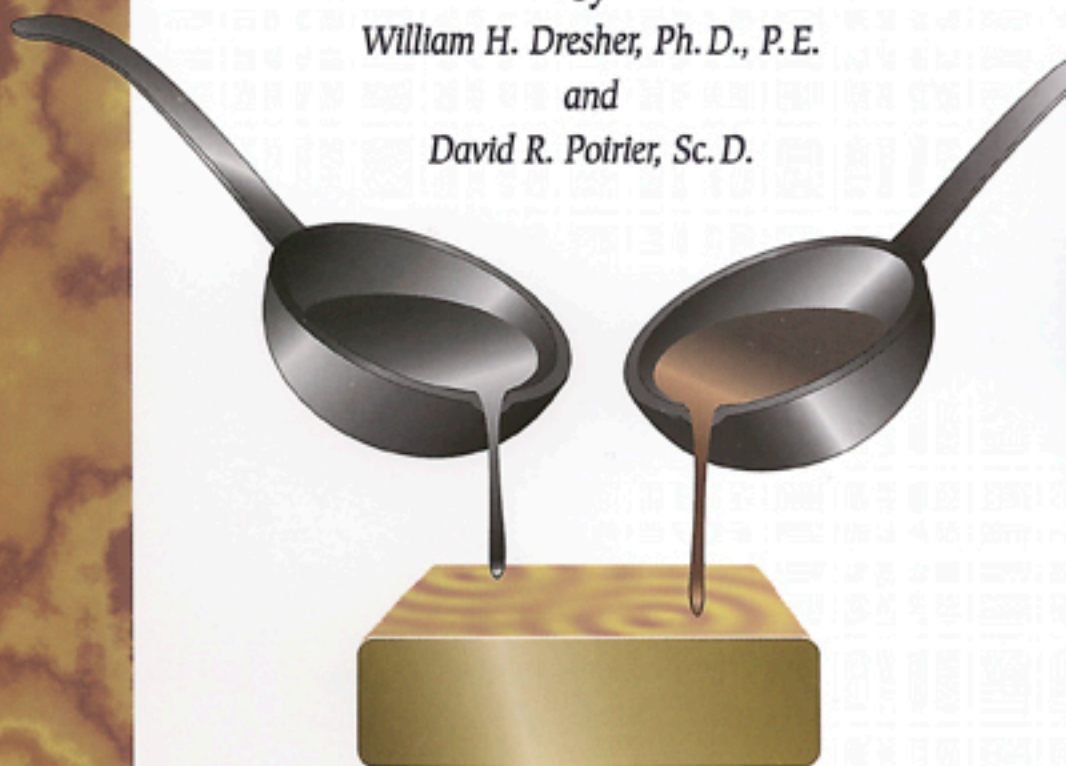

METALLIC ALLOYS AND MIXTURES: DEFINITIONS, BEHAVIOUR AND CHARACTERISTICS

with
Special Reference to the Environment

by
William H. Dresher, Ph. D., P. E.
and
David R. Poirier, Sc. D.



**A Publication by the International Council
on Metals and the Environment**

This book has been published by the International Council on Metals and the Environment (ICME) as part of a series of publications discussing issues relevant to environmental and/or health-related policies affecting the mining and metals sector. It is believed that the topics examined are of concern, not only to the non-ferrous and precious metals mining and producing sectors, but also to others, including policy makers, regulators, educators and the public at large. ICME hopes that these publications provide insight into what are often difficult and complex issues. While the views expressed in these publications are those of the authors, ICME welcomes questions and comments on their perspectives and the information they provide. The Council also appreciates suggestions regarding other issues of public importance for future publications.

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Foreword

While some metals are used in their pure, elemental state, the majority are used in the form of alloys containing two or more elements. Alloys represent an enormous family of engineered materials with a broad range of properties that find widespread application in the technological society of today. They can be precisely engineered to meet specific performance requirements by varying the proportion and/or kind of elements in their make-up and/or by changing their processing treatment. Each alloy is unique, with physical, mechanical and chemical properties that differ significantly from the components from which it was formed. Once formed, an alloy cannot be easily separated into its components by physical means.

This paper was prepared by Drs. William Dresher and David Poirier to provide, in easy-to-understand language, a scientific definition of alloys and an explanation of how and why they differ physically and chemically from simple mixtures and from their individual metallic or non-metallic components. As the paper demonstrates, proper classification of an alloy requires consideration of elemental composition, structure and processing history. Central to the issue of hazard identification and the determination of the toxicity of a substance is the rate of transformation of that substance to its bioavailable form(s). However, as this paper illustrates, the intrinsic properties of an alloy and the bioavailable species it may generate cannot be readily predicted based on the properties of its individual components. Indeed, one reason why alloys, rather than pure metals, are used is to reduce corrosion, and thus the availability of metallic ions to the environment. The bioavailability of these ions is then determined by a host of other factors. These are dealt with in this paper by Drs. Dresher and Poirier which should prove interesting to all those concerned with issues related to metals and the environment.

Gary Nash
Secretary General
ICME

Executive Summary

An alloy is a metallic material, homogeneous in outward appearance, consisting of two or more elements, that have been combined so that they cannot be readily separated by physical means. In contrast, a simple mixture is a physical blend of solids and is heterogeneous in appearance. It may be comprised of pure components, compounds or solid solutions which can be separated into its original constituents by physical means.

