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Introduction to the Science of Complex Metallic Alloys
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1.1 Introduction

Complex metallic alloys (or CMA for short), also called SCAPs (for structurally complex alloy phases) for some time [1] encompass a broad family of crystalline compounds made of metals, alloyed with metalloids or rare earths or chalcogenides. They exhibit large unit cells, containing up to thousands of atoms. The periodicity of the crystal unit cell is no longer a relevant property since it becomes much larger than the average first-neighbor distance, and more specifically exceeds the distance that characterizes basic interactions in the crystal. As a consequence, most physical properties, and especially transport of electrons and phonons, depart significantly from the ones observed in conventional metals and alloys that are characterized by smaller unit cells, containing just a few atoms. The conduction of heat for instance in an Al-Cu-Fe CMA of appropriate composition, although made of good heat conductors, is as low as in zirconia, a typical heat insulator used in aerospace industry [2].

Several types of CMAs exist, depending on the nature of the constitutive elements and their respective concentrations. The most widely studied so far are based on aluminum [3]. They comprise quasicrystals, which were first pointed out by Shechtman in the period 1982–1985 in metastable, melt-spun ribbons of an Al-Mn alloy [4, 5]. Later, the existence of stable quasicrystals was revealed by different groups, among which the most decisive contributions came from Tsai et al. who demonstrated that quasicrystals may be grown in various Al-based alloys at very specific compositions, but by slow cooling of the molten alloy [6–9]. A large research effort was dedicated to understanding better the crystalline structure of quasicrystals and its relationship to their properties, see reference 3 for a review of this work.

The challenge was indeed, and to a large extent still is, first to describe the atomic positions in quasicrystals (where are the atoms? as Bak used to write [10]) and secondly to discover the building principle that leads quasicrystals to abandon...
translational periodicity, although it is seemingly\(^1\) at work in the whole world of ordered solid matter known so far (why are the atoms where they are?). The first part of the challenge has been met very successfully and the new tools developed to match this goal have proven to apply to many complex materials, including the CMAs that we shall address in this book. This is not true as far as the second aspect of the challenge is considered. To the best of our knowledge, complexity is observed in metallic alloys, but no unifying principle has yet clearly emerged to show us why it is so in any given alloy, and help us design new alloys of controlled complexity based on a fully self-consistent theory. Empirical rules, and fragmentary understanding, nevertheless, do exist and will be explained in this book.

Most of this knowledge emerged from careful studies of a large variety of complex metallic alloys, which is the major focus of the present book. It started long ago, when the most famous chemist Linus Pauling was still a PhD student in the mid-1930s [12]. This research stopped, however, about 40 years later, when it appeared that the most complex crystalline structures known at that time could no longer be solved with the tools then available. The discovery of quasicrystals, which unfortunately arose in an undue controversy [13], forced crystallographers and physicists to reconsider very complex atomic architectures and revisit CMAs for their properties and potential applications. More than two decades after the discovery of quasicrystals, the crystallographic tools to describe complexity in metallic alloys were available. The moment had come to see whether the field of CMAs, to a very large extent unexploited until then, was offering a new frontier in condensed-matter physics or not.

### 1.2 Complex Metallic Alloy: What Is It?

A complex metallic alloy is characterized by (i) its chemical formula, (ii) the size of its unit cell, and (iii) the variety of atomic clusters that this unit cell contains. The composition often, but not always, is that of a ternary, or a quaternary, and so on, alloy, that is, a multicomponent alloy. Yet, quite a few binary complex crystalline compounds have been studied in depth in recent years, which led to the remarkable discovery of a stable binary quasicrystal [14]. The upper limit of the unit cell size is of course infinite in quasicrystals. It is more difficult to assess the lower limit. Conventionally, a crystal that contains a few tens of atoms in its unit cell is considered a CMA, which corresponds to lattice parameters of a few angströms. Very frequently, the atom clusters exhibit icosahedral symmetry. This leads to incorporation of Laves phases, with a small unit cell size and only 12 atoms per unit cell into the family of CMAs.

A simple definition of complexity in CMAs is difficult to express and different equivalent definitions may apply. For instance, the diffraction pattern of a CMA is characterized in reciprocal space by its many spots, some being close to the origin,\(^1\) A natural Al-Cu-Fe quasicrystal discovered recently in a million-year old rock tends to prove that Nature had discovered quasicrystals long before human beings [11].
and the closer as the size of the unit cell increases. If one is looking for a single parameter, the distance from origin to the first diffraction spot could be used. Theoretically, it would be equal to 0 in a perfect quasicrystal. However, due to the necessarily limited experimental resolution on diffracted intensities, the first measurable spot with nonzero intensity is located at some distance from origin, which opens a possibility to confuse a true quasicrystal with a high-order approximant. For this reason, we will rely on a more reliable definition in Section 1.2.2. We will see also in Section 1.2.3 how specific defects signal complexity in CMA.

1.2.1 Composition and Varieties

The best-studied example of a CMA system that comprises both quasicrystalline and crystalline CMAs is the Al-Cu-Fe system (for references, see ref. 3). An isothermal cut through the phase diagram is shown in Figure 1.1. Many different compounds appear: binary alloys comprise simple Al-Cu crystals, like the 0-A1_2Cu

![Figure 1.1](image.png)  
*Figure 1.1* Isothermal cut through the Al-Cu-Fe phase diagram in the Al-rich corner. See text for the labels of the compounds.

2) An approximant is a crystalline CMA the structure of which may be derived from the same high-dimensional lattice as the quasicrystal that lies nearby, in the same composition field.
phase with 16 atoms per unit cell (at/uc in the following), or more complex ones like the γ-brass Al₄Cu₉ compound with 52 at/uc (not visible on this diagram because it is located outside the concentration region drawn here). The nearly binary Al₁₀Cu₁₀Fe compound is labeled φ in this diagram. The letter η labels an hexagonal compound closely related to the B2-CsCl type β-phase that shows a broad stability region in the ternary system and plays an important role since it is the primary solidification phase that appears first when growth from the liquid state is applied [15]. Similarly, Al-Fe binary compounds comprise the λ-Al₁₃Fe₄ and μ-Al₅Fe₂ compounds, which are intermetallics of quite different complexity with, respectively, 102 and 12 at/uc.

The stable, ternary quasicrystal, marked ψ, shows up approximately in the middle of the diagram, in a narrow composition region located around Al₆₂Cu₂₅.₅Fe₁₂.₅ (at. %). Within the region labeled ψ, but not visible at this enlargement scale, coexist at least 3 high-order approximants of very similar compositions [16]. They contain hundreds of atoms per unit cell. In contrast, the much simpler ω phase, with 48 at/uc, lies only slightly apart from the previous composition region, and shows definitely different electron-transport properties [17].

Such a variety of compositions and structures in a metallic alloy system is a characteristic of CMA-forming alloys. It is an indication for the formation of a stable quasicrystal that has guided Tsai et al. in the hunt for these compounds at the beginning of the history of the field. Unfortunately, it does not supply us with a number that may be used to quantify complexity in a very simple way.

1.2.2 Complexity at a Glance

Indeed, we need a single number, preferably, that could possibly be used to correlate some, if not all, properties of a given alloy system to the complexity of its CMAs. This number does exist at least in Al-based CMAs, like the ones encountered in the Al-Cu-Fe phase diagram of the previous subsection. This is:

\[ \beta_C = \ln(N_{UC}) \]

where \( N_{UC} \) is the number of atoms in the unit cell.

By definition, \( N_{UC} \to \infty \) in a quasicrystal. However, since the size of the specimen is always finite, \( \beta_C \) is finite as well, and is close to \( \ln(N) \), where \( N \) is Avogadro’s number, that is, \( 23 \leq \beta_C \leq 55 \) depending on the size of the sample. We will take arbitrarily \( \beta_C = 23 \) in the following, which does not change our conclusions.

To exemplify, we show in Figure 1.2, two very different properties plotted as functions of \( \beta_C \) for a large number of Al-TM (TM: transition metal) CMAs of varying complexity according to the choice of TM and Al concentrations. In quite a few examples, a second TM’ element was added, like for instance in the Al-Cu-Fe ω-phase or in the quasicrystal. The first property, labeled \( n(E_F) \) is the density of Al 3p states obtained by soft X-ray emission spectroscopy (SXES) measurements at room temperature [18]. We will come back to this data in Section 1.3.1. The second
property is friction in vacuum against hard steel of the very same specimens, after correction for the plowing component of friction and noted $\mu_C$. This correction is explained later in this chapter (Section 1.4.3).

