CHEMISTRY OF METALS

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Contents

Summary

The chemical and physical classification of metals within the Periodic Table is outlined; their structural and physical properties, as well as their main production methods, are discussed.

The alloying behavior of metals is analyzed through the most representative binary diagrams. Intermetallic phases, that is solid solutions and intermetallic compounds, are defined and identified while examining the parameters influencing their formation and stability. A few intermetallic compound families are briefly described. A survey is given of the main synthesis methods as well as of the most important applications of intermetallic phases.

1. Introduction

Whether a particular element is a metal or not depends on certain of its properties. Which property or combination of properties defines a metal? To the chemist an element is a metal if its oxide reacts with acids to give salts, even though the chemical classification is rigorously applicable only to the elements of the main groups of the Periodic Table. Elements of blocks d and f are in any case considered metals. To the physicist an element is a metal if it displays good electrical conductivity, which decreases with increasing temperature. This criterion encompasses metals that are as different as sodium and gold.

In the Periodic Table reported in Figure 1 metals are positioned to the left, while to the right are the non-metals. Elements presenting borderline chemical behavior between the metals and the non-metals (for example semi-metals Be and Al whose oxides have an amphoteric character) are highlighted in Figure 1a, while Figure 1b highlights elements with a borderline behavior with respect to electrical conductivity (B, Si, etc.). In both cases, even though with some differences, semi-metals are arranged along a line which divides block p.

Figure 1. Periodic Table of the elements. a) chemical classification b) physical classification

Of the one hundred and three known chemical elements in the Periodic Table, approximately eighty are metallic. More than three-quarters of the metals are used industrially to some extent, but only eight are available at a low enough cost and in a sufficient quantity to serve as basis for common engineering materials: copper, iron,

lead and tin, used for thousands of years in various metallic forms, and aluminum, magnesium, nickel and zinc, relatively new additions.

Metals present physical properties that vary significantly with the position of the metal in the Periodic Table. Metals have variable densities, from 0.534 for Li to 22.48 g/cm^3 for Os; their melting point temperatures, at ambient pressure, vary from -38.8°C for Hg, the only liquid metal at ambient temperature, to 3422°C for W. The hardness of the metals may vary widely, going from soft metals such as Li, Na and Pb, to hard metals like W etc. Some metals have considerable vapor pressure at temperatures inferior to boiling T, a factor that must be kept into consideration during the various metallurgical operations. Metals are non-transparent solids, which display a particular luster; their color does not vary much going from Pb and Zn bluish gray to Ag white, with the only exception of two colored metals: Au and Cu.Ductility and malleability are typical of metals as opposed to other solid's fragility (ionic solids). Metals can withstand considerable permanent deformations before reaching the breaking point; they can be reduced into thin threads (ductility) and into thin foils (malleability).

Several metals can be classified in function of their properties and applications:

Light metals Li, Be, Mg, Al, Ti (used in light alloys); refractory metals Zr, Hf, V, Nb, Ta, Mo, W, Re (high melting points); soft solder metals Ga, In, Sn, Pb, Sb, Bi; ferrous alloy metals Ti, V, Nb, Cr, Mo, W, Mn; precious metals Ru, Os, Rh, Ir, Pd, Pt, Ag, Au. The precious metal family has a somewhat greater permanence than the other metals because they resist the action of many chemicals and hence are used as jewelry and monetary standards. Ag and Au together with Cu are also called coinage metals, because of their extensive use in coins and medals.

2. Structural and Physical Properties of Metals

The reason why metals and their alloys differ so greatly from other elements and more generally from non metallic solids depends on their characteristic metallic bond which is at the basis of their structure. Beyond the physical and chemical definition of metals given in the introduction, it is the presence of a metallic bond that characterizes and defines metallic solids.

