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REVIEW

Bonding, Structure and Uses of Metals

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ABSTRACT

This work briefly describes some of the different features of groups of metals. It highlights recent progress in research into metals. It details the structures and defects in solid metals. The common theories of metals including the free electron theory, band theory, the ions in a sea of electrons model and the soft sphere model are discussed and their merits are considered. It describes distinctions between the bonding in metals and inter-metallic compounds. It shows the influence of bonding on the properties of metals and alloys and provides a summary of tradition and newer uses of metals.

1. Introduction

1.1 Metals in Ancient Times

During the Stone Age human beings turned from hunter-gatherers to farmers and stock breeders. However, the main tools they used remain flint tools^[1]. Towards the end of the Neolithic Period copper metallurgy emerged in some regions. In the Indus valley metal technology involving the alloying of copper and tin was discovered^[2]. Researchers have found that ingots of tin found Bronze Age shipwrecks in the eastern Mediterranean dating from about 3200 years ago were smelted in the south west of England which suggests an ancient trade route existed

between the regions^[3]. The tin, formed into bars and plates was like destined for making bronze, a technology that influenced the development of ancient cultures. The Bronze Age played an important part in the development of Greek history and culture^[4]. The discovery and use of metals such as copper, gold, silver and iron^[5] and the use of alloys laid the foundations of many ancient civilizations. Well known archeological evidence shows Roman settlements were able to supply themselves with water with network of lead pipes. Recent study reveals that lead was a component of Roman ink. Metallic ink was detected in burnt papyri from the ancient Roman town of Herculaneum which was destroyed in the Mount Vesuvius eruption of 79AD^[6]. There is no argument that the discovery,

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manufacture, use and scientific understanding of metals and alloys are very important factors in the developments in civilization. This work describes the different groups of metals, the structure of metals, their bonding and summary of their uses.

1.2 Features of *s*, *p*, *d* and *f* Block Metals

The *s* block includes the alkali metals and alkaline earth metals. Unlike many other metals every member of both groups possesses only one valence. The alkali metals very electro-positive, very soft and the most reactive metals. Lithium, sodium and potassium are all less dense than water and react violently with it. Cesium has the third lowest melting point of all metals, after mercury and francium. Francium, the heaviest member of alkali metals, was only discovered in 1939^[7]. It is the most unstable element in the first 101 period table and all the 36 isotopes are highly radioactive. Alkaline earth metals are all denser than water. Beryllium, magnesium, calcium and strontium are less dense than all metals in the *p*, *d* and *f* block. Beryllium and barium have much higher melting points than other members of the group.

The *p* block metals are usually called main group metals and include gallium and germanium which are both vital in the transistor industry. Gallium has the lowest melting point in the whole group. After oxygen and silicon, aluminum, is the most common element in the earth's crust. Aluminum, while being a very reactive metal, can be made unreactive by a thin coating of aluminum oxide^[8].

The *d* block or the transition metals is the most diverse group metals. There is no typical *d* block transition metal. Mercury is the only metal that is a liquid at room temperature. The majority of *d* block metals have multiple valencies. Manganese possesses valencies from 1 up to 7. Many of these metals are high melting point solids and form many covalently bonded compounds. Osmium, iridium and platinum are the densest naturally occurring elements. Technetium was the first element to be produced artificially and was only discovered in 1937. There are 16 known isotopes with atomic masses ranging from 92 to 107^[7].

The *f* block includes lanthanides and actinides. With the exception of promethium, all the lanthanide elements were discovered in the nineteenth century. Promethium was first artificially made in 1941. The dominant valence is 3 although many of the lanthanides have variable valences. They are all high melting point solids and their densities vary from 5 to just over 9. Their physical and chemical properties are fairly well known^[9] and they are used in many industrial applications.

Many of the actinides were only discovered after World War II. All the actinides from atomic number 93 onwards

are artificially made. Although heavy elements were created long ago by cosmic collision of bodies such as neutron stars^[10] and evidence of actinide elements such as curium existed in the early solar system^[11]. Not much is known of the trans-uranium elements because until recently they were expensive, difficult to prepare and only small quantities were made.

1.3 Highlights of Recent Progress on Metals

There are a vast amount of research and studies on these materials. Research shows new compounds make dissolving gold simpler and safer. This discovery could offer new way to recycle electronics^[12]. Increasingly more metals are used in medicines including silver, gold and platinum^[13]. Researchers have evaluated the antimicrobial activity of 906 metal containing compounds submitted to the Community for Open Antimicrobial Drug discovery initiative. The study recorded a surprisingly high hit rate for metal containing complexes compared with organic molecules, underling their potential in the fight against antibiotic resistance^[14]. Metals such as copper and iron are essential for normal brain function. But it is a surprise to find the presence of elemental iron and copper embedded in brain samples of Alzheimer's patients. Determining the chemical pathway responsible for these elemental metals are crucial for the understanding their role in disease and potential drug targets^[15].