An alloy must be regarded as a separate substance, distinct from any of its components. The physical and chemical properties of an alloy can be modified by heat treatment and by mechanical working. Consequently, an adequate definition of an alloy must include, in addition to its elemental composition, a description of its processing history and the treatment it has undergone.

Metals and alloys, *per se*, are insoluble in aqueous media and therefore cannot be considered to be bioavailable. In order for metals to become soluble, and thus eligible for bioavailability, they must become ionized through a chemical reaction called *corrosion*. One of the principal reasons why alloys, rather than pure metals, are used is to reduce corrosion, which means that fewer metallic ions are available to the environment. Metallic elements, some of which may be considered toxic, are added to alloys in order to increase their resistance to corrosion. Even if corrosion does occur, the products of corrosion entering the environment from an alloy do not necessarily have the same elemental composition as that of the parent alloy. Thus, the ecotoxicity of an alloy cannot be predicted based on the bioavailability of its constituent elements.

Solubility itself does not constitute bioavailability. Bioavailability refers to the amount of a chemical compound in the environment that can be absorbed by an organism. The amount that can be absorbed is controlled by factors within the aqueous solution, such as the species of metal ion and other substances dissolved or in suspension in the water, and by the presence of factors within the organism itself. A potentially toxic species can become detoxified by chemical reaction or complexation with other species dissolved in the media.

CHAPTER 1

Introduction

While some metallic elements are used as engineering materials in their pure, elemental state, more than 90% of metals are used in the form of alloys — largely alloys of iron (the ferrous alloys) or of aluminum, copper, nickel or titanium (the non-ferrous alloys). Alloys represent an enormous family of engineering materials that provide useful properties to a wide range of products essential to our present standard of living. As will be discussed later, elements that are classified as toxic are often added to alloys for the purpose of stabilizing and inhibiting the release of these and other components of the alloys to the environment. A good case in point is stainless steel which is an alloy containing, among other additives, as much as 20% nickel. Under current EU legislation, preparations containing more than 0.1% nickel would be classified as Class 3 carcinogens and skin allergens based on this classification for pure nickel. The largest use of stainless steel is in kitchen sinks and food-handling equipment. As discussed below, it is this addition of nickel that helps to give stainless steel its outstanding corrosion resistance which prevents the contamination of food.

Central to the issue of environmental impact and toxicity are the *reactivity* — the rate at which a substance is transformed into a state which may be bioavailable — and the *concentration* of that substance under the conditions of environmental exposure. Under current reasoning, the fabrication of a substance (i.e., a change in its physical shape) does not change its classification. However, in many instances, a change in form can actually *increase reactivity* (for example, in the case of a powdered metal, by increasing the surface area available for reaction to take place) and consequently increase the amount of the substance entering the environment. Conversely, as will be discussed later, the alloying of two or more metals more often than not *reduces* the reactivity and consequently *reduces* the amount of the component metallic substances entering the environment. Indeed, the purpose of forming an alloy is to provide a metallic substance with physical, mechanical and/or chemical properties and characteristics *which are different* from those of any of its components. Improved corrosion resistance (*inertness*) is one of the benefits sought after in the design of many alloys. Stainless steel is an excellent example of this. Stainless steel alloys are resistant to corrosion (in ferrous alloys otherwise known as *rusting*), which means very little of their metallic components enter the environment.

In addition to the stainless steel alloys, there are many examples of toxic metals that are used to impart important characteristics to alloys. Indeed, much of modern technology depends on such materials.

- Beryllium-copper alloys (Cu-2%Be) are very strong and have higher electrical conductivities than other copper alloys. During heat treatment, called ageing, the beryllium leaves the solid solution and forms minute precipitates of a compound of copper and beryllium (CuBe) within the copper matrix. These precipitates strengthen the copper without interfering with electrical conductivity as is frequently the case with other alloying elements that go into solid solution with copper.
- Semiconductors are alloyed materials that possess a myriad of electronic properties and are the basic materials used in numerous electronic devices, such as computers, thermistors in fire detection equipment, etc. These are all dependent on the introduction of metallic and non-metallic elements into the silicon substrate of the device. Some of these elements, such as arsenic, antimony and boron are considered toxic.

In order to produce semiconductor-based electronic devices, microelectronic integrated circuits are formed on silicon chips. A single chip may have as many as a million transistors and other devices, each of microscopic size. This vast technology depends on intentionally and precisely dissolving impurity atoms (*dopants*) in the surface of the silicon crystal, forming microscopic alloys with the silicon. Some dopants, like arsenic, antimony and boron, introduce electrons into the silicon that increase the electrical conductivity of the silicon by forming n-type semiconductors. Other dopants, such as boron, aluminum, gallium and indium, create “electron holes,” and are used to form p-type semiconductors.

In recent years, semiconductors based on the alloy gallium arsenide (GaAs) are being used because electrons move two to five times faster in this alloy than in silicon-based semiconductors. New developments, involving light rather than electricity may provide still faster computers and communications systems than are available today. These will be based on compound semiconductors (e.g., GaAs, GaAlAs and InGaAsP) that produce laser beams.

