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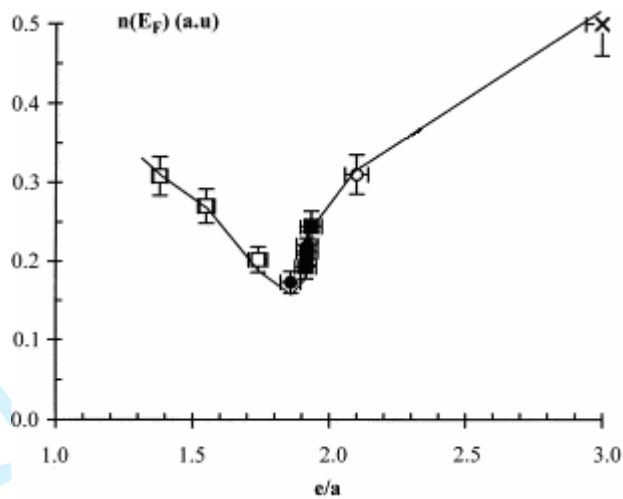


Figure 1

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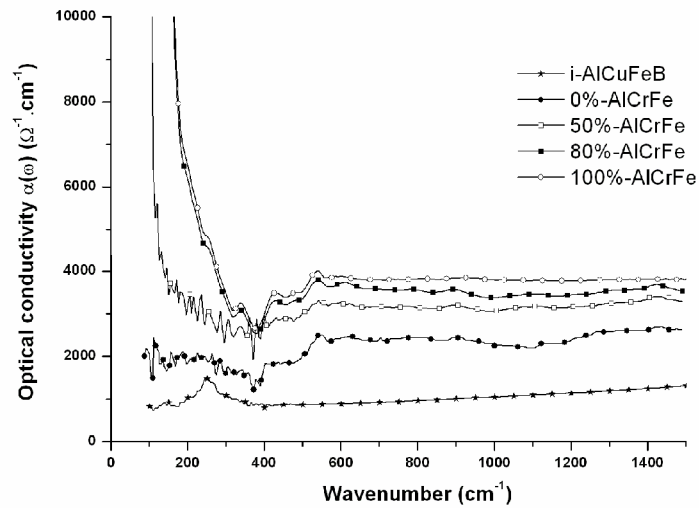