Aluminum is an essential element of some alloys and it is useful to understand the bonding between aluminum and other elements. Researchers have reported 2 copper complexes supported by aluminum or gallium metallo-ligands feature two centre/one-electron σ bonds^[16]. The first aluminum-aluminum double bond was reported in 2017^[17] also in a first for organo-metallic reactivity, aluminum has been found to selectively break biphenylene's strongest carbon-carbon bond while leaving sever weaker bonds intact^[18].

We now know more of the bonding of actinide elements. For example, for a californium borate the *5f*, *6d* and *7s* orbitals are all involving in bonding^[19]. Uranium forms an unusually strong triple covalent bond with nitrile groups, confounding predictions about the bond strength of actinides compared with the remainder of the periodic table^[20]. Neptunium forms a triple bond with oxygen in a solid state complex^[21]. These three examples demonstrate how much more research is needed to study the bonding of actinides.

There are much intense studies on newer alloys such as magnesium alloys and shape memory alloys. There are developments in titanium alloys for biomedical applications and health care products^[22]. Alloying non-toxic ele-

ments such as niobium, tantalum and zirconium with titanium produce materials for medical applications including dental products such as crowns and dentures. There is also research and development in magnesium alloys^[23,24] especially in industrial applications. There is a study on corrosion prevention of alloys^[25], work on shape memory alloys mainly on engineering applications^[26] and applying computer modeling on alloys^[27].

2. Metals

2.1 Types of Defects in the Solid State

In a perfect crystal of type say XY, the number of atoms of X is exactly equal to the number of atoms of Y. Each atom is surrounded regularly by the appropriate arrangement of atoms of the other kind. No site which should be occupied is vacant or there may be extra atoms of X or Y occupying positions which are not appropriate sites. In real solids, there are always defects in any crystal^[28].

Defects can be divided into intrinsic defects and extrinsic effects which arise from presence of impurities. Intrinsic defects can be point defects, line defects, area defects and volume defects. Point defects can be Schottky defects which consists of a vacant cation site and a vacant anion site. In a crystal which contains Schottky defects both the cation and anion lattices are incomplete. A Frenkel defect consists of a vacant lattice site, which the atom or ion should have occupied that site occupying a different type of position in the lattice. Line defects occur when there are dislocations of a line of atoms. There are two dimensional area defects when there are stacking faults. For example, in a crystal with cubic close packing the layers of atoms repeat according to ABCABCABC etc. pattern. The fault occurs when the layers become ABCBCABCABCAC etc. There are also volume defects when there are voids or pores in crystals and there can be a mixture of different faults.

2.2 Theories of Metals

Theories of metals were developed in the beginning of the twentieth century. In 1900, Paul Drude^[29] proposed his model of metals. He applied the universally acknowledged kinetic theory of gases to metals. Solids contain a free electron gas which can move within the material. The number of free electrons depends on the type of material and is responsible for the differences among conductors, insulators and semiconductors. A metal contains 6.022×10^{23} number of atoms per mole (where 6.022×10^{23} is the Avogadro constant) and ρ/A mole per cm^3 and ρ is the density (in grams per cm^3) and A is the atomic mass of the metal. Each atom contributes Z number of electrons

and the free electrons per cm^3 $n = N/V = 6.002 \times 10^{23} Z \rho / A$. Drude assumed that each atom contribute one or two electrons and in a typical metal there are in the order of 10^{22} conduction electrons per cm^3 . When Drude proposed the theory it was successful in explaining the Wiedemann-Franz law and satisfy Ohm's law on resistivity. The Wiedemann-Franz law is an empirical law which states that ratio of k/σ (where k is thermal conductivity and σ is electrical conductivity) of many metals is directly proportional to the temperature with a proportionality constant which is fairly accurate for all metals^[30]. Sommerfeld subsequently improved on this theory^[31] and it is now commonly called the free electron theory. Although this theory is more successful than other theories there are fundamental errors in basic assumptions of the theory^[32] and it is unable to calculate the Fermi energy correctly^[33].