The two properties, which cannot be related a priori, show the same decreasing dependence with increasing complexity of the crystal (in this system). Furthermore, a ln–ln plot of the data of Figure 1.2 demonstrates that they vary according to a same power law of $\beta_C$, that is, $n(E_F)$ and $\mu_C \approx \beta_C^{-1/3}$ (Figure 1.3).

To the best of our knowledge, this provides one of the scarce but clear indications available so far that friction in vacuum between two metals is dominated by adhesion

Figure 1.2 Variation with complexity index of the density of Al3p states at the Fermi energy $E_F$ (left) and adhesion against steel in vacuum (right) for a variety of Al-TM CMAs. The data selected in the right hand side figure comes from CMA samples with nearly identical concentration of valence electrons, see Figure 1.20.

Figure 1.3 Log–log plot of the data shown in Figure 1.2, demonstrating the same power law dependence towards $\beta_C$. The dashed lines have a slope of $-1/3$. 
of electronic origin. Most presumably, the underlying mechanism is the formation of a hybrid band between d states in the steel pin and sp states in the CMA sample (as is often observed in the CMA itself, see Section 1.3.1).

1.2.3
Defects

Generally, in CMAs all types of defects known from simple metallic structures, can occur. This includes zero-dimensional defects, for example, vacancies and interstitials, and planar defects, for example, stacking faults and antiphase boundaries. Line defects such as dislocations also exist in CMAs, but, due to the particular structural properties of CMAs, require more detailed discussion.

As a basic structural feature, CMAs possess large lattice parameters. A direct consequence is that conventional dislocation-based deformation mechanisms are prone to failure. The elastic line energy of a dislocation is proportional to $b^2$, where $b$ is the length of the Burgers vector [19]. For most materials, Burgers vector lengths larger than about 5 Å are energetically unfavorable. Accordingly, perfect dislocations in CMAs, which frequently would require Burgers vectors exceeding 10 Å in length, are highly unfavorable and not likely to form. In common materials, dislocations with large Burgers vectors split into partials. However, for the case of very large lattice constants as in CMAs, splitting into a high number of partials, each possessing its individual energy cost would be required. Moreover, the corresponding planar faults, which necessarily have to be introduced as soon as partials are involved, cost additional energy.

On the other hand, it has been shown that CMAs, at least at high temperatures, are ductile and that in all cases studied dislocations mediate plastic deformation [20–23]. It is therefore a central question in CMA research, to explore the deformation mechanisms structure of the defects involved.

Furthermore, in some CMA structures, salient one-dimensional defects exist. These defects, referred to as “phason lines” do not exist in simple metals. Even though they are linear in character, they are not dislocations. Nevertheless, they are pivotally involved in the deformation process of some CMA structures (see below) but also in phase transitions between related CMAs.

As a result of the structural hindrances for the formation of regular dislocations, in many CMAs novel types of dislocations are formed. Taking advantage of structural features of the host CMA, they allow, via their particular construction, for the accommodation of Burgers vectors corresponding to energetically acceptable strain fields. Particular examples of such defects in CMAs are the metadislocations.

Metadislocations were discovered in 1999 [24] and are today known to exist in various forms in different CMA structures. They mediate the plastic deformation process in these CMAs, which additionally involves phason defects. Metadislocations were firstly observed in orthorhombic ε-phases. These are based on ε$_6$-Al-Pd-Mn [25], which has an orthorhombic unit cell (space group $Pnma$) with cell parameters $a = 23.541$ Å, $b = 16.566$ Å and $c = 12.339$ Å. The structure can be represented in terms of a tiling of flattened hexagons arranged in two different orientations. The
vertices of the hexagons are decorated with 52-atom clusters of local icosahedral order, the so-called pseudo-Mackay clusters.

The compound $\varepsilon_{6}\text{-Al-Pd-Mn}$ is the basic phase of a family of superstructures with equal $a$ and $b$ but larger $c$ lattice parameters referred to as the orthorhombic $\varepsilon$-phases. The most prominent of these possesses a $c$ parameter of 57 Å and has been termed $\varepsilon_{28}\text{-Al-Pd-Mn}$. Other superstructures with $c = 32.4$ Å, 44.9 Å, and 70.1 Å have been reported [26].

Figure 1.4 displays transmission electron micrographs of dislocations in a deformed $\varepsilon_{28}\text{-Al-Pd-Mn}$ single crystal. Figure 1.4a is taken under two-beam Bragg conditions using the (10 0 0) reflection close to the [0 1 0] axis (inset). A high density of dislocations is seen in end-on orientation. No stacking-fault contrast is seen in the image, that is, the dislocations appear to be perfect dislocations. Contrast-extinction analysis [27] shows that the Burgers vectors of the dislocations are parallel to the [0 0 1] direction, that is, they are pure edge dislocations. Figure 1.4b shows the same sample area imaged using a symmetric selection of reflections of the (0 1 0) zone axis (inset). Under these conditions, it can be seen that each dislocation position is decorated by a small area of bright contrast. Figure 1.5a shows one of the single dislocations at a higher magnification. It consists of a dislocation-like structure with six associated half-planes. Note, however, that the dislocation-like structure resides on a length scale that is larger than the atomic scale by about one order of magnitude.

Figure 1.5b is a schematic representation of the defect structure of Figure 1.5a in terms of a tiling description [28]. The dislocation core is represented by the dark-gray polygon in the image center. The upper and lower edges as well as the right-hand side of the figure are represented by a tiling composed of pentagons, banana-shaped nonagons, and flattened hexagons in two different orientations. This is the representation of the ideal $\varepsilon_{28}\text{-Al-Pd-Mn}$ structure [29]. The pentagon–nonagon pairs represent phason lines, which periodically arrange along the [1 0 0] direction and form planes referred to as “phason planes.”
On the left-hand side of the metadislocation core is a triangle-shaped area, the tiling of which consists of flattened hexagons in alternating orientations. This tiling represents the ideal $\varepsilon_6$-Al-Pd-Mn structure [25]. In the upper and lower vicinity of the $\varepsilon_6$-Al-Pd-Mn triangle, the phason-plane arrangement, which in the undistorted $\varepsilon_{28}$-Al-Pd-Mn structure forms straight (0 0 1) planes, relaxes around the $\varepsilon_6$'-Al-Pd-Mn triangle.

The Burgers vector of the dislocation can be determined as $\mathbf{b} = c/\tau^4(0\quad 0\quad 1)$ by forming a Burgers circuit around the dark-gray core. The Burgers-vector length amounts to 1.83 Å, that is, the dislocation is a small irrational partial. The complete defect structure is inseparably formed by the partial dislocation on the atomic scale and the dislocation-like structure on the larger length scale formed by the associated phason half-planes. The latter accommodate the partial dislocation to the lattice in such a way that the ideal $\varepsilon_{28}$-Al-Pd-Mn structure can be continued above and below the dislocation core. As a direct consequence, the defect structure as a whole can move through the lattice without introducing any additional planar defects. Later, other types of metadislocation with 4, 10, and 16 associated phason half-planes were discovered [30]. It was demonstrated that metadislocations mediate the plastic deformation process in $\varepsilon_6$- and $\varepsilon_{28}$-Al-Pd-Mn [20]. The mode of dislocation motion has not been directly identified, but strong evidence was found that the movement takes place by a pure climb process [31].

Closely related but structurally different metadislocations were observed in $\varepsilon$-type phases in the system Al-Pd-Fe [32]. Figure 1.6a is a micrograph of a metadislocation in $\xi$-Al-Pd-Fe. The metadislocation core is located in the lower-left part of the image. It is associated with three planar defects extending to the upper right (dark contrast), which can be identified as phason half-planes. A Burgers circuit around the metadislocation core reveals a closure failure of $1/2\tau^4 [1\ 0\ 1]$ in terms of the $\xi$ lattice, which corresponds to the metadislocations Burgers vector. The Burgers vector length is 1.79 Å. Figure 1.6b shows two metadislocations in the structure $\varepsilon_{22}$-Al-Pd-Fe. The left metadislocation is associated with five phason half-planes and that on the right with eight phason half-planes. In the areas directly below both metadislocation cores, regions of $\xi$ structure can be identified. The metadislocations in Figure 1.6 are typical
for monoclinic host structures. As for the case of the metadislocations in orthorhombic ε-phases described above, we find series of metadislocation with different numbers of associated phason half-planes, corresponding to different Burgers vectors. While for the orthorhombic ε-phases we find that the numbers of associated phason half-planes follow double Fibonacci numbers, for the monoclinic case we find single Fibonacci numbers. In a tiling representation, the metadislocation cores are for both types described by the same tiles, which of course, correspond to the same Burgers vector length with respect to the individual lattice constant.