In the solid state all metallic materials are crystalline. Each grain of a metal is made up of a three-dimensional array of atoms comprising of what is called a space lattice. When free, or as separate entities with no neighbors, each of these atoms is composed of a nucleus made of protons (positively charged particles) and neutrons (uncharged particles), outside of which are electrons (negatively charged particles), each of which acts as though it were spinning about an axis through itself. The electrons exist, statistically, at various energy levels with respect to the nucleus, some of them being tightly bound to an individual atom while others apparently are relatively free to move throughout the crystal as a whole. Metals can be considered conveniently as an array of positive ions through which free electrons are in motion.

The engineering characteristics of metallic materials are determined either by the nature and conditions of the crystals or by the manner in which they are aggregated into larger masses.

The accepted theories of metallic bonding describe the delocalization process in terms of the creation of bands of energy levels, representing "molecular orbitals" over the entire metal crystal. In molecular orbital theory, the interaction of an atomic orbital of one atom with that of a second atom generates two new molecular orbitals. Interactions of N atomic orbitals in a metal will similarly produce N molecular orbitals. The difference between highest and lowest molecular orbital energy is the width of this band, depending only on the type of orbitals, not on their numbers. Certain gaps in the band may occur, however, where energy levels are forbidden, as determined by the wave characteristics of an electron moving in the periodic field produced by the lattice of positive ions. Then, if the lower part of a band (the valence band) is filled to capacity with electrons, electrical conduction cannot occur. Incompletely filled bands permit electrons to be promoted to the upper levels of the band (conduction band) and then conduct a current. If the conduction band is separated from the valence band by only a narrow gap or if they overlap the solid is a conductor.

In metals the valence band is only partially full (in Cu, for example, 4s electrons fill only half of the external s band, because there is only one 4s electron per atom). More details on this argument are reported in *High Temperature Materials and Solid State Chemistry*.

Since electrons in metals can, to a certain extent, be promoted to upper levels by absorbing any quantity of energy and not only a moderate amount implying a selective absorption, the result is the characteristic metallic luster, ascribable to the fact that metals absorb all incident radiations of the visible spectrum and then release them in all directions.

The physical properties of metals, in general, are controlled by the geometrical arrangement of the atoms relative to each other.

The regular arrangement of metal atoms in the solid state can be represented ideally as a space lattice. In general the metallic space lattices are highly symmetrical, although in some case, for instance for manganese, tin and plutonium they are complex and of lower symmetry. Because of the type of bonding in metals in which there is no direct linkage, each atom tries to surround itself with as many other atoms as possible. This leads to structures which are face-centered cubic (fcc), hexagonal close-packed (hcp) or body-centered cubic (bcc); about seventy percent of the metallic elements crystallize in these structures. The fcc and hcp structures represent alternate methods for close packing of spheres. There is a great deal of similarity also between the hcp, fcc and bcc structures, and in some cases, depending on the temperature, an element may allotropically change from one form to another.

The body-centered cubic lattice (bcc) results when two simple cubic lattices are so arranged that the corners of one fall exactly in the centers of the cubes of the other. Each cube now contains two atoms, one in the center and one from the simple cubic structure (eight corners with one-eight of an atom each) (See Figure 2a). At room temperature many of the stronger common metals (V, Nb, Ta, Cr, Mo, W, Fe) crystallize in this lattice. Also the alkali metals (Li, Na, K, Rb, Cs) are all bcc.

The face-centered cubic lattice results when an atom is placed in the center of each face of a simple cubic lattice. The unit cube now contains four atoms (one from the simple cubic lattice and one-half of an atom from each of the six faces of the cube) (See Figure 2b). At room temperature, many of the more ductile metals such as Cu, Ag, Au, Al, Pb crystallize in this type of space lattice.