Figure 2

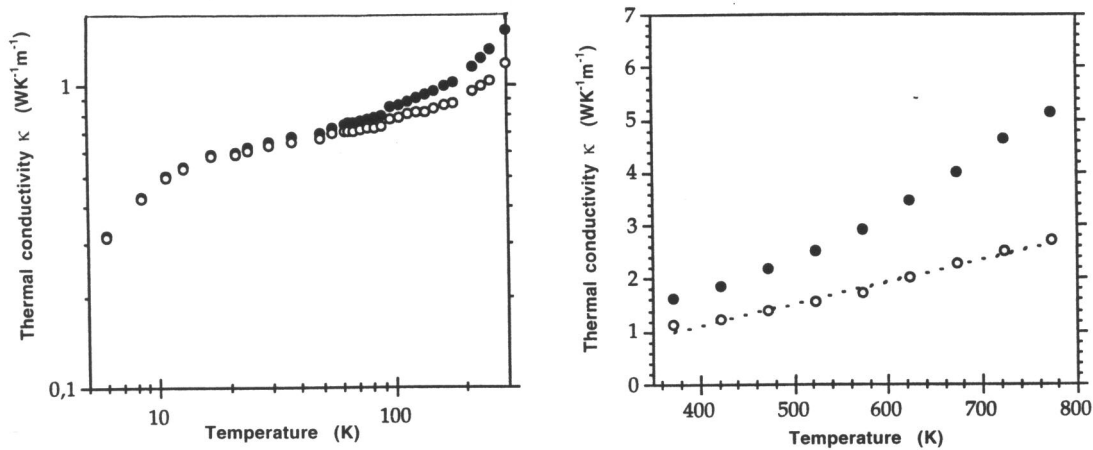


Figure 3

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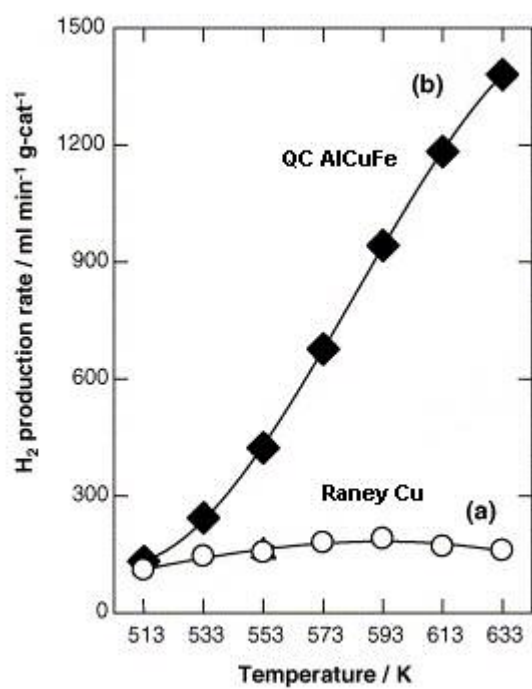


Figure 4

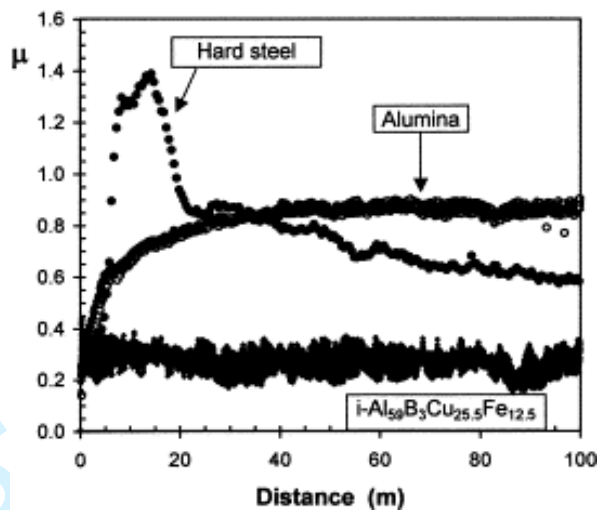


Figure 5

For Peer Review Only

# Quasicrystals and complex metallic alloys: Trends for potential applications

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Although the industrial development of Complex Metallic Alloys (CMAs) and Quasicrystals (QCs) has remained quite limited so far, these materials exhibit interesting and sometimes unexpected properties in terms of technological applications. A few selected examples of the most promising properties and trends for potential applications are presented.

*Keywords:* Quasicrystals; complex metallic alloys; properties; applications

## 1. Introduction

Complex Metallic Alloys (CMAs) are compounds essentially consisting of more than two (often three or four) metal components at comparable quantities. They are characterised by giant unit cells containing up to thousands atoms, a structure based on well-defined (often icosahedral) clusters and some amount of disorder due to the fact that icosahedra do not fill in three dimensional space. Although the first structural studies of CMAs date back to the 1920s [1] very little attention has been initially paid to the practical usefulness of these materials until the discovery of QCs, in 1982 [2], re-activated the interest for these materials. Although aperiodic, QCs exhibit short range order structures similar to CMAs. Attractive and sometimes unexpected properties were then evidenced, opening the way for technological applications [3-7].

In order to be of technological relevance, a material must not only present challenging properties, but also be easy to produce in the desired shape (bulk, powder or coating), stable in operating conditions, of low cost and its constituents must be free of any known toxicity. In addition, it must benchmark already existing devices. It is not that easy to fulfil these criteria in full and only a few devices, mainly based on the mechanical properties of these materials (high hardness and/or low friction coefficient), are commercially available so far. However, based on their physical and chemical properties, CMAs and QCs may prove suitable for a number of other applications.