- Superconductors are a class of alloyed materials in which electrical resistivity is zero at temperatures approaching absolute zero (-273°C). They offer the advantage of designing devices that utilize very high electrical currents with no power loss. In addition to energy conservation, the high magnetic fields that are possible using superconductors have become indispensable in certain diagnostic tech-

niques in the health fields, such as magnetic resonance imaging. Newer developments in this field are leading to ceramic superconductors that contain heavy metals, such as copper, strontium, thallium and barium. Ceramic superconductors make superconductivity possible at higher temperatures than do metallic superconductors. Therefore, these offer the potential of being translated into practical, energy-saving devices.

- A number of alloyed magnetic materials in our everyday life go largely unnoticed, but they are very important to the many devices that we depend on including electric motors, transformers and generators, video tapes or computer tapes and disks, television sets, medical diagnostic equipment, etc. An old “standby” in this class of materials is the iron-nickel alloys known as permalloys. A permalloy is a soft magnetic material that is used extensively in power transformers for minimizing electrical losses. Another application of this material is found in the electromagnetic heads that store or read information from computer disks.

Hard magnetic materials are needed in small motors, loudspeakers and headphones, etc. Hard ferrites are the most commonly used magnetic materials because they are inexpensive and relatively easy to grind to exact dimensions. Ferrites are composed of iron oxide containing barium or strontium. The strongest hard magnets are based on intermetallic compounds (also called intermediate compounds) of rare-earth metals and transition metals such as boron, cobalt, niobium and samarium. Examples of these are magnets based on SmCo_5 , on SmCo_{17} with iron and zirconium, and on $\text{Nd}_2\text{Fe}_{14}\text{B}$.

- The importance of nickel as an alloying element in stainless steels was mentioned earlier. Nickel- and cobalt-based alloys provide good corrosion resistance and good strength at relatively high temperatures. For this reason, these so-called “superalloys” are the main alloys used in aircraft and stationary-gas turbine engines. Nickel and cobalt alloys are also used extensively in chemical processing equipment and in thermal processing equipment (e.g., heat-treating furnaces, sintering furnaces, ceramic kilns, etc.)

In the following discussion, it is shown that two factors seem to be key when considering the difference between a simple mixture of two or more components and an alloy of two or more components. These are: (1) the ability to separate the components by physical means; and, (2) the relative chemical reactivity which transforms them to a potentially bioavailable state when in contact with the environment.

CHAPTER 2

Scientific Disciplines and Basic Definitions

Differences in Perspective

It is important to realize that there are fundamental differences in the approach taken by the several scientific disciplines involved in environmental considerations; namely, the fields of chemistry, biochemistry and physics as compared with those of metallurgy, ceramics and solid state physics. In addition, there are fundamental differences among the several types of substances involved in environmental considerations; namely, organic chemicals, inorganic chemicals and polymers as compared with metals and alloys.

Metallurgy, ceramics and solid state physics are sciences based on the structural approach to materials science, whereas chemistry and its subdisciplines, as well as physics, are based on the thermodynamic approach. Further, metallurgy and ceramics are strongly concerned with solid state phase relationships. It is these phases, not just the elemental composition, that give an alloy or a ceramic material its properties and hence behavioural characteristics. The relatively new field of material science and engineering (MSE) is an outgrowth of the sciences of metallurgy, ceramics, polymers, and solid state physics. Many of the areas of study of MSE parallel chemistry and physics. However, MSE distinguishes itself from classical chemistry and physics by emphasizing the important role that structure, properties and processing history play in determining the behaviour of materials.

The atomistic, or elemental, approach to science considers the structural aspects of a substance, beginning at the atomic level and extending to the phase level of structure. A chemist or physicist would describe a substance in terms of its composition and its phase (solid, liquid or gas), and the temperature and pressure at which the phase exists. On the other hand, no metallurgist would describe a piece of steel by using only these properties. Even the metallography (the microscopic examination of the phases present) of the specimen may not be regarded by the metallurgist as completing the description. In describing an alloy, the metallurgist often uses a description of the history of the material, from the time it was last melted, and sometimes from before. Included in this description would be the amount of heat treatment and mechanical working imparted to

