline constituent is retained out of equilibrium at room temperature together with the quasicrystal. Since crystals and quasicrystals exhibit significant composition and atomic volume differences, pores usually form at this stage with sizes distributed in the range up to micrometers. Exploitation of the physical properties of such samples, especially mechanical properties, is then rather desperate. Different tricks may be followed in order to reduce porosity to a minimum while pure quasicrystal is obtained, e.g. the Czochralski pulling technique or flux growth [12]. Sintering may also prove useful for the preparation of multi-grained, single phase bulk specimens [13]. It will soon become an industrial mean for producing pre-shaped parts. Whereas the mode of pressure application is not very important in view of preparing pure quasicrystalline samples, the temperature–time profile is critical. Pure icosahedral i-$Al_{59}B_3Cu_{25.5}Fe_{12.5}$ with virtually no phason strain may be prepared this way.

3. The industrial route

Up to now, this is essentially the way followed to produce thick coatings and sinters. The thick coating route goes basically in a three-step process [14]: (i) gas atomization of the liquid alloy, (ii) plasma spraying of this powder to obtain a thick coating on a substrate and (iii) mechanical polishing to get rid of the substantial roughness of the as-deposited coating. The first two steps are well known in powder metallurgy. In the third step, the roughness of the as-sprayed coating must be reduced down to a very smooth surface mandatory for most applications (friction, low adhesion). Due to the brittleness of the quasicrystal, this is not always a straightforward task and requires quite some know-how. Of specific importance is the possible occurrence of a brittle-to-ductile transition upon grinding the surface, see below.

Altogether, a plasma sprayed coating is substantially a composite material, comprising not only the deposited stuff but also pores, cracks, oxides, etc. More suitable techniques rely upon physical vapour deposition and are now routinely used for the production of a large variety of thin films. Once the variation of evaporation rates with chemical element is determined, it is easy to prepare quasicrystals right at the appropriate composition. This may be performed from targets either constituted from the separate constituents [15] or from sinters or even from plasma sprayed targets. Usually, films deposited on substrates at room temperature are amorphous but subsequent annealing does transform them into pure quasicrystal. To the best of my knowledge, it seems that quasicrystalline thin films were never prepared from electrolytes although this method would considerably enlarge the range of shapes and substrates of commercial interest.

Another route for using quasicrystals on an industrial scale is the manufacture of composites. Here, the term composite is used very broadly to include multiple phase materials produced by artificial mixing or by natural precipitation. In both forms, the brittleness which characterizes the bulk material is mitigated. Among the composites, a precipitation-strengthened steel [10] is currently marketed by Sandvik Steel in Sweden. Another type of bulk composite [11] is an Al-based alloy which can be formed by rapid solidification and powder processing. The quasicrystals form by precipitation, yielding nanoscale particles surrounded by an Al matrix. Certain compositions can exhibit especially high strength and high ductility.

A type of composite which is promising, but not yet marketed, involves polymers with quasicrystalline fillers [16]. Tests with certain high-performance thermoplastic resins have shown that quasicrystalline AlCuFe particles enhance the wear resistance of the polymers significantly. This effect is not understood, but may be related to a combination of the hardness, low friction, and low thermal conductivity intrinsic to the quasicrystal. At the same time, key thermochemical characteristics of the polymer — its glass and melting transitions — are unperturbed, indicating that the quasicrystal does not catalyse cross-linking or other disadvantageous chemistry in the resin. After Tsai et al. [17], metal-matrix composites may be designed by incorporating quasicrystal powders into an aluminium-based alloy for instance. This may be processed by mechanical alloying the different phase components and sintering or by mixing in the liquid state followed by a sintering step. Substantial increase of hardness, hence of wear resistance, and reduction of friction is observed [18] which compares very favourably with the state-of-the-art embodied by SiC fillers. These last two preparation methods — polymer- and metal-matrices — have the advantage to use fine particles, namely the granulometry range that is not useful for plasma spraying. Therefore, on top of the performance they offer on their own, these techniques will help industry to solve the environmental problem caused by storing (or wasting) the fine particle lots produced by gas atomisation.