The close-packed hexagonal lattice results when six atoms are placed in the hexagonal unit cell (namely one-sixth from each of the six corners of the basal faces, one-half from the centers of each of these basal faces and three atoms in the interior of the unit cell (See Figure 2c). At room temperature some of the more common metals crystallizing in this lattice are Mg, Ti, Os, Co, Zn, Cd. Mercury, when solid, also crystallizes in this lattice.
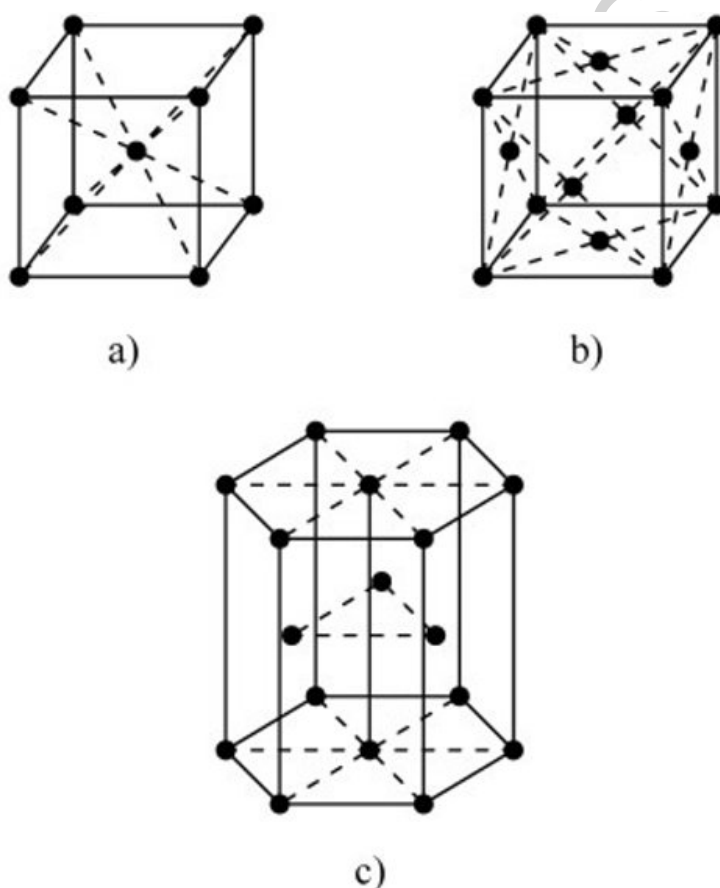
Figure 2. Typical metallic lattices. a) body-centered cubic (bcc) b) face-centered cubic (fcc) c) hexagonal close-packed (hcp)

The atom arrangements in the fcc and hcp lattices represent the two ways in which spheres of equal radii can be packed together most closely. For close packing a layer of spheres can be arranged in only one way, in which each sphere is in contact with six neighbors (layer A). A second layer (B) can be arranged on top of the first, again in only one way if close packing is to be preserved. There are two possible ways to adding the third layer, both preserving close packing: either directly above the first layer or in a

third position (C). The first case gives a repetition in an ABABAB... arrangement, giving rise to the hexagonal close-packed structure (for instance Mg-type), the second case gives an ABCABC… repetition giving rise to the face centered cubic close packed structure (for instance Cu-type) (See Figure 3).
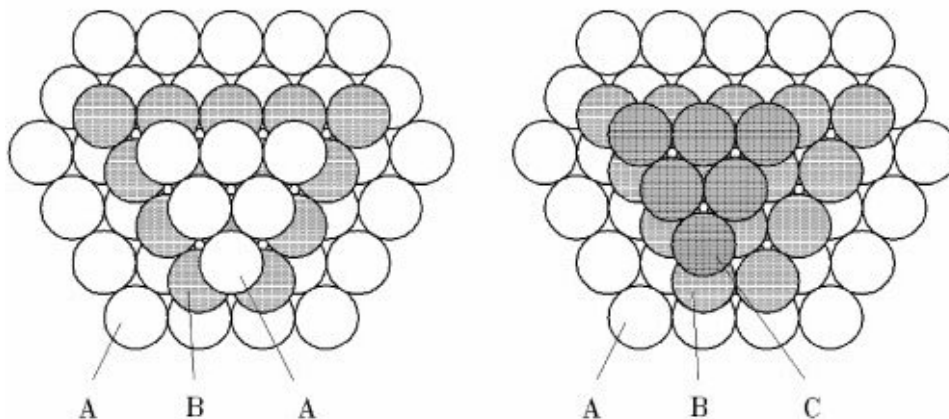

Figure 3. Arrangement of layers in close packed lattices. Left: hexagonal close packing. Right: cubic close packing.