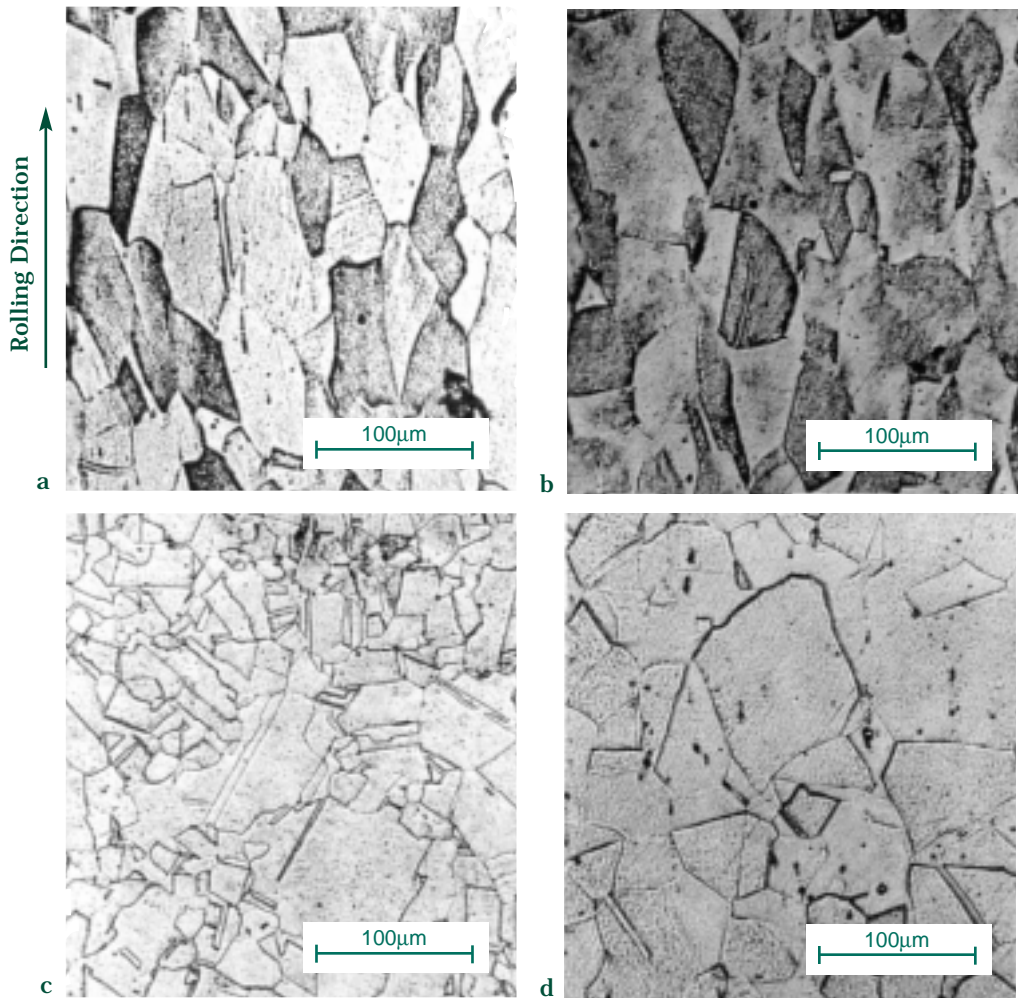


FIGURE 1.

The grains in a single-phase alloy, the recrystallization that occurs by cold-working and annealing, and the grain growth that follows complete recrystallization. (a) Following 50% reduction by cold-working, the grains are elongated in the rolling direction. (b) Little change in the microstructure is discernible after a heat treatment for 15 min. at 600°C, but recrystallization has just begun. (c) A completely recrystallized structure consisting of equiaxed grains has formed after one hour at 600°C. (d) Continued annealing at 600°C for two hours causes grain growth.¹

¹ Reproduced from Rolls, K.M., T.H. Courtney and J. Wulff. 1971. *Introduction to Materials Science and Engineering*. John Wiley & Sons, New York, NY, USA. p. 202 & 203.

the specimen. Failing this information, additional factors would have to be considered including: composition, hardness, corrosion resistance, morphology and grain size of microscopic phases, etc.

Figure 1, for example, shows photomicrographs of a single-phase alloy. The alloy has been subjected to a process called cold-working. In this case, the cold-working was accomplished by passing the sheet through a gap between two rollers. This is done to make the sheet thinner; however, in so doing, it also changes the physical properties of the alloy. At the microstructural level, the individual grains of the material have been deformed (Figure 1a); the alloy is also measurably stronger and harder in its cold-worked condition. Its composition has not been altered, but its properties certainly have been. It is, in effect, a different alloy by virtue of the cold-working. Should the metallurgist want to restore the alloy to its unworked condition, he or she would have to “anneal” (heat-treat) the alloy. Again, the alloy has not changed composition, but its microstructure, and therefore its properties, have undergone profound changes, as can be seen in Figures 1b and 1c. Longer time at an elevated temperature causes growth of the newly formed grains, as shown in Figure 1c.

The metallurgist understands and makes use of the microstructural changes that occur within the alloy during the processing sequence illustrated by Figures 1a-1d. To many chemists and physicists, however, the alloy would be defined simply by the compositional makeup of its elements and the temperature at which the measurements are made. In other words, what the metallurgist would consider different forms of an alloy, each with different properties, the physicist and chemist would consider as one.

A chemist defines a substance in terms of its valence states. For example, a metal is usually defined as an element having a valence of +1, +2 or +3.² On the other hand, a non-metallic element has a valence of +5, +6 or +7, and a metalloid has a valence of +4. However, to a metallurgist or a solid state physicist, a metal is defined by the nature of the bonds between the atoms that make up the metal crystal. Metals can be defined as solids composed of atoms held together by a matrix of electrons. The electrons associated with each individual atom are free to move throughout the volume of the crystal or piece of metal. This is why metals are good conductors of heat and electricity. Other

2 It should be noted that some metallic elements prove to be an exception to this; namely, the subgroup VIA elements of chromium, molybdenum, tungsten and uranium all can take on multiple valencies as high as +6. The +6 valence state is the most stable for molybdenum and tungsten, but for chromium it is the +3 valency that is the most stable. Of uranium's two valence states, +4 and +6, the +4 state is the most stable. Chromium in the +6 valence state is of the greatest environmental concern due to its ability to oxidize organic compounds to aldehydes. Sidgwick, N.V. 1950. *The Chemical Elements and Their Compounds, Vol II*. Oxford University Press, London, UK. p. 998.

properties that distinguish metals from other materials are their malleability (their ability to deform plastically), their opacity and their ability to be strengthened. The structural and historical modes of thinking are completely at odds with the approach of the chemist who is accustomed to thinking in terms of state properties that are measurable at the time of interest, no matter what their history might have been, and who defines the state of matter by thermodynamic descriptors. Thus, the state variables required to describe an alloy are quite foreign to the chemist.