4. Surface: preparation and properties

With the exception of thermal barriers, potential applications of quasicrystalline coatings exploit surface properties such as low friction, reduced apparent surface energy, corrosion and oxidation resistance and hardness. The corrosion behaviour of quasicrystals has not attracted yet considerable interest [19], maybe because it was shown to be dominated by compositional effects rather than by the atomic structure. Yet, it is essential that the coating process itself, then the final steps of polishing the surface preserve the appealing properties of the quasicrystal (use of PVD techniques does not require polishing in principle since the final roughness of the deposited film reproduces the initial roughness of the substrate). Basically, mechanical polishing is produced by fast, repeated and severe localized shearing within a very thin surface layer of the material under the effect of the abrasive grains. This is very reminiscent of the action of multiple pass scratches which may be applied using a tribology test device. It turns out that repeating a scratch test within the same track with a WC-Co rider produces a rather high friction, hence an important localized shear strain, and induces a significant ductility within the material volume beneath the scratch (see Fig. 5 in [20]). The bottom of a scratch track comprises of a number of micro-tracks of width typically below 1 μm, where the shear stress has been concentrated to far above the yield stress of the material. We have studied the microstructure and atomic structure in the region located beneath such micro-tracks [21]. In the region beneath the scratch trace where the Hertz contact pressure reaches its maximum, transmission electron microscopy allowed us to identify new particles of nanometer size. Micro-diffraction was employed to determine the structure of those small particles. Co-existing with the diffraction spots originating from the icosahedral matrix, periodically spaced spots demonstrated that a new b.c.c. phase with lattice parameter $a = 0.29$ nm had formed coherently within the icosahedral matrix, thus implying that those particles could not be re-deposited material. It must be stressed that the superstructure spots characteristic of the Cs–Cl-type, B2 equilibrium β-cubic phase in the Al–Cu–Fe system were not observed here. Hence, this out-of-equilibrium b.c.c. cubic phase was mainly due to the high shear strain achieved in the contact region with the indenter while temperature was most plausibly rather high owing to the poor thermal conductivity of both the WC-Co indenter and i-Al–Cu–Fe. A modulation of the quasicrystal structure was also found in the vicinity of the scratch.

Thus, the enhancement of ductility which goes along with repeated indenter sliding may arise from a stress-induced phase transition and appearance of a defective quasicrystal phase. Due to the strong coupling between electron localization on the one hand and influence of defects or of impurity phases with metallic character on the other hand, the present result has direct relevance to the control of quasicrystal surfaces subject to mechanical polishing or grinding in view of certain technological applications. Similar studies of the transformation of surfaces of technological quasicrystals should receive more attention in future.

5. Friction and wear

The initial report [22] that quasicrystalline samples exhibit low friction and wear was based upon a comparison with aluminium alloys. Although such an assessment is fair regarding composition, the largely different hardnesses of these materials makes its relevance rather unsounded. Therefore, we have reconsidered the friction coefficients μ of a variety of aluminium-based specimens with hardness H in a broad range (between 25 and 2000 Vickers units) as well as that of a Cr-containing hard steel of quite similar hardness than the icosahedral $Al_{59}B_3Cu_{25.5}Fe_{12.5}$ material. To this end, we used an (undeformable) diamond indenter although this has little technological relevance. The specimens we have studied include not only samples from quasicrystal forming Al(B)–Cu–Fe and Al–Pd–Mn systems, but also reference materials such as sintered alumina and common materials also examined in the next section (pure copper, aluminium and window glass). Full account of these results is given elsewhere at this conference [13]. The friction data are reported in Fig. 1 (indenter: diamond sphere of diameter 1.6 mm, load 5 N). Accuracy of these measurements is estimated to ±0.008. The pure quasicrystals, either single quasicrystalline or sintered and the orthorhombic (O1) approximant of the decagonal phase exhibit friction coefficients equivalent to those of the hardest materials, alumina as shown in the figure or diamond sliding on itself. The other materials gather close to the graph of $\mu \approx H^{-n} + \text{constant}$