A few selected examples of QCs and CMAs most promising properties will be presented in this paper together with trends for possible applications. Special emphasis will be put on the electronic structure of CMAs and QCs, in particular on the appearance of a pseudo-gap in the density of states at the Fermi energy, which plays a specific role in the stabilisation of these alloys and in most of their properties.

## 2. The pseudo-gap at the Fermi energy

At equilibrium, the stability of a given structure is induced by the minimisation of the free energy  $F = U - TS$ . The internal energy  $U$  mainly depends on atomic size ratios, electronegativity differences and a band structure term. As many complex metallic phases only have small differences in electronegativity and atomic sizes, the band structure term dominates the stabilisation conditions. CMAs and QCs can thus be considered as a special class of Hume-Rothery alloys [8]. In particular, for Al-based complex alloys, the

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combination of the Hume-Rothery scattering of electron waves by Bragg planes and sp-d hybridization effects leads to the opening of a well-defined pseudo-gap in the Al 3p partial density of states at the energy of the Fermi level. The first experimental evidence of the existence of such a pseudo-gap was obtained on quasicrystalline AlMn thin films [9] and was subsequently confirmed for a large number of quasicrystals and complex alloys. In particular, a detailed study of the variation of the density of Al 3p states at Fermi level as a function of valence electron per atom  $e/a$  (electronic concentration) for a number of AlCuFe intermetallics has shown that  $n(E_F)$  is much lower in the compounds based on the icosahedral structure (quasicrystalline or approximants) than in simple  $\beta$ -cubic CsCl-type phases or tetragonal  $\omega$ -Al<sub>7</sub>Cu<sub>2</sub>Fe crystals [10; 11] (see Figure 1). In short, a deep pseudo-gap seems to be characteristic of icosahedral short range order and to increase with structural complexity.

Insert Figure 1

The pseudo-gap is not only playing an important role in the thermodynamic stability of the complex materials but it has also important consequences on some of the most exciting properties of these alloys, such as transport properties. In addition it must be noted that the lowering of the density of states close to the Fermi edge is maintained on the CMAs and QCs smooth (sputtered and annealed) surfaces [12] and surface properties such as friction and wetting will thus also be strongly influenced by the electronic structure.

### 3. Optical conductivity and solar selective absorbers

The optical conductivity response  $\sigma(\omega)$  of QCs is characterized by very low values and the absence of a Drude peak at low frequencies, together with the appearance of a peak conductivity in the visible range [13-19]. The absence of the Drude peak can be interpreted in the frame of the generalised Drude law proposed by Mayou [20]:

$$\tilde{\sigma}(\omega) = e^2 n(E) \Gamma(2\beta + 1) A \left( \frac{\tau}{1 - i\omega\tau} \right)^{2\beta-1}$$

where  $\tilde{\sigma}(\omega)$  the complex conductivity,  $n(E)$  the total density of states,  $\Gamma$  the gamma function,  $\beta$  the diffusion exponent,  $A$  a constant,  $\omega$  the frequency,  $\tau$  the lifetime of the valence electrons.

The shape of  $\sigma(\omega)$  (hence the existence of a Drude peak) is fixed by the value of  $\beta$  which varies from  $\beta=1$  for simple metals to values close to  $\beta=0$  for pure icosahedral samples.

The optical conductivities  $\sigma(\omega)$  of a mixture of two orthorhombic approximants of the decagonal O<sub>1</sub>/O<sub>2</sub>-AlCrFe phase and of a pure rhombohedral  $\gamma$ -AlCrFe brass phase have been recently investigated [21] and compared with those of the icosahedral AlCuFeB phase (i-AlCuFeB) in a broad range of frequencies  $\omega$ . It has been shown that, in all complex alloys of large (or infinite) unit cell, the optical conductivity remains very weak at low frequencies. In addition, both the i-AlCuFeB and the O<sub>1</sub>/O<sub>2</sub>-AlCrFe are characterized by the absence of the Drude peak whereas the  $\gamma$ -brass phase exhibits a clear Drude peak albeit several orders of magnitude weaker than in pure aluminium (see Figure 2). Moreover, as shown in Figure 2, for mixtures of orthorhombic approximants and  $\gamma$ -brass phase (x % Al-Cr-Fe means x %  $\gamma$ -brass phase), the metallic character increases with the proportion of the  $\gamma$ -brass phase. In other words, the larger the unit cell the lower the conductivity at low frequencies.