Inorganic chemistry is the branch of chemistry of closest concern to metals and alloys. Inorganic chemistry deals mainly with metallic elements in ionic combination with one or more non-metallic elements, e.g., acids, bases or salts (NaCl, CuSO₄, etc.). These compounds are soluble in water, which makes them available for possible assimilation by organisms, i.e., they can become bioavailable. Generally, the dissolved fraction of metals in natural waters and sediment porewater is thought to best represent the fraction that is bioavailable.³ It is the ionic nature of these compounds that allows them to dissolve in water. Thus, for a metal to be potentially bioavailable, *it must first be transformed into an inorganic compound by a chemical reaction*. This will be discussed in detail below.

Organic chemistry, on the other hand, is based on compounds of carbon which are non-ionic. Most of these compounds contain hydrogen, and a large number of them contain oxygen as well. Other elements, such as nitrogen, the halogens, sulphur and phosphorus, may also be present. Relatively few organic compounds contain metallic elements, and when they do, they are generally present in an exchangeable form such as in a coordination compound. Most organic compounds are not soluble in water and are therefore not directly bioavailable. Although alcohol, acetic acid, sugar and a number of other organic compounds are readily soluble in water, water solubility is the exception rather than the rule. Those that are water-soluble generally contain hydroxyl (OH) groups; those that are insoluble generally do not. Some organic substances are subject to ionization of a degree comparable to that typical of inorganic compounds, and hence exhibit water solubility, but the dissociation usually occurs at some site in the molecule other than the carbon atom; for example, at an attached oxygen (such as a ketone) or nitrogen atom (such as an amine). Organic compounds exist as liquids, gases and low-melting solids (generally < 400°C). Many are soluble in other organic substances — including animal fat. Thus, the bioavailability of an organic compound is more a function of its volatility and solubility in the organic materials making up biological life than of its aqueous solubility.

3 Parametrix, Inc. 1995. *Persistence, Bioaccumulation and Toxicity of Metals and Metal Compounds*, International Council on Metals and the Environment, Ottawa, Canada. p. vi.

Some organic compounds are plastics, or more correctly, polymers. A number of polymers are used as engineering materials, sometimes replacing metals and alloys in application. Polymers are substances composed of long-chain molecules, made up of repeating units derived from the starting chemicals (which are known as monomers). In most cases carbon forms the backbone of the chain. The atoms in the larger repeating molecule are strongly bonded (usually covalently), and the bonds between the large molecules may be due to weaker secondary bonds or similar covalent bonds. Some polymers display a high degree of crystallinity, and in this characteristic, are analogous to metals; others do not crystallize. Long-chain polymers are usually weaker than metals because the molecular chains (i.e., the large molecules) are bonded to each other with rather weak electrostatic forces called van der Waals bonds. When mechanically loaded, the long-chain molecules slip past each other causing the material to deform or break. Strengthening is accomplished by techniques that retard chain movement: by the addition of fillers, cross-linking of chains, chain branching, crystallization and the like.⁴

As in metals, unique properties can be developed in polymeric materials by the formation of copolymers — polymerization of two or more monomers of different formula. Examples of these are two engineering materials — the copolymer of ethylene and butane which form low-density polyethylene and the copolymer of acrylonitrile, butadiene and styrene which form ABS plastic. Contrary to metals, these are not called “alloys” because the different elements are covalently bonded making them different molecules or compounds. Polymer alloys are polymer blends which are produced by the mechanical mixing of two or more different polymers in the molten liquid phase. No chemical reaction between polymer types occurs to produce the blend. Nonetheless, the properties of the blend can be considerably different from the starting polymers.

States of Matter

In a regulatory context, *matter* is regarded as a *substance*. It is generally inferred that a substance is a *chemical or chemical compound*. Matter exists in three states — liquid, gas or solid. Each of these states is conventionally defined by thermodynamic terms — temperature, pressure and composition. However, as discussed above, metals, and alloys in particular, require additional descriptors to complete their definition. This is the principal reason why metals and alloys cannot be treated in the same manner as chemicals for environmental regulatory purposes. Further, *alloys are unique substances and differ in chemical and physical properties from their components*.

⁴ Budinski, K.G. 1996. *Engineering Materials — Properties and Selection*. 5th ed. Prentice Hall, Englewood Cliffs, NJ, USA. p. 15.

Where metals and alloys are concerned in matters of environmental impact, the solid state is the state of principal importance. Liquid metals and alloys occur only at temperatures that are well above those encountered in biological processes. Indeed, the melting-point temperatures of most metals are completely destructive to biological life forms. In so far as gases are concerned, few metals have a vapour pressure sufficiently high at ambient temperatures (mercury being the major exception) to be of consequence to the biosphere.