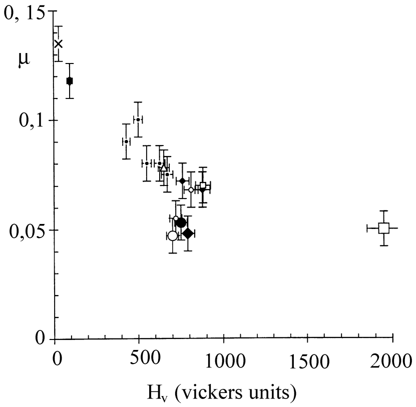

Fig. 1. Friction coefficient μ measured in an alternating sliding scratch test with a diamond indenter (see text) for a number of specimens with variable hardness. Symbols are as follows: (○) twinned icosahedral quasicrystal i-$Al_{70.5}Pd_{21}Mn_{8.5}$; (●) sintered $Al_{70}Pd_{20}Mn_{10}$; (o) tetragonal ω-$Al_{70}Cu_{20}Fe_{10}$, orthorhombic O1-$Al_{71.2}Cu_{9.8}Fe_{8.5}Cr_{11}$ and monoclinic λ-$Al_{73.5}Cu_3Fe_{23.5}$ ($Al_{13}Fe_4$-type); (•) AlCuFe β-cubic CsCl-type (≤5% in volume); (⬩) sintered AlCuFe icosahedral + β-cubic; (◆) sintered single-phase i-$Al_{59}B_3Cu_{25.5}Fe_{12.5}$; (×) f.c.c.-Al; (□) sintered cubic alumina; (▫) hard Cr-steel; (▪) f.c.c.-copper; (△) window glass.

with $n \approx 0.4$, a kind of universal power law which is expected if ploughing dominates the friction behaviour. Assuming indeed that the diamond indenter is not deformed under the applied load, and in the absence of a third body, friction arises from deformation of the scratched material in front of the indenter, from roughness of the contacting surfaces (this becomes negligible after a small number of passes except for lattice mismatch effects) and from electronic interactions. For a typical quasicrystal with Young's modulus $E = 100\,\mathrm{GPa}$, a rough estimate of the ploughing deformation corresponds to $\mu = 0.03$, hence to $\mu = 0.02$ for lattice roughness and electronic interactions. Solids examined here like the hard steel with comparable hardness but twice as large Young's modulus, thus supposedly a smaller contribution from elastic deformation, show a more significant contribution from sticking effects, most plausibly due to enhanced electronic interactions. To summarize, Fig. 1 clearly demonstrates that the low friction of quasicrystals of excellent lattice and microstructure quality (no cracks, no pores, no crystalline impurities) is not solely related to their high hardness and Young's modulus but primarily to reduced electronic interactions. Nevertheless, brittleness is still a main limitation for the use of quasicrystals in tribology. In this respect, phase purity is important, as assessed in Fig. 1, as well as chemical interactions with the counterpart. Again, this domain of mechanical properties of quasicrystals still suffers from insufficient knowledge.

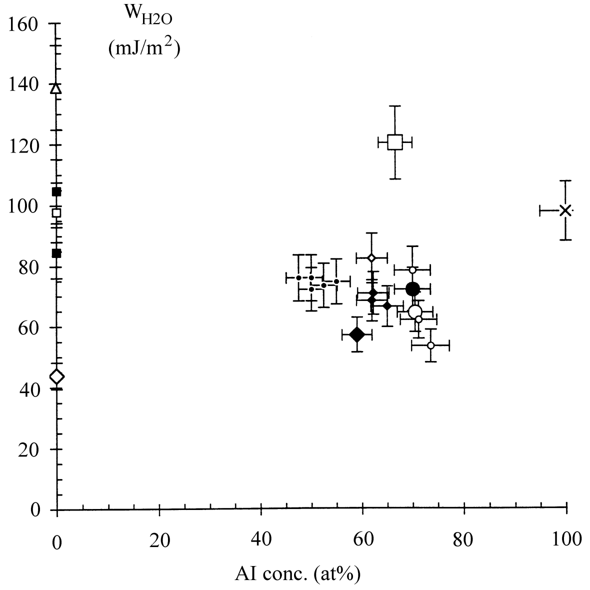

Fig. 2. Reversible adhesion energy of water at room temperature versus Al concentration in a number of Al-based intermetallics and reference samples. Symbols have the same meaning as in Fig. 1 plus: (◇) amorphous $Al_{62}Cu_{25.5}Fe_{12.5}$ prepared by PVD; stainless steel (■) and teflon (◇).

