

SVC Topics

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PVD Processes: Alloys, Compounds & Dispersions

The term *alloy* is generally applied to metallic materials. The term can also be applied to nonmetallic materials, however, such as oxide compounds. An alloy is a stable mixture of two or more elements (or compounds) where there is mutual solubility such that the atoms (or molecules) are evenly dispersed among each other. Some materials, such as silver and gold, have total solubility one-in-another. Others have limited solubility and when the solubility limit is exceeded, the excess material may precipitate as regions of second-phase* material dispersed in a matrix of the alloy. Typically, the solubility limit increases with temperature. An alloying agent, therefore, can be uniformly distributed in the alloy at high temperature, but if cooled slowly, the excess alloying agent will agglomerate into second-phase regions at low temperatures.

Some combinations of elements, such as Fe-Ag and Cd-Bi, exhibit almost no solubility at any temperature-even in the liquid state. The solubility limits, under equilibrium conditions, can be obtained from the phase diagram, which gives the phase composition of the solid and liquid mixture as a function of the composition and temperature under equilibrium thermodynamic conditions. When the elements react to form a compound, the kinetics (rate of reaction) is important. In some cases, a long time at a specific temperature is necessary to establish equilibrium conditions.

Uniform mixtures of different atomic species in concentrations beyond the solubility limit can be obtained from solutions by rapidly cooling (quenching) from a high temperature, where there is high solubility, to a low temperature, where the material is solid and the atoms do not have a chance to agglomerate into a second phase. These unstable or "metastable" solutions may change composition, grain size and phase distribution with temperature, stress and/or time, as regions of different phases develop. Such mixtures can also be formed by PVD techniques by co-deposition of the atoms at low substrate temperatures where diffusion and reaction rates are limited.

Small amounts of alloying elements ("alloying agents") are added to the primary constituent(s) to enhance a variety of properties, such as strength, hardness or corrosion resistance, or to allow the formation of second-phase materials that are dispersed in the alloy, with the proper thermal treatments. Many engineering and structural alloy compositions can be found on the website <www.matis.com>.

The composition of an alloy can be specified either as a weight percent (wt%) or as an atomic percent (at%). For example, Zr:24at%Cr has the same composition as Zr:14wt%Cr (one of the Zr-Cr eutectic** alloy compositions), and W:10wt%Ti has the same composition as W:30at%Ti (alloy used in silicon device metallization). Quite often in the literature, wt% or at% is not specified. Generally, if not stated, weight percent is being used.

In a crystalline solid, atoms of one material can either be located at lattice sites (substitutional alloys) or be in spaces between the lattice sites (interstitial alloys). Carbon is a small atom that is often located at interstitial sites in an alloy. Above a specific composition, a crystalline lattice may be stained by these "foreign" atoms to the point that it will assume a different crystalline structure. For an alloy, therefore, the crystalline structure may differ depending on the composition and/or the temperature. The equilibrium crystalline phase(s) can be obtained from the phase diagram.

In PVD processing, alloys of metallic materials may be used as the substrate (see P&SF December 1998), or films of alloy materials—such as Al:2%Cu:1%Si (a silicon device metallization alloy)-can be deposited by PVD processes. Compounds may also form alloys if the compounds are soluble in each other. For example, 10wt%SnO, can be alloyed with 90wt%In₂O₂ to form an indiumtin-oxide (ITO) alloy, which is used as a transparent electrical conductor film material. Above 10wt%SnO₂, the excess tin oxide may segregate from the alloy as a separate phase.

A compound is a combination of the atoms of two or more elements in a specific ratio. The atoms combine as a result of the interaction of the electrons of the atoms. This interaction is called "chemical bonding."

An atom consists of a nucleus containing protons and neutrons in nearly equal numbers, surrounded by electrons in specific energy ranges called shells or orbitals. For an uncharged atom of an element, there are as many electrons as there are protons. If there is a deficiency in electrons, the atom becomes a positive ion. If there is an excess of electrons, the atom becomes a negative ion. The number of protons in the nucleus determines the atomic number, or "Z" of the material. The total mass of the atom is the sum of the masses of the protons, electrons and neutrons, and is given in atomic mass units (amu)*** of the material. All the shells except the innermost shell are subdivided into several energy levels. The inner atomic shells can be filled to a specific number of electrons that they can contain (2,8,18,—). The outermost or valence shell can be "full" or not dependent on the number of electrons available. If the outermost shell is full, then the atom is relatively chemically inert, such as in the case of the "inert gases" (He, Ne, Ar, Kr, Xe). If the outermost shells are not full, then they can donate or accept electrons in the chemical bonding process. For some materials, shells below the valence level may not be full and can also participate in the chemical bonding process.