Solid phases exist in four different forms:

1. **Pure components**, such as arsenic, bismuth, cadmium, copper, iron, nickel, etc.
2. **Compounds**, formed by a reaction between the pure components. Examples are MgZn_2 in the system Mg-Zn; CuAl_2 in the system Al-Cu; $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ in the system $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$; and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in the system $\text{FeCl}_3\text{-H}_2\text{O}$. Such compounds have a definite composition, are stable over a definite range of temperature, pressure and solution concentration, possess definite melting or transition temperatures and have a characteristic crystal structure.
3. **Solid solutions**, homogeneous solids, whose composition may vary within a certain concentration interval (as determined by the composition of the solution from which the solid crystallizes) and which have the same crystal structure over the entire range of compositions. In spite of being homogeneous, the chemical reactivity, and therefore potential availability to biological systems, will vary with chemical composition. Such variability in composition differentiates a solid solution from a compound which has a fixed composition.
4. **Mixtures**, a physical blend of solids which themselves may be pure components, compounds or solid solutions.

Nature of Chemical Elements

Three-quarters of the naturally occurring elements of the periodic table are metals.⁵ Their difference from non-metals begins at the atomic level. Hume-Rothery⁶ has divided the elements, except the rare gases, into three classes: Class I, metals; Class II, intermediate elements; and, Class III, non-metals.

5 74 elements of the 103 naturally occurring elements. This excludes the 15 transuranic elements which are synthetically derived.

6 Hume-Rothery, W. 1962. *The Structure of Metals and Alloys*, 4th ed. Inst. of Metals, London, UK.

The elements of Class I constitute about two-thirds of the naturally occurring elements. With the exception of one form of manganese and one form of tungsten, every Class I element crystallizes in one or more of the following lattice structures: (1) face-centred cubic (fcc); (2) hexagonal close-packed (hcp); or, (3) body-centred cubic (bcc).

Class II may be defined as comprising those elements whose crystal structures fall in neither Class I nor Class III. Zinc and cadmium crystallize in a modified hcp arrangement in which the axial ratio is 1.856 and 1.886, respectively, instead of the 1.633 expected in an ideal hcp structure. Mercury crystallizes in a rhombohedral structure which may be regarded as a distorted simple cubic lattice. Thallium and lead are included in this class in spite of the fact that they crystallize in typical metallic structures. The reason for this is that their rather large interatomic distances, in conjunction with other factors, is sufficient to relegate them to Class II.

Compounds

With the exception of metals and gases, it is rare for a chemical substance to occur, or be used, in elemental form (the elemental gases, such as oxygen and nitrogen which form the atmosphere, and sulphur are exceptions). Rather, chemical substances are generally compounds comprised of more than one element. Compounds exhibit chemical and physical properties quite different from those of the parent elements from which they are formed. Most inorganic chemical compounds are reaction products of metals (sodium chloride [table salt], for example, being a product of the reaction between sodium, a metal, and chlorine, a gas). Organic compounds, on the other hand, are products of the reaction between carbon and such non-metallic elements as oxygen and hydrogen, and may include other non-metallic elements, such as sulphur or phosphorus. Indeed, even alloys, as will be discussed later, may also be solid state compounds comprised of more than one metallic element. Thus, most chemical substances that are candidates for classification are chemical compounds, not mere mixtures of the component elements. Consequently, their properties differ substantially from the properties of the elements from which they are formed. For this reason, they must be treated differently for classification purposes.

CHAPTER 3

Alloys

For the purposes of this discussion, a practical definition of an alloy is:

“An alloy is a metallic material consisting of two or more elements, homogeneous to outward appearance, and so combined that they cannot be readily separated by physical means.”

An alloy is formed by the thermal treatment of a mixture of two or more elements. The major element in an alloy is a metal, and the alloying elements can be either metallic or non-metallic. While alloys are generally regarded as being of two or more metallic elements, alloys often contain non-metallic components and/or non-metallic microcomponents. Examples include carbon in steel (where it is dissolved), graphite in cast iron (where it is a non-metallic phase) and silicon in Al-Si alloys (where it is both dissolved and also exists as a non-metallic phase). Figures 2a and 2b are photomicrographs of microstructures in a cast iron and Al-Si alloy, respectively. These alloys are used as castings in automobiles, as well as in many other useful devices.

The reason for forming alloys from two or more elements is to provide properties that are not available in the elements individually. Indeed, it was the discovery that additions of other elements to metals imparted new and useful properties to those metals that enabled man to progress into the technical society that we enjoy today. For example, the first alloy used by mankind, around 3200 BC, was arsenical copper. Here arsenic, a toxic substance, was added to copper to increase its mechanical strength. Artefacts recovered from this era contain as much as 7% arsenic. Copper, being a normally soft metal, and thus amenable to shaping by hammering, had been used largely for decorative purposes until it was discovered that a very hard alloy of copper could be produced by hammering the copper with small amounts of arsenic. (Note: this illustrates that it is not composition alone that imparts the properties to an alloy, but that subsequent mechanical working can play an important role as well.) Consequently, arsenical copper was found to be useful for more utilitarian purposes than copper alone. Arsenic is still used in copper alloys today, serving to stabilize brass alloys for use in sea water.