6. Apparent surface energy and wetting

Indirect evidence that the surface energy of quasicrystals is actually small may be deduced from a comparison of contact angles measured by depositing small liquid droplets on the surface of a quasicrystalline sample as well as on reference samples such as teflon, metals, or a bulk oxide, namely alumina. Developments along an equation already introduced two centuries ago by Young take us to a fairly simple expression [23] of the reversible adhesion energy of a given liquid onto the surface: $W_L = \gamma_L(1 + \cos\theta)$, where γ_L stands for the surface energy of the liquid. This assumes that the contact angle θ is well defined, which is only true if the solid surface energy is comparable to or smaller than γ_L. This does not hold true also for metals, alloys or oxides. On other solids, and especially teflon, water does not wet: the contact angle is clearly larger than 90°. It happens that finely polished quasicrystal surfaces do not wet as well [24]. Their reversible adhesion energy with water in only 25% larger than that of teflon (namely 55 and 44 mJ/m^2, respectively), whereas it is $\frac{1}{3}$ of that of window glass. Alumina, which is the oxide always found at the surface of aluminium metal and of its alloys, is comparable to window glass in this respect.

We have re-measured the reversible adhesion energy of ultra-pure water W_{H_2O} for the samples used for friction measurements, stainless steel and teflon. The term W_{H_2O} is directly and easily accessible to experiment since it requires only to measure the contact angle of a minute water droplet (volume between 1×10^{-9} and $3 \times 10^{-9}\,\mathrm{m}^3$) at room temperature. It assumes no specific formalism to interpret the data but only a well-defined contact angle, hence a negligible film pressure. As we see below, this condition is fulfilled by our samples since their surface energy, except for alumina and window glass, is smaller than that of water $\gamma_{H_2O} = 72\,\mathrm{mJ/m^2}$. Specific care has to be taken to identify correctly the advancing front angle as described in [25].

It turns out that the best quasicrystals exhibit W_{H_2O} data rather comparable to teflon (Fig. 2). They are indeed only 25–30% above the W_{H_2O} value for this solid and by no means comparable to the W_{H_2O} value typical of pure aluminium, or more specifically to that of the Al_2O_3 oxide. Above the quasicrystals and approximants of lowest W_{H_2O}, i.e. i-$Al_{59}B_3Cu_{25.5}Fe_{12.5}$ and λ-$Al_{73.5}Cu_3Fe_{23.5}$, we find the other samples closer to stainless steel. The more metallic they are, the less difference we see in comparison to this steel. Such a difference may be related to different factors first studied by Rivier [26]. Specifically, Rivier [26] considered a direct overlap of wave functions at the solid–liquid interface, but due to the oxide layer always present at the surface of our samples, such an interaction most plausibly results from electrons tunnelling through the oxide barrier or preferably from electrostatic image forces generated by the dipolar moments of the molecules. For Al–Cu–Fe intermetallics, the thickness of the oxide layer decreases smoothly with increasing aluminium content of the substrate [27] within a range of 0.4–0.8 nm when oxidation is performed in ambient air. Our data, also presented elsewhere at this conference [25], confirm a previous report [24] in which we showed that W_{H_2O} correlates with parameters of the Al 3p partial density of states [28], i.e. the density of the less localized states found at the Fermi energy. In all respects, quasicrystals are found in between stainless steel and teflon, but closer to teflon as soon as their lattice quality, phase purity and surface preparation is adequate. A complete understanding of this phenomenon — for quasicrystalline surfaces of technological interest as well as for metallic materials at large — remains to be worked out.

7. New potential applications

Possible application of quasicrystalline materials was also pointed out in various domains of energy savings, namely thermal insulation (which I have already mentioned above), light absorption, power generation and hydrogen storage. Thermal barrier demonstrators [29] could be assessed in real conditions during an aircraft engine ground test. For the other issues, development of devices is not as mature, but nevertheless a number of technical characteristics emphasize how quasicrystalline materials may become useful. These results will be briefly elaborated in the following.

The design of selective quasicrystalline light absorbers [30–32] take advantage of the specific optical properties of quasicrystals [33]. Furthermore, the emissivity of thin films may be reduced down to less than 3% by using triple-layer sandwiches having a quasicrystal film like i-Al–Cu–Fe of a few nanometers thickness deposited between two dielectric films as was first suggested by Eisenhammer and Lazarov [30]. This device shows performances equivalent to those of more conventional materials like Ti–N–O films already on the market but resists to higher temperatures of the order of 300–350°C. Its corrosion resistance to humid air may be significantly improved by using instead Al–Cu–Fe–Cr approximant materials [34]. Other potential applications of the optical properties of quasicrystals comprise IR detection (bolometers) and temperature sensors.