In the orthorhombic Al$_{13}$Co$_4$ phase, metadislocations that are less closely related are found. Al$_{13}$Co$_4$ is an orthorhombic phase with space group $Pmn2_1$ and lattice parameters $a = 8.2$ Å, $b = 12.3$ Å, and $c = 14.5$ Å [33]. The main structural features are pair-connected pentagonal-prismatic channels extending along the [1 0 0] direction. Within the (1 0 0) plane, the structure can be matched by a tiling consisting of regular pentagons and rhombs, where the rhombs are arranged in an antiparallel manner.

Figure 1.7 displays a transmission electron micrograph of a deformed Al$_{13}$Co$_4$ single crystal [34]. A high density of dislocations (black arrow) and trailing planar defects (white arrow) can be seen. The dislocations have [0 1 0] Burgers vectors and [1 0 0] line direction, and their movement takes place in (0 0 1) planes. That is, the dislocations are of pure edge type and move by pure glide.

Figure 1.8a is a micrograph of the dislocation core at higher magnification. A tiling representing the unit-cell projection along the [1 0 0] direction is superposed. Rectangular tiles represent the orthorhombic Al$_{13}$Co$_4$ phase and rhomb-shaped tiles represent a closely related monoclinic modification [33, 35]. The dislocation core is localized in the open center, and the stacking fault stretches out to the right. It can clearly be seen that the planar fault consists of a slab of monoclinic structure within the otherwise orthorhombic lattice. Figure 1.8b is a schematic of the defect in terms of a pentagon tiling [36]. The superposed unit-cell projections correspond to those
shown in the experimental image. The dislocation core is represented by the dark-gray tile. The planar defect corresponding to the slab of monoclinic phase stretches out to the right and is represented by a parallel arrangement of pentagon and rhomb tiles, while the surrounding orthorhombic phase is represented by an alternatively oriented arrangement of pentagon and rhomb tiles.

Other types of metadislocations were observed in the orthorhombic Taylor phases based on Al$_3$Mn. A review, describing all types of metadislocations in great depth, is given by Feuerbacher and Heggen [37].
An apparently different mechanism was observed in C$_2$-Al-Pd-Fe. The structure of this phase was determined by Edler et al. [38]. It is cubic with a lattice constant of 15.5 Å and a unit cell containing 248 atoms. The structure can be described in terms of icosahedral cages generated by Pd atoms. These cages are alternatively filled with two different cluster motifs. The resulting two types of clusters are distributed on a cubic lattice such that the different fillings lead to a face-centered ordering.

Figure 1.9a shows a bright-field Bragg-contrast image of a typical defect arrangement in plastically deformed C$_2$-Al-Pd-Fe. The presence of dislocations attached to planar faults showing fringe contrast is clearly seen. The inset presents a contrast-enhanced enlargement of the boxed area, showing two dislocations separated by about 300 nm terminating a stacking-fault fringe contrast. Figure 1.9b shows a high-resolution TEM image of such an arrangement along the [−1 1 0] direction. The defect appears as a dumbbell-shaped object with two almost rectangular-shaped extremities. The stacking fault is seen in edge-on orientation. The terminating dislocations, marked by white arrows, are located at the upper ends of the rectangular brighter-contrast areas.

The defect can be analyzed by back-transform Fourier filtering analysis. This yields a Burgers vector $a_0/2 [0 0 1]$ for both terminating dislocations. The whole arrangement hence has Burgers vector $a_0 [0 0 1]$ and consists of a perfect [0 0 1] dislocation with a Burgers vector length of 15.5 Å, which is split into two energetically more favorable partials with Burgers vector lengths of 7.8 Å at the cost of a stacking fault between the latter.

Fourier filtering analysis reveals that the rectangular bright-contrast areas are of body-centered structure, that is, a structure locally differing from the face centered host. Phase-diagram investigations [39] revealed that in the Al-Pd-Fe system indeed a
body-centered phase, C\textsubscript{1}-Al-Pd-Fe, exists in the compositional range around Al\textsubscript{63}Pd\textsubscript{31}Fe\textsubscript{6}. This phase possesses a slightly smaller lattice constant of 15.4 Å.

These findings are consolidated in the following interpretation: In order to lower the elastic line energy of the perfect dislocation the latter splits into two partials. These, however, still possess rather large Burgers vector lengths of 7.8 Å, which have to be accommodated by the structure. The experimental findings suggest that it is energetically favorable to transform a small portion of the structure, which is lying in the compressive part of the dislocation strain field, to a body-centered structure possessing a slightly smaller lattice constant. By this means, the dislocation with the large Burgers vector can be more easily accommodated into the face-centered structure at the cost of a portion of “wrong” structure considering the composition of the crystal.

In CMAs, hence, dislocations of different nature from that in simple metals occur. Besides metadislocations in a number of CMA phases, we also find other unusual mechanisms, such as the dislocations in cubic Al-Pd-Fe described above. While these mechanisms at a first glance seem completely different, they have one major common property: in all cases we find that accommodation of the dislocation in the host structure involves a local area of different but related structure. This locally differing structure occurs in the form of a slab in the wake of the moving dislocation (e.g., in the case of Al\textsubscript{13}Co\textsubscript{4}) or in the form of a bar around the dislocation core. We should, however, note that in some CMA phases investigated, for example, the Samson phase β-Al\textsubscript{3}Mg\textsubscript{2}\textsuperscript{27} or the Bergman phase in the system Mg-Zn-Al [40], rather conventional deformation mechanisms, involving ordinary partial dislocations trail- ing stacking faults, have been observed.

1.3 Complex Metallic Alloy: Why Is It Complex?

For many years, the key point in understanding CMAs, and especially quasicrystals, was to know where the atoms are [10]. This question is now solved to a very satisfactory degree [41], using various techniques derived from high-dimensional crystallography and, as often as possible, comparison to a known, high-order approximant when it exists [42]. Nowadays, the central question is to understand “why the atoms are where they are,” which by the way is a question that is simply not solved in all crystals of simpler structure known so far. We address this issue in the following section from the electronic structure standpoint, in a way that is very much reminiscent of the early works by Hume-Rothery [43], Jones [44] and Blandin [45] and in more recent years Friedel and Dénoyer [46] and Mizutani [47].

1.3.1 Electronic Densities of States and Hume-Rothery Rules

Does the particular atomic structure of complex metallic systems engender characteristic features in their electronic structure? A theoretical approach is most often pretty uneasy because of the too large number of atomic sites in the unit cell that, in addition, may not be all fully occupied. Information is gained from experimental
results derived from resistivity and specific heat measurements or densities of states (DOS) investigations using spectroscopic techniques, but results are available only for a restricted number of these compounds. Hence, to figure out what the electronic structure may be in CMAs, one may rely on data obtained either for stable quasicrystalline compounds (QCs), which we shall consider as the ultimate state of complexity in CMAs, with a single unit cell containing an infinite number of sites, or their approximants, also with large unit cells, but of finite size.

For quasiperiodic lattices, theoretical studies of the energy spectrum pointed out that the wavefunctions should be critical, hence the corresponding electronic states differ from conventional systems since they are neither extended nor localized [48, 49]. Due to the lack of periodicity, exact DOS calculations cannot be carried out for QCs. However, they are available for structures whose atomic order mimics the local arrangement of the QCs [50–52] and in some cases, also for true QC systems owing to the Rietveld method applied to experimental diffraction patterns combined with first-principles methods [53]. Many calculations have been also carried out for series of Al-TM conventional intermetallics [54, 55]. In all cases, a pseudogap was found at or nearby the Fermi energy ($E_F$).