The coordination number of an atom (CN) indicates the number of equidistant near neighbors that an atom has in a given crystal structure: CN is 12 in the fcc and hcp lattices, 8 in the bcc lattice.

In the closest packing of equal spheres (fcc and hcp lattices) there are, among the spheres, two kinds of interstices: tetrahedral holes (smallest holes) and octahedral holes. An atom inserted in a tetrahedral hole has four neighbor spheres at the corners of a regular tetrahedron; an atom inserted in an octahedral hole is surrounded by six neighbor spheres at the corners of a regular octahedron (See Figure 4). There are as many octahedral sites as there are spheres and twice as many tetrahedral sites as spheres.

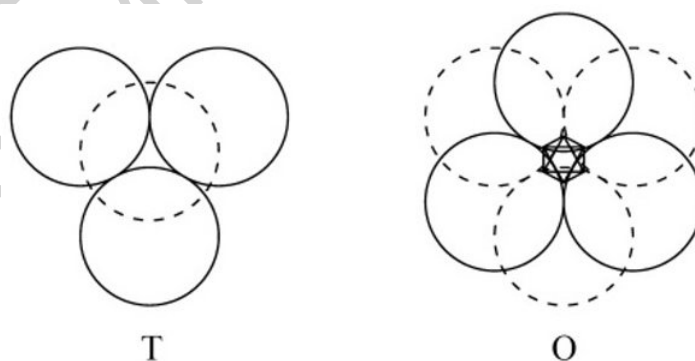Figure 4. Interstices in close-packed lattices: tetrahedral (T) and octahedral (O) holes
As an example, the lateral view of the stackings of the layers in hexagonal close-packed (Mg) and face-centered cubic (Cu) structures are reported in Figure 5.
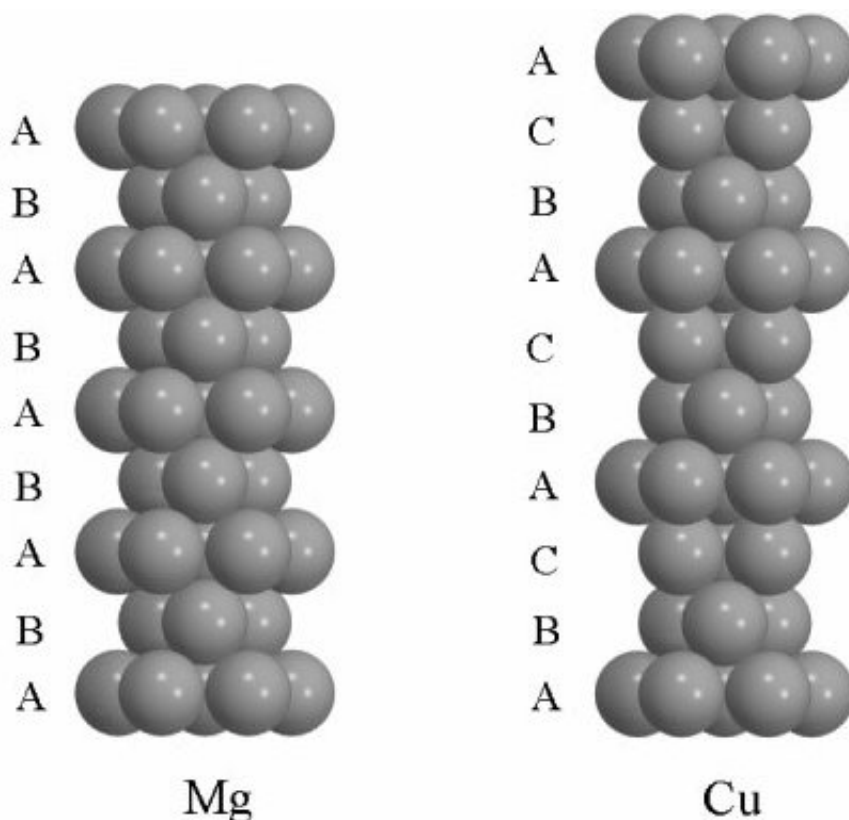
Figure 5. Stacking of layers in close-packed structures a) Mg (...ABABAB...) b) Cu (...ABCABC...)