To my knowledge, Cyrot-Lackmann [31] was the first to point out with her colleagues in Grenoble that certain quasicrystals may become useful for thermopower generation. Some quasicrystals indeed show appreciable thermo-electric power of the order of $S = 70\text{–}80\,\mu\text{V/K}$ in the vicinity of room temperature. Since they exhibit also weak electrical and thermal conductivity, the corresponding figure of merit is already close to 0.1–0.2. However, modern thermoelectric materials like narrow band-gap semiconductors present figures of merit larger by an order of magnitude. The composition and structural perfection of the quasicrystal influence drastically the thermoelectric power [35] which may change from large and positive to weakly negative within a few percents of concentration change. The hopes to apply quasicrystals to competitive thermopower generators rely upon enhanced stability at high temperatures, further increase of thermopower above its present room temperature value whereas, meanwhile, the lattice thermal conductivity should not increase too much. Target numbers to achieve a respectable figure of merit of about 1 will obviously require tailoring specific compositions. In this respect, the Umklapp process will add a positive (and favourable) contribution to S in (supposedly perfect) quasicrystals in strong contrast to the case of regular crystals, since it allows transferring arbitrarily small momentum of phonons to the quasilattice [35]. With the combined pressure for environmentally green materials for civil applications and silent power generators for military applications, it is easy to predict that thermo-electricity of quasicrystals will soon become a focus of interest for RD programs (and funding).

Titanium-based icosahedral quasicrystals may be categorized as belonging to the Bergman family according to the kind of elementary cluster which builds up their atomic skeleton (see [36] for more information on the cluster types). Hence, a large number of tetrahedral interstitial sites may be occupied by protons. One composition, namely $Ti_{45}Zr_{38}Ni_{17}$, was shown to give a stable icosahedral phase at low temperature [7]. It turns out that this composition, as well as its 1/1-cubic approximant, store large quantities of protons, approaching the ratio of about twice as much H atoms than constitutive metals. In weight percentage, this leads to 2.5% hydrogen in $Ti_{45}Ni_{17}Zr_{38}$, which compares very favourably with metal hydrides currently used in devices of technological interest, for instance rechargeable batteries. Severe hindrance to this kind of application of quasicrystals may result, however, from limited reversibility during storage–desorption cycles. It is clear that Ti–Ni–Zr compounds have been successfully operated during a small number of cycles in different hydrogen-storage media such as the gas phase, including at room temperature, or electrolytic cells but feasibility over thousands of cycles has not yet been fully demonstrated.

8. Conclusion

With technological applications, potential or demonstrated, the science of quasicrystals has entered a new era. Many patents relative to quasicrystals are already close to 10 years-old, and last (and late) but not least, private companies show now interest in quasicrystals. Especially in US and Japan, public funding is associated with research programs focused at applications of quasicrystals, for instance tribology or thermopower generation. Many fundamental questions are still far from a solution however and require a better understanding if our community seeks for an efficient collaboration with scientists in industry. Here, I shall list only a few of those questions. First, composition tailoring requires to know where all the atoms are in the quasicrystal, still an open question although great progress has been done along this line in recent years [36]. It demands a complete knowledge of at least ternary phase diagrams not only in metallic systems but also in metalloid-based ones. For sure, the recent demonstration that Si and Ge possess a phase with close relationship to quasicrystals will (re-)open the hunt for a truly semi-conducting aperiodic compound [37]. Mechanical properties, especially in the brittle phase below 450°C, offer a real challenge because they are intimately linked with all kinds of applications. Of special interest is the coupling between ductility and transport properties since the former is mandatory for shaping and durability, whereas the latter are involved in sensors, low wettability, heat insulation, etc. Processing is therefore central to the actual use of our materials, but as yet was considered only by a very few groups in the world. Many other questions of this kind, relevant to the relationships between microstructure, properties and processing, wait for an answer. Altogether, we shall not doubt that the applied science of quasicrystals will entail considerable renewal of our discipline.

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