Insert Figure 2

In view of their high absorbance in the solar wavelength region and their high reflectance at longer wavelength, CMAs and QCs soon appeared as good candidates for use as solar selective absorbers. Extensive studies have been performed by Eisenhammer *et al.* on AlCuFe thin films and cermets [22-27].

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Devices consisting of sandwich systems of Al<sub>2</sub>O<sub>3</sub>/AlCuFe/Al<sub>2</sub>O<sub>3</sub> films deposited on copper films on Al<sub>2</sub>O<sub>3</sub> coated silicon were produced, showing 90% solar absorbance and low thermal emittance. Reasonable chemical and thermal stabilities in air were observed up to 400°C making these materials appropriate candidates for high temperature applications. However, rapid degradation in humid conditions as well as diffusion of copper through the Al<sub>2</sub>O<sub>3</sub>/AlCuFe sandwich at higher temperatures still are serious limitations to the usefulness of these devices in extreme conditions (i.e. beyond house ware).

#### 4. Thermal conductivity and thermal barriers

The first evidence of the peculiar behaviour of the thermal conductivity  $\kappa$  in QCs was given in a pioneer work performed by Kuo and co-workers on Al<sub>65</sub>Ni<sub>20</sub>Co<sub>15</sub> and Al<sub>62</sub>Si<sub>3</sub>Cu<sub>20</sub>Co<sub>15</sub> decagonal crystals [28]. These authors have shown that the thermal conductivity of these 2D quasicrystals was abnormally low compared to that of their metallic constituents. Moreover, the values of  $\kappa$  measured perpendicular to the stacking axe (i.e. along the aperiodic direction) were an order of magnitude lower than in the periodic direction. The thermal conductivity  $\kappa$  can be expressed as the sum of a lattice contribution due to structural scattering of phonons  $\kappa_{\text{lat}}$  and of the electronic contribution  $\kappa_{\text{el}}$ :

$$\kappa(T) = \kappa_{\text{lat}}(T) + \kappa_{\text{el}}(T)$$

The electronic contribution, which can be described by a modified Wiederman-Franz law [29], is negligible at low temperature where  $\kappa$  is dominated by umklapp scattering of phonons and phason-phonon interactions (see Figure 3a). Above room temperature the electronic contribution becomes comparable to the lattice contribution (see Figure 3b) but is hindered by the reduced density of states at the Fermi energy. It is worth noticing that the value of the thermal conductivity at room temperature ( $\approx 1 \text{ Wm}^{-1}\text{K}^{-1}$ ) is close to the value corresponding to pure zirconia and orders of magnitude lower than that of simple metals (200  $\text{Wm}^{-1}\text{K}^{-1}$  for Al and 400  $\text{Wm}^{-1}\text{K}^{-1}$  for Cu).

Insert Figure 3

The low thermal conductivity exhibited by these materials, combined with a thermal expansion close to metals and good corrosion and oxidation resistance made them interesting candidates for applications as barriers coatings for heat insulation. In particular coatings consisting of a AlCoFeCr approximant of the decagonal phase have been extensively studied for potential applications as coatings for components of aeronautical and power generation turbines [30; 31]. Excellent results were obtained in terms of thermal and corrosion properties. However, a strong interdiffusion between the coating and the substrate was observed at high temperatures (above 950°C), which drastically hinders potential applications to aeronautic devices, even though some diffusion barriers proved reasonably efficient to slow the interdiffusion effect. Nevertheless it is very likely that the excellent thermal properties exhibited by CMAs and QCs will find applications in less demanding fields in terms of temperature range.