Band theory^[34] is another theory of metals. A metal crystal can be considered as being made up of a number of the same kind of atoms, the energy levels composed of the electrons form a vast number of energy bands. Each band consists of many closely spaced discrete energy levels. The energy bands are separated by gaps in which there are no available energy levels. At zero degree only the lowest energy levels are occupied. When energy from an electric field is added to the electrons, those in lower energy levels cannot accept the energy because they cannot move into already occupied higher energy levels. Only electrons in the highest levels can accept energy and only if the energy is enough to raise them to slightly higher unoccupied levels. In metals, which are conductors, the highest energy band, which is the conduction band, is only partly occupied so that random movement of electrons is allowed. When there is a potential difference between the ends of such a solid electrons in the conduction band can freely move down the potential gradient forming an electric current. In insulators, there is a large energy gap between the highest occupied band and the next empty energy band. Since the highest band is fully occupied in an insulator, electrons cannot move across the solid to create a current. Molecular orbital theory has a slight different description of band theory^[35]. Band theory clarifies the mechanism of electrical conduction precisely but does not account for other metallic properties.

Some texts describe a metal as “ions in a sea of delocalized electrons”. It is claimed that metals are good conductors of heat because when metals are heated the delocalized electrons in areas of high temperature can move rapidly towards the cooler regions of the metal transferring energy to the cooler parts of the metal. It is also argued that when a force is applied to a metal crystal the layers of atoms can slide over one another, which is why

metals are malleable and ductile. It is also said that metals are malleable because there are defects in the solid state. Experiments^[36,37] have demonstrated that metals do not behave as “ions in a sea of electrons”. Defects in the solid occur also in non-metallic solids, so it is poor explanation for metallic properties^[38]. If layers of metal atoms can slide over one another the result is some kind of wrinkle or crimp and not a smooth bend. When one part of a metal is heated and if the delocalized electrons in areas of high temperature really move rapidly from areas of high temperature towards cooler regions of the metal an electric current is created and this is not observed in experiment. More details are available in previous work^[38] to show that the ions in a sea of electrons model is an erroneous representation of metallic bonding and structure.

A model that assumed that atoms and ions are like soft or compressible spheres have been used inter-nuclear distances in ionic and covalent compounds with excellent results^[39,40] and this is extended to model metallic structure and bonding^[41].

The highest electron density in an atom is found around the space near the nucleus and decreases with increasing distance from the nucleus. The soft/compressible sphere model assumes that in a metal solid, there are “fractions” of electron density separated from the bulk of electron density around the nucleus and take up the spaces directly in between individual atoms of the solid. To keep the description simple, but not entirely correct because of quantum mechanical principles, the term detached electron(s) is used in this work^[38]. The detached electrons are those electrons which occupy the highest energy band and only some these electrons in the highest energy level can move at random within the unit cell. Hence, it does not contradict band theory.

The outermost electron(s) is/are separated/detached from the atom which forms a positive ion with one or more of the “detached” electron(s) acting like negative ions as shown in Figure 1. The detached outermost electron(s) occupy equivalent positions that are at the midpoint between the nearest neighbors of the positive ions and can move within these midpoint positions in a unit cell^[41].

Depending on the crystal structure of the metal the number of outermost electrons that are detached from each individual metal atom can range from zero to six. The maximum number of detached electrons cannot exceed the number of available sites. Consider cubic closed packed metal unit cell, each atom has twelve nearest neighbors and each atom in the unit cell can have up to six detached electrons or as few as one detached electron or a half if only half the atoms in the unit cell has an electron

detached and occupying a midpoint site.

Different transition metals have different electron configurations and so the number of detached electrons is liable to be different for different elements. The maximum number of detached electrons may not be reached because of defects in the solid state. The number of detached electrons per atom may not always be exactly the same for the same reason. Hence, different transition metals possess different specific electrical resistance, atomic volume and hence distinct densities.

Detached electrons occupying one or more sites midway between metal ions

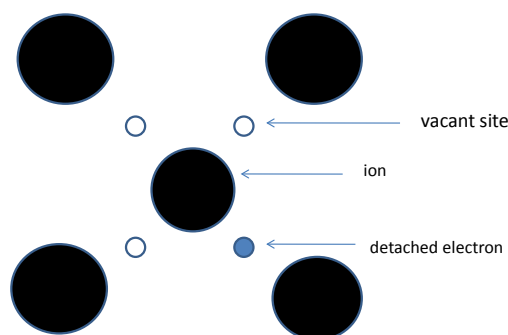


Figure 1. A layer of metal atoms showing the mid-point sites occupied by detached electrons

2.3 Structure of Metals

Many metals possess one or more of the hexagonal or cubic closest packed (face centered cubic) or body centered cubic structures^[42]. At room temperature metals may have more than one structure such as cobalt which exists in hexagonal closed packed or cubic close packed form. Some metals possess many allotropic forms. For example, there are 6 crystalline forms of selenium. Plutonium exists in 6 allotropic variants, uranium and neptunium exist in 3 structural modifications^[42]. A few metals have highly complex crystallographic structures such as manganese, tin and gallium. α -manganese is reported to have a cubic structure with 56 atoms per unit cell. There are two forms of tin at atmospheric pressure, gray tin and white tin. Gray tin has the diamond structure with 8 atoms per unit cell and white tin is tetragonal with 3 atoms per unit cell. α -gallium is orthorhombic, β -gallium is monoclinic and a third form of solid gallium (γ -gallium) is orthorhombic with 40 atoms per unit cell.