Hume-Rothery found empirically that in many systems such as Cu-Zn, Al-Cu, and so on, for specific values of the valence electron to atom ratio ($e/a$), there exist alloys displaying different crystal structures that do not behave as free-electron systems do, but are stabilized owing to the creation of a depletion in the DOS at $E_F$, namely a pseudogap [43]. These specific alloys are denoted Hume-Rothery (H-R) phases. The mechanism by which such a pseudogap occurs may be summarized as follows [56]. Electronic waves in the alloy are scattered by the Bragg planes of the Brillouin zone. This mechanism opens up gaps in reciprocal space. For specific electron concentrations, the Fermi sphere overlaps with the Brillouin-zone boundary, which in turn produces a depletion in the DOS at the Fermi energy after integration over all directions in reciprocal space of the scattered waves. As a consequence, electronic states from the top of the valence band (VB) are repelled towards lower binding energies as shown in Figure 1.10, thus stabilizing the crystal structure for that specific electron concentration.

![Figure 1.10](image-url)  
*Total density of states (DOS) of a free-electron system (dotted line) and of a H-R alloy (full line).*
Friedel and Dénoyer [46] noticed that (i) many quasicrystals and approximants are made from elements with small differences in atomic radii and electronegativities and (ii) there is a large number of spots, several with high intensity, in their X-ray diffraction patterns the position of which in reciprocal space demonstrates that the Hume-Rothery rule introduced above is obeyed. Actually, a pseudo-Brillouin zone (PBZ) can be constructed from the location of the most intense peaks in reciprocal space, although a true Brillouin zone cannot be defined due to the loss of translational periodicity. This assessment was successfully taken as a thumb rule for the search of new stable quasicrystalline compounds and, indeed, many QCs and approximants were found this way with $e/a$ values around 1.86 e$^-$/at (electrons per atom) and 2.04 e$^-$/at, mainly in Al-based systems as for example Al-Pd-Mn, Al-Cu-Ru, Al-Mg-Zn, ... QCs [7–9].

The pseudogap at the Fermi energy is perhaps one of the most emblematic features of QCs as well as of CMAs and is of great importance to interpret many of their physical properties [3, 57, 58]. Its existence was checked experimentally for a number of Al-based QCs and CMAs as well as for conventional H-R crystals using spectroscopic techniques among which soft X-ray emission spectroscopy (SXES). SXES scans separately occupied partial and local DOSs in a compound, whatever it is [18, 59–63]. It was ascertained that the intensity of the Al 3p states distribution at $E_F$ (I(Al3p/$E_F$) reflects the metallic character of the specimens and is directly connected to the importance (depth and width) of the pseudogap [18].

Furthermore, it was established that the Hume-Rothery mechanism alone cannot explain the formation of the pseudogap since in genuine H-R alloys such as 0-Al$_2$Cu or $\varphi$-Al$_{10}$Cu$_{10}$Fe, it is rather faint as compared to Al-based approximants and QCs that contain the same transition metals. This is shown in Figure 1.11 as a plot of I(Al3p/$E_F$) in various simple and complex phases versus the $e/a$ ratio [64]. The data is the same as the one in Figure 1.2, but is shown versus the $e/a$ ratio that is directly related to the position of the CMA specimen in the composition field, assuming a contribution to the valence band of +3 electrons for Al, +1 for Cu and a negative valence of Fe of $-2.6$ e$^-$/at. Clearly, I(Al3p/$E_F$) is almost constant for the true Al-Cu H-R alloys and decreases progressively when going to approximants and QCs, a signature of increasing complexity of the lattice, as we pointed out earlier in this chapter. From the study of all electronic distributions in the VB of these samples, it was pointed out that sp states at the top of the VB are mixed to TM d states in agreement with the above-mentioned DOS calculations done on series of conventional Al-transition metal (TM) alloys [18].

Further studies of complex alloys highlighted the importance of hybridization between p and d states [63]. A beautiful assessment of the respective weights of H-R and hybridization mechanisms was given recently by Mizutani and coworkers [65–68] while studying a series of $\gamma$-brass phases to determine whether they are stabilized following or not the e/a rule (or H-R mechanism). The authors pointed out that the H-R stabilization mechanism produces a pseudogap across $E_F$ as a result of a resonance between electron waves and particular sets of lattice planes that differ from each other, depending on the studied specimens. They also pointed out that $e/a$ does not keep the canonical 21/13 value for all the $\gamma$-brass samples, but rather varies from 1.6 e$^-$/at for example in Cu$_9$Al$_4$ to 1.8 e$^-$/at in Fe$_7$Zn$_{11}$ and
1.46 e⁻/at in Al₈V₅. For this latter alloy, using LMTO-ASA DOS calculations, they clearly demonstrated the key role played by V 3d – Al 3p hybridization in the formation of the pseudogap across the Fermi level (Figure 1.12, left side). This theoretical result was confirmed experimentally, again using soft X-ray emission spectroscopy, as displayed in the same figure (Figure 1.12, right side) [63]. The interaction between the Al and TM states can be viewed as a Fano-like interaction, namely an interaction between extended and localized states, as described by Terakura [69].

To summarize, in CMAs made of Al (or Mg) alloyed with other elements among which TMs, the pseudogap present in the DOS at \( E_F \) results from the combination of two mechanisms, on the one hand, the so-called H-R mechanism and on the other hand, hybridization (interaction) between extended and localized states at \( E_F \) and nearby, which results in the presence of states with a localized character at the top of the VB.

1.3.2

Self-Hybridization in Al-Mg Alloys

What is the situation in CMAs made only of sp elements, for which there are normally no real localized states at the top of the VB? Let us consider the case of an emblematic...
CMA, namely the so-called Samson phase [70]. This is cubic $\beta$-Al$_3$Mg$_2$, with cell parameter $a = 28.24$ Å, containing 1168 at/uc distributed over icosahedra and Friauf polyhedra. Many atomic sites are not fully occupied, which induces an important degree of disorder. As far as transport properties are concerned, this compound behaves similarly to a simple mixture of the pure metals. This result is to be contrasted to the extremely complex structure of the Samson phase ($\beta C = 7.07$), which raises the question to understand why the two simplest ways of staking metal atoms (Al is fcc and Mg is hcp) end at this specific composition in such a complex architecture. So, what is the electronic structure? Clearly, exact DOS calculations are extremely difficult to carry out or even impossible in this system, at least for the moment. On the contrary, experiments, again using X-ray emission spectroscopy that analyzes separately Al and Mg contributions to the VB, may give qualitatively valuable information about the bulk specimen.

The data presented in Figure 1.13 may be summarized as follows [71, 72]. First, Al 3p and Mg 3p states overlap over the extent of the VB, which points to the strong covalency in this energy range of the VB. However, chemical bonding is not so simple, since the maximum of the Mg 3p curve coincides with a depletion of the Al 3p curve, which indicates some degree of repulsion existing between Mg and Al 3p states in this energy range [69]. Secondly, the intensity of both Al and Mg 3p curves at $E_F$ is about $25 \pm 2\%$ of the maximum intensity (set to 100%) and the edges are shifted towards lower binding energies since they are distant from $E_F$ by $0.3 \pm 0.05$ eV at half-maximum intensity. Note that in both pure metals, the intensity at $E_F$ is 50% of the maximum intensity and the edges very steeply crossing the Fermi level axis at half-

Figure 1.12 Left: DOS calculations by the LMTO-ASA method for Al$_8$V$_5$ with (top panel) and without (low panel) accounting for the V3d-Al 3p hybridization. In the low panel, clearly the pseudogap has disappeared as compared to the top panel. Right: Partial DOS as obtained from SXES experiments. The various distribution curves are normalized to their own maximum intensity. The mixed Al3p-V3d states are found at about 2 eV below $E_F$ whereas in the calculation the V states are set at 1 eV below $E_F$. 

1 Introduction to the Science of Complex Metallic Alloys
maximum intensity of their respective distribution curves. All these observations suggest that in cubic $\beta$-Al$_3$Mg$_2$, a faint pseudogap is present at $E_F$. The maximum of the Al 3p curve is found at the same energy as a depletion of the Al 3s,d curve and of a plateau on the Mg 3s,d curve, indicating repulsive interaction between the Al 3p and the 3s,d states.