#### 5. Catalysis and hydrogen production

The interest in catalytic properties of CMAs arises from the fact that they often contain transition metals as typical constituents (which are good catalysts and can eventually be cheap raw materials!). In addition their brittleness turns to be an advantage as they can easily be crushed into powders. Extensive studies of the activity of AlCuFe alloys toward steam reforming of methanol ( $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}_2$ ) have been performed by Tsai and co-workers [32-35] in pressure and temperature conditions reflecting those used in catalysis. Various compositions were evaluated based on the production of hydrogen gas. As these materials are covered with an aluminium passive layer, leaching treatments similar to that applied to Raney Al-alloys based catalysts, were followed by reduction in a hydrogen atmosphere before carrying the

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steam reforming of methanol experiments. Following such treatments, the prepared catalysts can be viewed as copper and copper oxide particles located on the surface of a complex metallic alloy core. The rate of hydrogen production was found to be comparable to that of the presently available commercial Cu-based catalysts. Furthermore, higher production rates were obtained at high temperature for the AlCuFe quasicrystalline particles compared to conventional Cu-Raney catalysts (see Figure 4). This increase in the performance has been ascribed to a better dispersion of the copper metal in the porous aluminium oxide layer which is formed on the quasicrystalline catalyst surface and to the inhibition of sintering of the copper particles due to the presence of iron. However, as the catalytic activity and stability of the quasicrystalline Al-Cu-Fe phase is much higher than that of other Al-Cu-Fe phases (e.g. Al<sub>55</sub>Cu<sub>25</sub>Fe<sub>12</sub> beta- and Al<sub>2</sub>Cu theta- phases) specific interactions between copper particles and the quasicrystalline support leading to stabilisation of the copper clusters were also invoked [35]. Although it is not yet clear which specific property determines the good catalytic performance of the quasicrystalline phase [36], it seems that the catalytic activity could be related to a size effect that gives to Cu an atomic-like character [37].

Insert Figure 4

## 6. Friction under vacuum and cold welding

It was recognized soon after the discovery of QCs that the friction coefficient of these materials against antagonists like hard steel is significantly reduced compared with the friction coefficient measured in comparable conditions on conventional metallic alloys of similar mechanical characteristics [38]. Hence, reduced friction was for long taken as one of the best example of potential application of QCs and CMAs [3; 7]. However, the friction coefficient observed in air is only low in a transient regime [39]. It increases with time during the test and many artifacts due to tribo-oxidation are appearing.

Investigations performed in vacuum have shown that the friction coefficient strongly varies with the oxidation state of the surface [40-42]. In addition, on clean surfaces, the friction coefficient is lower for QCs and CMAs than for conventional metals and alloys [40-46]. As an example, a recent AFM investigation performed on a clean 2-fold decagonal d-Al-Ni-Co surface clearly evidenced the strong anisotropy of the friction force between the periodic 10-fold and the aperiodic 2-fold directions [47], the latter direction exhibiting much lower friction.

A comparison of the friction coefficients measured under vacuum in similar conditions on hard steel, sintered alumina and icosahedral Al<sub>59</sub>B<sub>3</sub>Cu<sub>25.5</sub>Fe<sub>12.5</sub> using a pin-on-disk test (hard steel ball) is shown on Figure 5. The most striking feature in this figure is the constant value observed for the AlBCuFe phase even for long riding distances, which contrasts with the strong variations observed for alumina and hard steel. These variations have been ascribed to the appearance of wear debris which either originate from the hard steel substrate and can form a lubricating third body by sticking to the pin surface (friction on hard steel) or originate from the pin and stick to the alumina surface which is ultimately covered with steel (friction on alumina). The low and constant value observed in the case of i-AlBCuFe indicates that wear is reduced and that steel does not stick on the substrate [42].