The lattice constants and detailed descriptions of the structures are provided in *The Structures of the elements*^[42]. Individual experimental measurements of lattice constants of metals are also available in *Crystal Data Determinative Tables*^[43,44].

2.4 Bonding in Metals

The ions in an electron sea model cannot explain why metallic bonds are strong and free electron theory does not provide an account of metallic bonding. The soft sphere/compressible sphere model shows there are four major components involved in the bonding of metals. They are ionic bonding, covalent bonding, weaker three center bonding and exchange interactions^[45]. Three center bonding takes place when two bonding electrons are connected to three separate sites^[46] and occurs only between nearest neighbors. Recent research demonstrates that single electrons can form three center bonds^[47]. In any instant each detached electron can participate in any one of the type of bonding. The ionic and covalent bonding accounts for transition metals being good heterogeneous catalysts and are malleable and ductile. Only the electrons in three center bonds participate in electrical conduction and a very small percentage of electrons (about 0.01%) participate in current flow^[48] when there is a potential difference between the ends of a metal solid, otherwise too many electrons will collide with each other releasing energy in the process and the temperature of the solid will increase rapidly.

2.5 Inter-metallic Compounds

Inter-metallic compounds are a special group of alloys. Unlike most ordinary alloys they are stoichiometric compounds and they possess different bonding. Many inter-metallic compounds have the formula XY ^[49] where X and Y stand for separate metals. There are many inter-metallic compounds with the formula XY such as BeCo, MnV, CuSc. The most common is the CsCl structure^[50] which is a cubic structure with chlorine atoms occupying the corners of a cube with the cesium atom at the centre with eight chlorine nearest neighbors. Unlike ordinary alloys, covalent bonding is the main type of bond that binds X and Y together^[49].

3. Uses of Metals

Metals and alloys have great many uses, from everyday items such as pots and pans to vehicles for air, land and sea transport. One of the most important applications is as catalysts^[51]. Fuel is essential for modern life. Latest research shows that a copper complex can split water at neutral pH^[52] and both hydrogen and oxygen are very useful. A transition metal carbide dotted with gold nano-particles could provide fuel cells with high purity hydrogen^[53]. A recent study shows that nickel dissolved in molten bismuth catalyses hydrogen production^[54]. There are numerous new findings on catalysts and below are a few

results of recent work. A catalyst comprising a tiny amount of platinum dissolved in liquid gallium makes it three orders of magnitude more active than solid platinum catalysts^[55]. Inducing different amounts of tension or compression dramatically changes the catalytic activity of platinum^[56]. Titanium complex converts methane to alkenes at room temperature^[57]. Stereochemical control of construction of carbon-carbon bonds is achieved using nickel catalyst^[58].

A new method has been designed to produce millions of different metal nano-particle alloys in a single pass^[59] and metal/alloy nano-particles can be used in applications including imaging, therapeutics or catalysis. A newly created magnesium alloy with minute amounts of calcium has showed an exceptional corrosion resistance^[60].

There are many other uses of metals and alloys and here are some examples. A first interaction between neon and a transition has been demonstrated, opening up the possibility of a new method to capture inert gas and other unreactive elements^[61]. The ability of an excited metal to emit light of a particular frequency is useful in communication and some elements such as technetium, show characteristic luminescence^[62]. Technetium is also very useful in a host of medical applications such as a tracer, diagnosis of bone diseases, and cancer and skeletal imaging agent. More details of using technetium in medicine are available in the Journal of Nuclear Medicine and the journal Radiology.

4. Conclusions

There are numerous publications on metals and a few are included in the reference list^[63-67] for readers that want to find out more. Although the crystal structures of metals and alloys are well known the bonding of metals and alloys are still not fully understood. The bonding and structure influence heavily the properties of metals and alloys. There are many discoveries in the studies on catalysts. New research constantly shows many new possibilities for metals and alloys.

Conflict of Interest

There is no conflict of interest.

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