The most striking feature is the rather narrow peaks present at about 1.5 eV below $E_F$ in the 3s,d distribution curve for both Al and Mg in the compound. These narrow peaks are distant by about 0.2 eV from each other, which suggests that some repulsion takes place between the spectral distributions at the top of the VB, whereas the peak in the Al 3s,d curve overlaps totally the Al 3p and Mg 3p curves. Here, we shall mention that SXES studies of compounds containing Al and two TM that are neighbors in the classification of the elements, have shown that the d states are located at the top of the VB and repel each other [62, 63]. Thus, the narrow shapes of the Al and Mg 3s,d curves close to $E_F$, their slight separation along the binding energy scale and the presence of the faint pseudogap suggest that these states are to some extent localized, namely have a d-like character. Let us mention that in fcc Al, as well as in hcp Mg, only a very small fraction of states with a d-like character is found near $E_F$ [73]. In $\beta$-Al$_3$Mg$_2$ we see that the proportion of the d-like states is strongly enhanced, in line with the results described in the previous section where we reported that in Al-TM CMAs, localized states present at the top of the VB hybridize to sp states for a pseudogap is formed and stabilizes the system. Therefore, the mechanism in $\beta$-Al$_3$Mg$_2$ is not the same as in compounds containing a TM bringing d states to the VB.

Instead, achieving stabilization of the $\beta$-Al$_3$Mg$_2$ system is a little more complex. First, Al and Mg states self-hybridize in such a way that states with a localized character are found at the top of the VB. Secondly, the localized Al and Mg states thus formed slightly repel each other and interact with Al-Mg covalently bonded states. It is
interesting to mention that the same mechanism occurs in other Al-Mg compounds, but of lesser complexity such as the Zn$_2$Mg Laves phase ($N_{UC} = 12$, $\beta_C = 2.48$), the low-temperature variant of the Samson phase [74], or the Al-Mg-Zn Bergman phase ($N_{UC} = 148$, $\beta_C = 5$). In these latter compounds, the same peak of localized d states is pointed out by SEXS at the same energy position, but with intensity (amplitude) varying smoothly with the complexity index and almost unchanged width [72]. The result of this analysis is presented in Figure 1.14. It has an interesting issue, namely that Nature selects preferably a complex structure when the self-hybridization mechanism is at work, although far simpler atom packings exist nearby in the phase diagram (not taking into account the role of configuration entropy that is able to further reduce the free energy of the system).

1.4
A Brief Survey of Properties

1.4.1
Transport Properties

Resistivity measurements performed for specimens with increasing structural complexity up to quasicrystalline compounds have pointed out a different behavior
from that of conventional alloys. This is exemplified in Figure 1.15 as a plot of the variation of the electrical resistivity against temperature for a series of Al-based alloys. The curves at the bottom of the figure, with resistivity below 100 $\mu\Omega$ cm, correspond to structurally simple alloys, namely CsCl-cubic Al$_2$Cu-B and tetragonal $\omega$-Al$_7$Cu$_3$Fe. They show a normal increase of the resistivity with temperature, characteristic of conventional alloys and metals. The curves in the middle of the figure were obtained from approximants of quasicrystalline compounds. Their resistivity values are much larger than for conventional alloys and the variation with temperature is almost zero or very weak. In strong contrast to normal alloys, genuine quasicrystals exhibit
resistivity values at low temperature that are high to very high and the variation of the resistivity with increasing temperature is of opposite sign to that of simple alloys and metals [58].

Hence, attention was paid to the electronic properties of CMAs in relation to their structures. Magnetic, electrical and thermal transport properties have been probed so far for series of CMAs [75]. Recent data refer to Al₄TM and Al₁₃TM₄ families whose atomic structure can be viewed as a stacking of flat and corrugated atom layers with structural complexity and unit cell size increasing from Al₄TM to Al₁₃TM₄ families. For completeness, the investigations were carried out perpendicular as well as along the stacking direction. These data are detailed in Chapter 3.

Basically, magnetic susceptibility, electrical resistivity, thermoelectric power, Hall coefficient and thermal conductivity all displayed anisotropic behavior that is more marked with increasing structural complexity from Al-Ni-Co to Al₁₃Co₄ and Al₄(Cr,Fe). The temperature coefficient is of Boltzmann-type in Al-Ni-Co and Al₁₃Co₄ for all crystallographic directions and non-Boltzmann as far as the temperature-dependent in-plane resistivity is concerned for Al₄(Cr,Fe). The thermal conductivity of the same specimens behaves similarly to the electric conductivity. It is about one order of magnitude lower when measured along the stacking axis than in-plane [76]. The Hall coefficient is also anisotropic. It is the lowest when the external field is applied along the stacking axis and higher when it is applied in-plane. However, no clear connection with structural complexity was evidenced in these series of samples. All these investigations pointed out strong differences in the respective contributions of the lattice and conduction electrons. They led to the conclusion that the anisotropy of the atomic structure of CMAs extends to their electronic properties, thus departing from those of conventional alloys and their elemental constituents. These results are detailed in Chapter 3.

1.4.2 Surface Physics and Chemistry

The physical and chemical properties of the surfaces of CMAs depend on their preparation, namely whether it is a clean surface worked out in ultrahigh vacuum (UHV) or a “dirty” surface kept in ambient atmosphere with an important contribution of the native oxides lying above the top layers of the CMA material.

The outermost layers of clean CMAs surfaces (including quasicrystals) as prepared in UHV by successive cycles of sputtering and in situ annealing are similar to simple bulk terminations with steps and islands. So far, no reconstruction of the surface and no chemical segregation effects were observed on highly complex CMAs. The atomic density is high and the topmost layers host the elements that have the lowest surface energy. This latter characteristic governs nucleation and growth on CMA surfaces used as templates for nanostructuration of foreign atoms.

The electronic structure of such sputtered-annealed CMAs surfaces has been investigated using several spectroscopic techniques. A main issue is that the pseudogap that exists at the Fermi level in the electronic density of states of the bulk specimen is also present in the surface top layers. However, this is no longer true for surfaces obtained from mechanical fracture in UHV with no further treatment.
Actually, such cleaved surfaces display a more metallic character, as shown by the reduction of the importance of the pseudogap with respect to the bulk sample. Band gaps have also been predicted by theoretical means in the phonon density of states, but this is still a matter of experimental investigations. These characteristics of the electronic and phononic structures at the surface of CMAs influence physical properties such as adhesion, friction and energy dissipation [77]. Chemical reactivity is also affected by the electronic structure and atomic structural complexity, but to a far lesser extent.

Oxidation in UHV of CMA surfaces shows selective oxidation of Al and the formation of a passive amorphous overlayer that is similar to the one that forms on pure Al. The thickness of this oxide layer depends on the conditions under which oxidation is carried out [78]. Note that the oxide layer formed on Al-Cr-Fe CMAs after water immersion is relatively thin, giving this CMA a significant corrosion resistance, especially with respect to the action of water [79].

Wetting by ultrapure water of Al-based CMA surfaces kept in ambient air and cleaned using a strict protocol avoiding contamination was studied by measurements of contact angles. Strong differences were pointed out from sample to sample, despite their outermost oxide layer being the same from the chemical point of view (Figure 1.16). It was concluded [59] that the reversible adhesion energy of water

![Figure 1.16](image_url)

**Figure 1.16** Variation of the reversible adhesion energy of water, $W_{H2O}$, against $n^2/t^2$ where $n = n(E_F)$ is the intensity of the Al $3p$ partial DOS at $E_F$ and $t$ is the oxide thickness. The two straight lines correspond to specimens with different contributions of 3d states at $E_F$. The line with the largest slope corresponds to Al–Cr–Fe(–Cu) samples, whereas the other is for Al–Cu(–Fe) specimens. The open symbols located on the y-axis are for Teflon (diamond) and alumina (square). They define, respectively, the lowest and largest values that can be observed with the present set of Al-based samples. The inset presents an enlargement of the data in the region $n^2/t^2$ below 0.003.
(\(W_{H_2O}\)) deduced from contact angle depends on the Al 3p density of states at the Fermi level of the bulk CMA substrate and on the inverse of the squared thickness of the oxide layer. Using image force theory, the wetting properties of the oxidized surfaces of Al-based CMAs appeared to be dependent on long-range forces between the dipole sitting on water molecules above the oxide top layer and their image dipoles developed into the conduction sea, far beneath the surface oxide. For the \(i\)-Al-Pd-Mn quasicrystalline phase, the oxidation, low adhesive properties and reduced surface reactivity as compared to pure Al were found to be consistent with the more ionic character of alumina that grows on this sample in ambient air [80]. It was also found that the oxidation kinetics of CMAs significantly departs from that of classical intermetallics [81]. In addition, the adsorption behavior of molecules other than oxygen or water suggests that CMAs surfaces can be more reactive than their pure metal constituents or related conventional intermetallics.