7 Modified from Eurométaux. March 1996. *Classification of Alloys — A Feasibility Study*. Brussels, Belgium. p. 40.

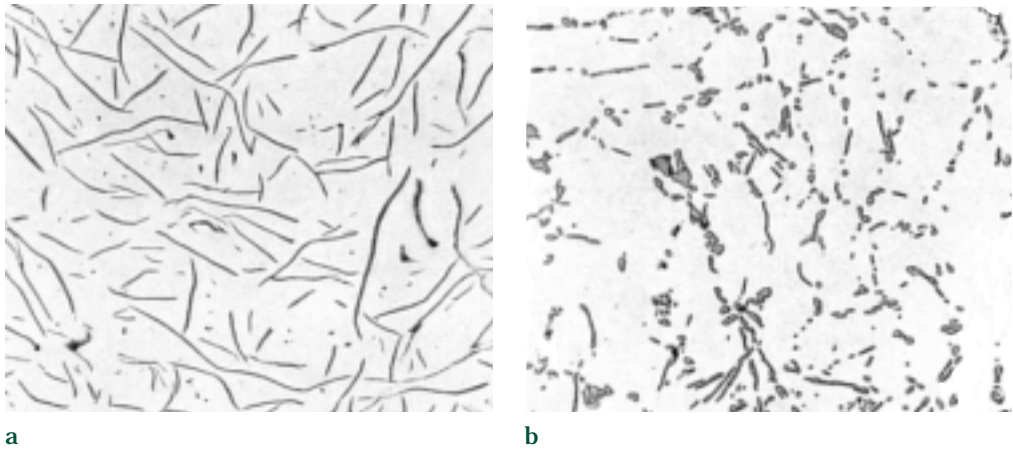


FIGURE 2.

The microstructures of two commonly used casting alloys (magnified 100X). (a) Cast iron with graphite flakes, i.e., carbon, dispersed in a matrix of iron. A small amount of carbon is also dissolved in the iron. (b) An aluminum alloy with silicon particles in an aluminum matrix. A small amount of silicon is also dissolved in the aluminum-rich phase.⁸

Pure copper was difficult to cast, not only because of the need to keep the temperature of the metal above its high melting point of 1084°C, but also because it had the tendency to oxidize and to form bubbles from trapped gases. However, it was undoubtedly noticed that the presence of some other metals in the molten copper made it flow more readily and over a wider range of temperatures. Eventually, it was found that the addition of tin to copper would reduce the temperature necessary to melt the metal and that the molten metal flowed more freely into moulds and did not form bubbles. The first tin bronze — in which the percentage of tin in the alloy is high enough to suggest that it was a deliberate addition — appears in the archaeological record around 3000 BC. Since bronze provided infinitely more practical uses, mostly as tools and weapons, than either copper or arsenical copper, it quickly replaced these materials in engineered products. Thus, until electricity was brought to practical use, unalloyed copper was relegated to being used solely for decorative purposes. So important was the discovery of this alloy to the advancement of civilization, that an era has been named after it: The Bronze Age.

⁸ Reproduced from: Lyman, T., H.E. Boyer, W.J. Carnes, P.M. Unterweiser (editors). 1972. *Metals Handbook, 8th ed., Vol 7, Atlas of Microstructures of Industrial Alloys*. American Society for Metals, Metals Park, OH, USA. p. 82 and 258.

The Bronze Age was replaced by the Iron Age when it was discovered that swords made of “good” iron — probably an alloy of iron, carbon and silicon — were stronger than swords made of bronze. The expertise of early Iron Age metallurgists, and an early example of corrosion resistance formed by alloying, is demonstrated by a dagger found by the side of King Tutankhamun during the excavation of his tomb. The dagger has a gold hilt and a blade not of gold, silver or copper, but of shining, virtually untarnished iron!

Iron had been known, in meteoric form, for as long as man had been familiar with native metals. But unlike the other, and more commonly used, native metals, gold and copper, iron was of little interest to early man because they could neither melt nor cast it. Pure iron melts at 1537°C, a temperature that was quite unobtainable. Nonetheless, when it was discovered that a spongy, semi-metallic mass could be recovered from Bronze Age furnaces, which after hammering would take on metallic properties, wrought iron, a mixture of iron and silica slag, was born. However, wrought iron was inferior to bronze for use in tools and weapons. The improvement in the properties of iron was achieved, probably accidentally, by the addition of carbon (a non-metallic element) to form an alloy which was a forerunner of what we know today as “steel.” The effect of “steeling” on the hardness of iron is dramatic, especially in comparison to bronze. Pure iron is much softer than unworked bronze, but the addition of even 0.3% carbon makes steeled iron as hard or harder than bronze. Raising the carbon content to 1.2% makes the iron even harder than cold-worked bronze. And, if the blacksmith then cold-hammers the steeled iron, it develops twice the hardness of cold-worked bronze.