Insert Figure 5

Further experiments carried out on various materials (AlCuFe and AlPdMn quasicrystals, approximants of the decagonal phase like  $\lambda$ -Al<sub>13</sub>Fe<sub>4</sub>, orthorhombic O- and  $\gamma$ -brass AlCrFe compounds, Al-based intermetallic compounds like  $\omega$ -Al<sub>7</sub>Cu<sub>2</sub>Fe,  $\phi$ -Al<sub>10</sub>Cu<sub>10</sub>Fe,  $\beta$ -Al<sub>50</sub>Cu<sub>35</sub>Fe<sub>15</sub>,  $\gamma$ -Al<sub>4</sub>Cu<sub>9</sub> and o-Al<sub>3</sub>Cu<sub>4</sub>, pure Al and pure Cu) have shown that the friction coefficient scales with the inverse of the hardness of the material and with the density of d-states at the Fermi energy which can interact with the d-states of the iron-containing rider. A low density of d-states at the Fermi energy leads to low interaction hence low adhesion

and friction [42; 44]. These results can be of primary importance for applications such as hindrance of cold welding in aerospace or vacuum industries.

## 7. Conclusion

Due to their remarkable diversity of properties, metallic materials will remain of utmost technological importance in the coming years. Although the industrial development of CMAs and QCs has remained quite limited so far, a number of interesting potential applications can be foreseen based on the specific properties of these materials. A few examples of these properties and potential applications have been briefly described in this paper. However, this description is far from being exhaustive and a number of other applications can also be foreseen, such as hydrogen storage, high-performance alloys, metal and polymer composites, thermo-power generation, quantum dots.... Furthermore, it must be pointed out that perhaps the most promising future for QCs and CMAs is the possibility they can offer to combine properties which are mutually excluding in conventional materials (e.g. metallic electric conductivity combined with low thermal conductivity, good light absorption and high temperature stability, high metallic hardness and low wetting by polar liquids...). However it must be kept in mind that, in order to successfully compete with other materials such as polymers and ceramics, QCs and CMAs must offer superior solutions at competitive costs together with environmental harmlessness and low energy consumption during production, service and recycling. In addition, due to the intrinsic brittleness of these materials at low temperatures, many applications are foreseen in the form of surface coatings. Therefore tailoring thin films or coatings with reproducible characteristics, stability and low cost in large quantities is a major issue for industrial success. Finally, due to the huge number of possible combinations between the 80 possible constitutive metals, it is likely that a high throughput combinatorial approach will be necessary for identifying the most promising materials.

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## Figure captions

Figure 1. Variation of the density of Al 3p states  $n(E_F)$  as a function of electronic concentration in fcc Al (cross),  $\beta$ -cubic crystal (open squares),  $\omega$ -Al<sub>7</sub>Cu<sub>2</sub>Fe crystals (open dot), AlCuFe approximants (solid squares) and icosahedral Al<sub>62</sub>Cu<sub>25.5</sub>Fe<sub>12.5</sub> (solid dot). From [10].

Figure 2. Optical conductivity at low frequency for an icosahedral AlCuFeB phase (i-AlCuFeB) and mixtures of AlCrFe orthorhombic approximants of the decagonal phase and  $\gamma$ -brass phase (0%-AlCrFe means pure O<sub>1</sub>/O<sub>2</sub>-AlCrFe and 100% means pure  $\gamma$ -brass phase). Courtesy V. Demange, Nancy.

Figure 3. Total thermal conductivity (solid circles) and lattice contribution (open circles) at a) low temperature in i-Al<sub>62</sub>Cu<sub>25.5</sub>Fe<sub>12.5</sub> and b) above room temperature in Al<sub>59</sub>B<sub>3</sub>Cu<sub>25.5</sub>Fe<sub>12.5</sub>. After [7].

Figure 4. H<sub>2</sub> production rate for the steam reforming of methanol as a function of the reaction temperature for Cu-based catalysts leached in NaCO<sub>3</sub> aq. for a) Raney Cu (commercial Cu-based catalyst); b) quasicrystalline Al-Cu-Fe crushed by wet milling in ethanol and leached at 323K. From [34].

Figure 5. Friction coefficient in vacuum against a hard steel ball observed during a pin-on-disk test for hard steel, alumina and i- Al<sub>59</sub>B<sub>3</sub>Cu<sub>25.5</sub>Fe<sub>12.5</sub>. After [42].