The high chemical reactivity of CMAs makes them good candidates for catalysis purposes. Actually, the performance of powdered quasicrystals was investigated for several specific catalytic reactions after various chemical treatments. It has been shown that, for example, Al-Cu-Fe or Al-Pd-Mn CMAs are good candidates for replacing at low cost, expensive catalysts that are necessary to the chemical industry [82].

1.4.3 Surface Energy

Surface energy is an essential property of a material. It determines the equilibrium shape of a single crystal, it is directly related to its cleavage energy, it is involved in the height of the crystal nucleation barrier when the crystal grows from the liquid state, it is related to its adhesion energy to another solid, and so on. It is, however, very difficult to measure experimentally and as far as CMAs are concerned, it is nearly impossible to compute owing to the limited power of present computers. A variety of experimental facts, based on friction measurements or on contact-angle measurements of small droplets deposited at the surface of CMAs, indicates that the surface energy of CMAs with large unit cell may be characterized by a reduced surface energy. Experiments performed in ultrahigh vacuum show the same trend, namely that the surface energy of icosahedral compounds might be much smaller than that of the constituent species.

A series of pin-on-disk friction experiments performed in high vacuum allows us to quantitatively estimate the surface energy of a large number of CMAs [3, 83]. A pin-on-disk experiment is housed in a vacuum chamber in which the residual pressure of oxygen is small enough to forbid the growth of a complete oxide layer between two successive passages of the indenter. Under such conditions, and if the applied load is small enough to produce no third body, or equivalently, if friction is performed at equilibrium, friction takes place between the two naked bodies (pin and surface of interest) after just a few rotations of the disk during which the native oxide layer is destroyed by the contact and escapes from the trace due to the rotation of the sample. The friction coefficient is given by \(\mu = F_T/F_N\), where \(F_T\) stands for the force that works against the movement of the sample relative to the pin, in the
plane of the contact, and $F_N$ is the applied load. To first order, for hard enough samples, we may write:

$$\mu = \alpha/H_V + \beta W_{SP}$$

with $H_V$, the (Vickers) hardness of the disk material, $W_{SP}$ the work of adhesion between surface of interest $S$ and pin $P$ and $\alpha$ and $\beta$, two fit parameters that can be determined experimentally for that specific experimental setup, using materials of known, or measurable, hardness and surface energy (see why below). Assuming friction does indeed take place at equilibrium, which can easily be ascertained after the end of the experiment by inspection of the trace, $W_{SP}$ becomes the reversible adhesion energy between $S$ and $P$:

$$W_{SP} = \gamma_S + \gamma_P - \gamma_{SP}$$

with $\gamma_S$ and $\gamma_P$ the surface energy, respectively, of the studied CMA surface and pin, and $\gamma_{SP}$ the interfacial energy developed between (naked) $S$ and $P$ bodies.

In a very crude assumption, we will take the term $\gamma_P - \gamma_{SP}$ equal to 0, which leads to an overestimate of $\mu$ by combining the equation above to the previous one:

$$\mu \geq \alpha/H_V + \beta \gamma_S$$

and therefore estimate the upper limit of the surface energy of the CMA specimen:

$$\gamma_S \leq (\mu - \alpha/H_V)/\beta$$

Despite this model being very crude, compared to more sophisticated ones published in the literature [84], it turns out to fit very satisfactorily the hardness and surface energy of many reference samples like transition metals, window glass, aluminum, aluminum oxide, and so on, which were used to calibrate the pin-on-disk apparatus used in the present study, thus delivering reliable values for $\alpha$ and $\beta$ (Figure 1.17). It must be stressed, however, that a few metals, like Co and W, do not obey the same simple model, essentially because the sticking coefficient of oxygen on those metals is so high that friction is always lubricated in the conditions of the experiment, and therefore forbids naked surfaces to come into contact.

Application of the previous equation to CMAs of unknown $\gamma_S$, but easily measurable hardness, delivers an upper value for their surface energy [83]. The results are summarized versus the experimental $m$ data in Figure 1.18. They are consistent with other experimental data supplied by ultrahigh vacuum growth experiments [85] and show that the surface energy of a quasicrystal of high crystal perfection is smaller than that of its pure constituents by a factor comprised between 2 (Al) and 4 (Cu, Fe).

Furthermore, the term $\mu_C = \mu - \alpha/H_V$ represents the adhesive part of friction, when $\mu$ is corrected for the mechanical deformation of the specimen under the stress developed by the contact to the pin. Relevant values of $\mu_C$ were presented earlier in this chapter in the right side of Figure 1.2 for a series of Al-Cu-Fe CMAs of varying crystal structure and complexity. Another view at the adhesive part of friction against hard steel in vacuum is given in Figure 1.19 as a function of the partial densities of Al 3p, Al 3s,d and TM 3d states probed separately at the Fermi energy by XSES. The
Figure 1.17 A set of pin-on-disk experiments in vacuum allows us to measure the friction coefficient $\mu$ against hard steel for various reference samples of known hardness and surface energy. Right: the plot shows that $\mu$ values calculated according to Equation 1.1 fit very well the experimental data, except when the hardness is small (arrow) since Equation 1.1 diverges when $H_v \to 0$. Left: same data, from which calibration parameters $\alpha$ and $\beta$ applicable to our specific experiment are deduced with satisfactory accuracy.

Figure 1.18 Summary in a single chart of all upper limits of the surface energy data deduced from friction experiments in vacuum against hard steel. The lower data is for an Al-Cu-Fe quasicrystal of high lattice perfection and falls in the range $0.5-0.6 \text{ J m}^{-2}$, well below the surface energy of the pure constituents (Al: $1.2 \text{ J m}^{-2}$; Cu: $1.8 \text{ J m}^{-2}$; Fe: $2.4 \text{ J m}^{-2}$). The other data are for CMAs of decreasing complexity and increasing density of d states at the Fermi level (see below).
CMA crystals are all of about the same complexity and belong to the B2 CsCl-type of cubic phases. The overall trend observed on the figure is that the adhesive part of friction increases with increasing TM 3d DOS in the CMA sample, whereas it decreases with increasing Al 3p and Al 3s,d intensities. Since the DOS in the pin is determined by the nature of the hard steel used for the pin ball, this behavior is equivalent to that expected from the formation of a band between CMA sample and pin when the two bodies come into contact.

The tendency to decrease adhesion in vacuum (once more, against hard steel) with the filling of the band is further exemplified in Figure 1.20 where we show an overview on all surface energy data gained from the same specimens as in Figure 1.18, but plotted as a function of VCE, the total number of valence electrons of the sample. The surface energy decreases with increasing VCE, until a minimum is reached at VCE = 8 e⁻ /at. Beyond this value, a copper-rich sample and fcc Cu itself show the opposite trend. It is worth noting that the quasicrystal in this family of CMAs (star in Figure 1.20) is found significantly below the other specimens. This result, again, stresses the electronic origin of adhesion in vacuum between the solids considered herein. Empirical rules may be derived from the present study to optimize the choice of materials that are placed in contact under severe load, whereas vacuum hinders the formation of a diffusion barrier at the contact interface. We will come back to this aspect later in this chapter.

1.4.4 Plasticity

The plasticity of CMAs is a novel field of materials science. To date, only a very limited number of different CMA phases have been experimentally investigated. It is a
common property of all these materials that they are brittle at room temperature. Ductility sets in at temperatures of the order of 70% and higher of the melting point of the individual materials. This is a feature discriminating CMAs from essentially all other simple crystalline metals – the latter typically show ductile behavior at room temperature and even below. In this respect, the plastic behavior of CMAs rather resembles that of covalently bond crystals such as for example, silicon.

In the following, we will discuss experimental results on three CMA phases, \( \varepsilon \)-Al-Pd-Mn, \( \beta \)-Al\(_3\)Mg\(_2\), and Al\(_{13}\)Co\(_4\). The phases \( \varepsilon \)-Al-Pd-Mn and Al\(_{13}\)Co\(_4\) are orthorhombic and have 320 and 102 atoms per unit cell, respectively. Their structures were described in Section 1.2.3. The compound \( \beta \)-Al-Mg is cubic, space group \( Fd\bar{3}m \). We already mentioned that the lattice parameter is \( a = 2.82 \text{ nm} \) and the unit cell contains about 1168 atoms \([70]\). The coordination polyhedra in the structure comprise 672 icosahedra (ligancy 12), 252 Friauf polyhedra (ligancy 16), 24 polyhedra of ligancy 15, 48 polyhedra of ligancy 14 and 172 more or less irregular coordination shells of ligancy 10–16. Because of incompatibilities in the packing of the Friauf polyhedra, this structure features a high amount of inherent disorder, which is apparent as displacement disorder, substitutional disorder and fractional site occupation.