The structures of a number of metals deviate markedly from close packing. Bi, Sb, Ga have an atomic arrangement with rhombohedral symmetry, rather than a cubic structure. These metals have so-called open structures, meaning that there is a substantial amount of empty space surrounding each atom, considered as a hard sphere. It is interesting to notice that these metals decrease in volume when they melt, whereas most metals have a greater specific volume in the liquid state than in the solid state.

Many metals, particularly among the elements in the transition series of the Periodic Table have two or more crystalline forms. These forms are called allotropic forms (polymorphism). Iron is bcc at temperatures ranging up to 912°C, but at this temperature it undergoes an allotropic transformation and becomes fcc. The fcc phase is stable up to 1394°C at which temperature it transforms back to the bcc structure which it then retains up to the melting point. An interesting example of allotropy is known for tin; at 25°C β-Sn (white tin, body centered tetragonal structure) is the thermodynamically stable allotrope, but lowering the temperature to 13°C results in a slow transition to α-Sn (grey tin). During the $\beta \Rightarrow \alpha$ transition the coordination number decreases to 4, because α-Sn adopts a diamond type lattice, losing the metallic properties. The density of Sn decreases from 7.31 to 5.75 g cm^{-3}, whereas an increase in density is more usual in going from a higher to a lower temperature allotrope.

The structures described refer to perfect crystals. The presence of imperfections, such as lattice vacancies, interstitial or substitutional atoms, and dislocations constitutes a departure from the ideal structure.

The physical properties of metals can be differentiated in two classes: structure-insensitive, characteristic of the perfect crystal, and structure sensitive depending upon departures of the structure from perfection. The structure-insensitive properties are well-defined properties of a metallic phase, whereas the structure-sensitive properties are dependent not only on the composition and crystal structure of the materials but also on structural details (microstructure) that depend upon the previous history of the sample. Thus the structure-sensitive properties are properties of a particular sample of a material, while the structure-insensitive properties relate to the material. Different samples of the same material have essentially identical structure-insensitive properties, but the structure-sensitive properties are identical only when the previous treatment has been equivalent. Examples of structure-insensitive properties are: density, elastic behavior, melting point, specific heat, thermal expansion, thermal conductivity, resistivity, electrochemical potential, reflectivity. Among these peculiar properties of metals are electric conductivity, which decreases with the temperature increase, and thermal conductivity.

Among the structure-sensitive properties examples are fracture strength and plasticity. In particular the application of a stress to a metal may cause any of the following changes: a) elastic deformation, in which the strain appears and disappears simultaneously with the application and the removal of the stress; b) anelastic deformation, in which the strain reaches its maximum value after the stress has reached its maximum peak and in which the strain disappears after the removal of the stress; c) plastic deformation, in which the strain occurs simultaneously with the application of the stress but does not vanish if the stress is removed; d) creep, in which non recoverable strain occurs while the stress is held at a fixed value; e) fracture, in which physical separation takes place. These processes do not necessarily occur separately. Of these processes, only the first (elastic behavior) is structure-insensitive; the other four processes are structure-sensitive and must be considered in relation to crystals that are imperfect.

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