There are several types of chemical bonding based on the interaction of the electrons associated with an atom. In metallic bonding, the valence electrons are free to move easily through the material, which gives rise to good electrical and thermal conductivity. The individual charged atoms (ions) are in an "electron cloud," which provides the chemical bonding.

In ionic bonding, electrons from one type of atom (donor) are accepted by another type of atom (acceptor), giving oppositely charged ions that then bond by electrostatic attraction. In sodium chloride (NaCl), for example, the sodium (Na⁺) has given up an electron and the chlorine (Cl⁻) has taken up an electron. In some cases, an atom can give up or accept more than one electron. For example, in magnesium chloride (MgCl₂), the magnesium has given up two electrons (Mg⁺²) and combined with two chlorine atoms. Ionically bonded materials generally have poor electrical and thermal conductivity because there are no free electrons. If there is an excess of electrons due to missing acceptor atoms, "defect conductivity" can occur in the ionic material. Two different metallic atoms can be ionically bonded. Aluminum and copper, for example, can form an intermetallic compound of Al₂Cu by ionic bonding. Aluminum is called an amphoteric element as it can act as

either a donor or acceptor in chemical bonding, depending on the nature of the atom with which it reacts.

In covalent bonding, electrons are shared by atoms, such that a valence electron on one atom can help fill the valence shell of another atom. This can occur between atoms of the same type, such as carbon-carbon, or atoms of a different type, such as hydrogencarbon. The covalent bond is important in the formation of chainmolecules, such as those found in many polymers and in some elements, such as tellurium. Covalent bonds are often represented by electron-dot formulas, where the valence electrons are depicted as dots and are arranged about the chemical symbol of the element in such a way that the sharing of the electrons is obvious.

Chemical bonding can be a mixture of bonding types. This may mean that there is some metallic bonding mixed with some ionic bonding. There are other weaker bonding forces—such as van der Waal's bonding and dispersion bonding—that can come into play.

Stoichiometry is the numerical ratio of the atoms in a molecule of a compound. A compound that has a composition such that the bonding capacity for each atom is satisfied, is called a stoichiometric compound $(e.g., SiO_2)$. If there is a deficiency of one type of atom, the compound is called substoichiometric. For example, in SiO_{2-x} (e.g., $Sio_{1,8}$) there is a deficiency of oxygen. Substoichiometric compounds often have the same crystalline structure as the stoichiometric compound until the deficiency becomes so large that there is a change in crystalline type. This may result in a stoichiometric compound of the material with a different crystalline structure. Iron oxide, for example, has stoichiometric compound compositions of FeO, Fe_2O_4 and Fe_2O_2 , each of which has a different crystalline structure. In some cases, a specific stoichiometric composition can exist in several crystalline phases. SiO₂ can exist as cubic (cristobilite), hexagonal (quartz) or rhombohedral (tridymite) crystalline structures, as well as a noncrystalline glass.

Compound phases and alloy phases containing the same materials can coexist. Carbon can be found in an iron-carbon system both as an Fe-C alloy and as an iron carbide. The composition and cooling rate from the melt are important in the kinetics of forming of multi-phase phase systems.

Dispersion of one phase in another phase can be desired for a number of reasons. Steel, for example, can be hardened by having a dispersed phase of carbide particles, which inhibit plastic flow, in the alloy matrix (precipitation or age hardening). The size, number and separation of the particles is important to the resulting hardness. Dispersed-phase materials may have the disadvantage that the two phases in contact can form a galvanic corrosion couple that will corrode if an electrolyte is present. This can lead to pitting or pinhole corrosion. In the deposition of Al:2%Cu for silicon device metallization, for example, if the film is heated, Al₂Cu is precipitated in the aluminum grains, and if a photoresist containing a liquid electrolyte is applied to the surface, pitting can occur by galvanic corrosion.

The composition of alloys, compounds and dispersions depend on the possibility of forming a composition, as given by the phase diagram, as well as the probability of forming the compound that is related to the kinetics of the precipitation or reaction process. In PVD processing, just because you deposit equal numbers of titanium and carbon atoms does not mean that you will form titanium carbide (TiC). The film may be a mixture of TiC, Ti and C. In PVD processing, substrate heating or "activation" of reactive species and concurrent bombardment by energetic particles during deposition (ion plating) are used to increase the reaction probability. P&SF

^{*}A phase is a physically identifiable region of material that has specific characteristics. There are solid, liquid and gaseous phases, as well as various liquid phases characterized by differing compositions, and various solid phases that are characterized by crystalline structure (or lack of it—glassy phase) and chemical composition.

^{**}A eutectic composition is a composition that exhibits a local temperature minimum in the solid-liquid phase boundary in the phase diagram.

^{***}An amu is defined as 1/12 the mass of the ¹²C atom, or 1.66 x 10⁻²⁴ gram.