Figure 1.21 shows the stress–strain curve of an \( \varepsilon \)-Al-Pd-Mn sample, deformed at 700 °C with a strain rate of \( 10^{-3} \text{ s}^{-1} \). The compression axis was chosen parallel to the \([0 1 0]\) lattice direction. For a discussion of the main features of the stress–strain curve, ignore the three sharp dips, which are the result of stress-relaxation tests to be discussed below. The course of the curve is at the positions of the relaxation dips interpolated by dotted lines. At very small strains \( \varepsilon \), the curve shows an almost linear behavior. This is the elastic regime, where the deformation is reversible and,
according to Hooke's law, the stress $\sigma$ is proportional to the strain. Plastic deformation sets in at about 0.70% strain, where first deviations from a linear course occur. At 1% strain the curve reaches an upper yield point at about 350 MPa. Subsequently, the stress decreases down to a value of about 280 MPa, where it reaches a lower yield point at about 2.5%. After the lower yield point, the stress–strain curve goes through two further stages. First, from about 3 to 5% strain, the stress decreases with strain, that is, the material shows a work-softening stage. Second, from about 5% to the termination of the experiment at 8%, the stress–strain curve is essentially horizontal. In this stage, the material is in a dynamic equilibrium, corresponding to a steady state where hardening and softening processes in the microstructure balance.

Figure 1.22 displays a set of stress–strain curves of Al$_{13}$Co$_4$ samples, deformed along the $\langle 6 4 5 \rangle$ direction at a strain of $10^{-5}$ s$^{-1}$ and temperatures between 650 and 800 $^\circ$C [23]. Each curve shows signatures of additional temperature cycling tests and a stress-relaxation test, marked “TC” and “R,” respectively, in the uppermost curve. The corresponding results will be considered below.

At all temperatures the curves have common qualitative features. After the elastic regime, a strong yield-point effect is observed in the strain range between 0.25 and 0.55%. At 700 $^\circ$C, for instance, a stress difference as large as 45% between the lower and upper yield stress was measured. Additional yield-point effects are seen after the temperature changes and after stress relaxation. At high strains, above about 2%, the curves show an almost constant flow stress or, at some temperatures, a very weak work-hardening stage. The deformation behavior is strongly temperature dependent: the stress strongly decreases with increasing temperature, leading to high-strain flow stresses between about 320 MPa at 650 $^\circ$C to 120 MPa at 800 $^\circ$C.

Figure 1.23 displays stress–strain curves of $\beta$-Al$_3$Mg$_2$ samples at $10^{-4}$ s$^{-1}$. The black curves represent deformations of single crystalline samples along the $[1 0 0]$
direction, the gray curves represent deformations of polycrystalline samples (grain size about 20 μm). Temperature changes and relaxations were carried out during most of the experiments. The single-crystal deformations show similar features to those of Al$_{13}$Co$_4$, with a generally smaller yield-point effect. The polycrystals deformations, on the other hand, show considerably different behavior. The yield points are much broader, the curves show work softening, and the high-strain flow stresses are considerably smaller than for the single-crystalline case. Also, the single-crystalline samples can be deformed at temperatures down to about 225 °C, while the polycrystals are ductile only above 300 °C.

Figure 1.22  Stress–strain curves for single grains of Al$_{13}$Co$_4$ deformed at various temperatures as indicated.

Figure 1.23  Stress–strain curves of β-Al$_3$Mg$_2$ at different temperatures as indicated.
The activation parameters are determined by dedicated incremental tests, that is, stress-relaxation tests (R in Figure 1.22) and temperature changes (T in Figure 1.22). Figure 1.24a displays the activation volume of \(\varepsilon\)-Al-Pd-Mn, determined by stress relaxation as a function of stress. The activation volume is strongly stress dependent. It decreases with increasing stress, following a hyperbolic curve. The absolute values vary within the range of about 0.5–2 nm\(^3\). This stress dependence and the absolute values of \(V\) are typical for CMAs. Let us compare different CMA phases for a given stress value of 300 MPa: Values of \(V = 0.45\) nm\(^3\) (\(\varepsilon\)-Al-Pd-Mn), \(V = 0.8\) nm\(^3\) (Al\(_{13}\)Co\(_4\)), and \(V = 0.6\) nm\(^3\) (\(\beta\)-Al\(_3\)Mg\(_2\)) are found. Scaled by the respective atomic volumes, we find \(V/V_a = 30\) for \(\varepsilon\)-Al-Pd-Mn. For Al\(_{13}\)Co\(_4\) and \(\beta\)-Al\(_3\)Mg\(_2\) we find \(V/V_a = 53\) and \(V/V_a = 32\), respectively.

The values found for the activation volume of different CMAs obviously exceed the atomic volumes by more than an order of magnitude, which indicates that large obstacles containing some tens of atoms control dislocation motion. Recall that we have accounted for the presence of a cluster substructure as a distinct structural feature of CMAs. Accordingly, it was concluded for several CMA phases, that the cluster substructure provides the rate-controlling obstacles for dislocation motion [20, 22].

Figure 1.24b shows the activation enthalpy and the work term of \(\beta\)-Al\(_3\)Mg\(_2\) single crystals as a function of deformation temperature, obtained from combined temperature-change and stress-relaxation tests. The values for the activation enthalpy \(\Delta H\) are shown as solid squares. Values increasing with temperature from about 1.8 to 2.6 eV are found. A linear fit under the boundary condition \(\Delta H(T = 0\, \text{K}) = 0\, \text{eV}\) is shown as a dashed line. The work term, corresponding to the part of the energy, which is supplied by the applied stress, is shown by circles. It is roughly constant in the observed temperature range and amounts to about 0.4 eV.

The activation enthalpy \(\Delta H\) is larger by about a factor of six than the work term. It can hence be concluded that the deformation is a thermally activated process. Similar behavior of the energetic activation parameters is also found for other CMAs. For Al\(_{13}\)Co\(_4\) \(\Delta H = 2.2\) eV\(^2\) and for \(\varepsilon\)-Al-Pd-Mn \(\Delta H = 5\) eV is found [20]. The activation

![Figure 1.24](image-url)
enthalpy is always much larger than the work term, and the enthalpies are considerably larger than the corresponding self-diffusion energies. As the latter finding indicates that the deformation-rate-controlling mechanism is not given by a single-atom diffusion mechanism, this is consistent with the conclusions drawn from the results for the activation volumes.

1.5
Potential Applications

1.5.1
Applications Related to Surface Energy

It is a well-known fact that technological developments often anticipate a full understanding of the property they are based upon. This has been the case for Al-Cu-Fe-Cr quasicrystals and approximants, which were shown to yield appreciate antistick properties and interesting corrosion resistance, making them suitable for a new generation of cookware [86]. This type of utensil was combining low adhesion and excellent mechanical resistance to scratch, in contrast to many modern devices that do not offer both performances together. Figure 1.25 summarizes the basics behind the performance of such utensils. It is based on the reduction of the apparent surface energy of a CMA coating, equipped with its native Al₂O₃ oxide that forms in ambient conditions. The reversible adhesion energy of water (taken as a model material representative of food, although the chemical reactions that take place during cooking are far more complicated) is then related to the contact angle, as discussed earlier in this chapter. It may be divided into two parts, coming respectively from fluctuations of the electric charges on both sides of the water/oxide interface.

![Figure 1.25 Lifshitz–Van der Waals (left) and IₐB (right) components measured using various liquids for pure alumina (square), fcc aluminum (star) and a series of Al-Cu-Fe-Cr CMA materials of changing complexity and therefore, different Al₃p DOS at Eₚ (n(Eₚ)). Observe that IₐB cancels for selected samples when n(Eₚ) ≈ 0.12, which corresponds to quasicrystals and high-rank approximants in Figure 1.11.](image-url)
and from a component accounting for the presence of permanent electric charges at the interface and its vicinity. The first component is called the Lifshitz–Van der Waals term, and the second is often termed simply $I^{AB}$.

Then, the reversible adhesion energy of water reads:

$$W_{H2O} = \gamma_L(1 + \cos \theta) = 2(\gamma_{LS}^{LW} + \gamma_{LL}^{LW})^{1/2} + I^{AB}$$

where the subscripts $S$ and $L$ stand for solid and liquid, respectively, $\theta$ is the contact angle, and LW is for Lifshitz–Van der Waals. The part of the surface energy of water $\gamma_L$ that accounts for LW interactions is well known. The equation above is valid only if the film pressure of water on the surfaces of interest is negligible, which is the case in the present work for all CMA samples of large complexity that were studied. Now, using various liquids, which allows us to vary the ratio $\gamma_L/\gamma_{LS}^{LW}$, it is possible to assess the respective weights of $\gamma_{LS}^{LW}$ and $I^{AB}$ for a given solid (Figure 1.25). It turns out that $I^{AB}$ vanishes for CMA materials of high complexity, like the Al-Cu-Fe quasicrystal and the Al-Cu-Fe-Cr orthorhombic approximant of the decagonal phase that was designed for this purpose [87], in strong contrast to fcc aluminum or conventional Al-based intermetallics. Since $\gamma_{LS}^{LW}$ is merely constant in all alloys, the low stick property pointed out for those CMAs is an intrinsic property related to complexity, via the $I^{AB}$ component and its reduction with the decreasing Al3p DOS at $E_F$ (or equivalently, increasing $\beta_C$, Figure 1.2).

Definite attempts were made by one of the present authors to transfer this discovery to industry. A process able to produce large amounts of atomized powder (up to 1000 kg/day) was designed in association with the preparation at large scale of coatings by plasma spray (Figure 1.26). Demonstrators were supplied to restaurants and to a number of participants in the study. Unfortunately, when marketing started, the pans that were sold had not undergo the thermal treatment designed to stabilize the mixture of icosahedral and $\beta$-CsCl type phase that are quenched in a metastable state during the fast cooling that follows the projection from liquid state [88]. As a consequence, the high corrosion resistance characteristic of the alloy selected for this application was lost, especially in washing machines. It resulted in a massive return of the products, and customers claimed for reimbursement, which sadly concluded the story. The inventor, who had never been informed of the change in the process, gave up with this type application of quasicrystals and approximant CMAs.

Other possible applications related to the surface energy of Al-based CMAs were looked at over the years. They revolve around friction and adhesion in vacuum, which is a concern for the aerospace industry and microelectronics. Satellites, for instance, make a broad use of mechanical devices, which must be kept closed under high mechanical stress during launch and travel, to avoid uncontrolled movement, and must open when they arrive at their final destination. A lot of vibration during the travel phase, and event later, produces what is called cold welding in the vacuum of space. Metallic alloys usually bond under such conditions, and the parts do not separate when demanded from earth, which causes the loss of the mission, that is, billions of US Dollars or Euros. To avoid such problems, surface coatings are often
used, with the purpose to forbid direct contact between the naked metal surfaces. Fretting tests performed at Austrian Institute of Technology, in Seibersdorf, Austria [89], have shown that Al-based CMAs are excellent candidates for this purpose (Figure 1.27). They exhibit both high hardness, which is mandatory to sustain the high applied stress during launch of the rocket, and do not bond against hard steel or aluminum alloys. For the moment, the limitation to the use of these coatings is basically the process of covering complex shapes like the ones encountered in this field with a coating made of a CMA of excellent lattice perfection, and no macroscopic defects like cracks or pores. A later chapter deals with this side of CMA metallurgy.

In order to insist a little more on the care that must be taken to produce coatings of excellent microstructural quality to achieve the level of performance expected for CMA materials, we show in Figure 1.28 a successful attempt made at the Josef Stefan Institute by Cekada et al. [90]. The starting point (Figure 1.28a) is a multilayer stacking of Al, Cu and Fe films the respective thicknesses of which are selected in order to reproduce the adequate stoichiometry of the material. After thermal mixing (Figure 1.28b), a homogeneous thick coating is formed. It can be used for example, to coat cutting inserts made of a WC-Co sinter, covered by the Al-Cu-Fe film. Alternatively, physical vapor deposition (PVD) can process the same quality of
coatings, starting from a target the composition of which was designed to take into account the shift from stoichiometry that results from preferential sputtering rates encountered for different elements like Al, Cu and Fe. Standard tests defined according to the state-of-the-art prove that the lifetime of the tools under representative machining conditions is increased by 25% (Figure 1.29), which represents a very significant saving for the profession, provided the production costs are kept low. This step for the time being is not yet achieved.

1.5.2 Applications Related to Transport Properties

Applications related to transport properties are of four types: heat insulation, light absorption in view of solar heating of houses, applications connected with the
magnetocaloric effect (MCE), namely the heating or cooling of a magnetic material in response to the variation of an external magnetic field and finally, applications referring to the thermoelectric effect, namely the transformation of caloric energy into electric energy or vice versa. These two latter aspects are treated in Chapters 8 and 9, hence we will not detail them any further. Let us just mention that as far as the magnetocaloric effect is concerned, much effort is done nowadays with the purpose of finding materials with a high MCE around room temperature [91], easy to prepare and suitable for designing the first magnetic refrigerator usable in everyday life. Also, an investigation is being carried out with the goal of discovering new environmentally friendly energy sources, as for example, for achieving electricity generation from waste of heat via thermoelectric modules. These two potential applications of CMAs are dealt with in Chapters 8 and 9, respectively.

The potential of CMAs for applications in the domain of heat insulation, namely the production of thermal barriers for the automotive and aeronautic industries, and solar-light absorption for the purpose of low-cost house heating was recognized and secured by one of the present authors quite some time ago (see references in Ref. 3). Thermal barriers were produced by plasma spray technology and demonstrators were submitted to tests [92]. A limitation comes from the too low melting point of the CMA coatings known so far. However, for certain niche applications like turbine blades of helicopter engines or military aircrafts, the potential of CMA coatings has been recognized and studied to some extent (Figure 1.30).

Successful attempts were also carried out by Eisenhammer [93] to replace the so-called TiNOₓ technology by Al-Cu-Fe films of equivalent light-absorption performance, but much higher working temperature, and therefore better thermodynamic

![Figure 1.29](image-url)
efficiency. In fact, all trials have failed so far due to the nonmature film deposition industrial processes of CMAs layers and coatings, which increase the cost of the layers above the thresholds that industry may accept.

1.5.3 Applications Related to Dispersion of Particles in a Matrix

In Section 1.4.4, we have seen that CMAs are ductile only at elevated temperatures. In temperature ranges of 70% of the melting temperature and above, the flow stresses are of the order of some hundreds of MPa. The flow stress is strongly temperature dependent and increases with decreasing temperature. Accordingly, at lower temperatures, for example, at room temperature, the yield strength of CMA materials is very high, albeit at very low ductility. Consistently with the low surface energy, the toughness constants are small, if not negligible.

These properties can be taken as an advantage for using CMA particles to harden ductile metals and alloys of lower yield strength. For instance, in situ precipitation of nanoparticles of icosahedral symmetry was used long ago to produce maraging steels [94] of amazingly large yield strength that are used in a commercial application by Philips (razor blades). Other metal–matrix composites can be produced under such conditions that CMA particles precipitate in a soft matrix, for example, in Al-based alloys, or by mechanical alloying and sintering. It has, for example, been demonstrated that volume fractions of β-Al₃Mg₂ as low as 20% spread in an Al-matrix lead to an increase of strength by 400% at a still high ductility of about 40% (Eckert et al., Chapter 7). Particle strengthening using CMA composites is treated in detail in Chapter 6.

A real breakthrough was recently achieved using laser selective sintering, a rapid prototyping method able to produce a variety of composites based either on polymer or aluminum matrices [95, 96]. Figure 1.31 shows an example of a toy part made according to this process, with very high mechanical properties that exceed the current state-of-the-art and may find application in many areas of the transport industry.
1.6 Conclusion and Introduction of the Following Chapters

This book is intended to introducing the reader to a state-of-the-art comprehension of the most salient features of the science of CMAs, which the editors selected in view of their relevance to potential technological applications. The book is organized in 10 self-contained chapters. In addition to the present introduction, the following chapters are dedicated to the study of the properties of CMAs from theoretical and experimental standpoints (Chapters 2 and 3), to the surface science and surface chemistry of CMAs (Chapters 4 and 6), to metallurgy, preparation, processing and engineering properties of CMAs (Chapters 5 and 7), to magnetocaloric properties and thermoelectricity (Chapters 8 and 9) and finally to CMAs as catalysts (Chapter 10).

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References

References


References