As described above, the process of alloying occurs as a result of melting the components together. However, using modern technology, it is also possible to form an alloy at temperatures below the melting point of any of the components by using solid-state diffusion processes. Thus, the first attribute of an alloy not found in a physical mixture of metals is that *an alloy is the result of a fabrication process, involving heat, whereby the mixture of components undergoes a transformation that changes the physical and/or chemical form of the components.*

Composition of Alloys

Typically, an alloy contains more than two components, although they are generally classified in terms of their major binary system. Bronze, for example, is nominally an alloy of copper and tin. However, as shown in Table 1, commercial bronze alloys in use today contain, in addition to copper and tin, varying amounts of lead, zinc, iron, antimony, nickel, cobalt, sulphur, phosphorous, aluminum and silicon. Hence, many alloys contain

TABLE 1.
Copper-Tin Alloys (Tin Bronzes) — Composition, Percent Maximum Content

Alloy No.	Cu	Sn	Pb	Zn	Fe	Sb	Ni/Co	S	P	Al	Si
C90200	91.0-94.0	6.0-8.0	.30	.50	.20	.20	.50	.05	.05	.005	.005
C90300	86.0-89.0	7.5-9.0	.30	3.0-5.0	.20	.20	1.0	.05	.05	.005	.005
C90500	86.0-89.0	9.0-11.0	.30	1.0-3.0	.20	.20	1.0	.05	.05	.005	.005
C90700	88.0-90.0	10.0-12.0	.50	.50	.15	.20	.50	.05	.30	.005	.005
C90710	Rem.	10.0-12.0	.25	.05	.10	.20	.10	.05	.05-1.2	.005	.005
C90800	85.0-89.0	11.0-13.0	.25	.25	.15	.20	.50	.05	.30	.005	.005
C90810	Rem.	11.0-13.0	.25	.30	.15	.20	.50	.05	.15-.8	.005	.005
C90900	86.0-89.0	12.0-14.0	.25	.25	.15	.20	.50	.05	.05	.005	.005
C91000	84.0-86.0	14.0-16.0	.25	1.5	.10	.20	.80	.05	.05	.005	.005
C91100	82.0-85.0	15.0-17.0	.25	.25	.25	.20	.50	.05	1.0	.005	.005
C91300	79.0-82.0	18.0-20.0	.25	.25	.25	.20	.50	.05	1.0	.005	.005
C91600	86.0-89.0	9.7-10.8	.25	.25	.20	.20	1.2-2.0	.05	.30	.005	.005
C91700	84.0-87.0	11.3-12.5	.25	.25	.20	.20	1.2-2.0	.05	.30	.005	.005

Source: Copper Development Association. Application Data Sheet — Standard Designations for Wrought and Cast Copper and Copper Alloys. New York, NY, USA, p. 15.

trace amounts of metals classified as toxic without these metals being identified in the name of the alloy type. In many cases, the addition of these trace elements provides important changes to the properties of the parent alloy.

Types of Alloys

In practice, alloys are prepared in several forms, depending on their composition and sometimes their intended use:

Solid solution alloys — alloys in which one or more elements are dissolved in the crystal structure of the dominant metal (copper-based alloys, nickel-based alloys, etc.). Such alloys may also contain a separate compound formed by one or more of the solutes with the solvent metal. Solid solution alloys are the most common.

Because of their bonding characteristics, solid metals can act as solvents and dissolve at least a limited amount of most other elements — both metallic and non-metallic (such as oxygen). Alloy elements and impurity elements may occupy either atom positions in

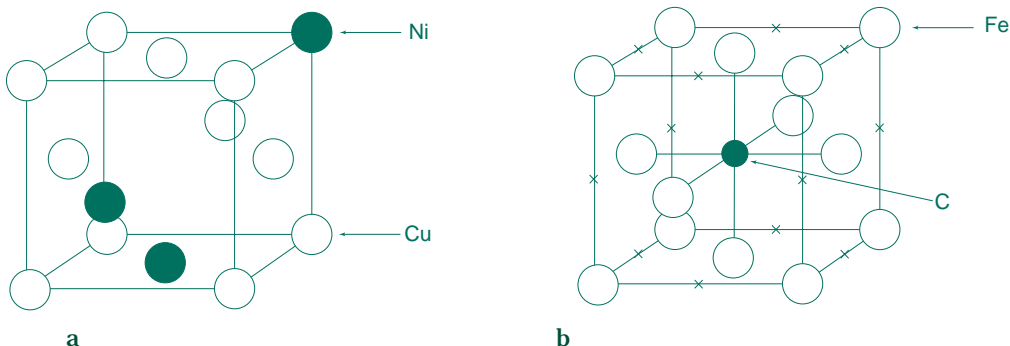


FIGURE 3.

Crystal structures of alloy solid solutions. (a) A substitutional solid solution of Ni and Cu atoms in a unit cell. The Cu and Ni atoms substitute in atomic positions (i.e., the lattice sites) in the face-centred cubic lattice. (b) The interstitial solid solution of C atoms in the unit cell of face-centred cubic iron. As much as 2.1% of C can dissolve in fcc iron at elevated temperatures. The position where the C atom resides as well as the x-positions, are the interstitial sites.⁹

the crystal structure of the solvent or small interstitial sites between solvent atoms; i.e., *substitutional* solid solution or *interstitial* solid solution as shown in Figures 3a and 3b, respectively.

Solid solutions are common in metallic systems and frequent in other inorganic systems (ceramics, for example) at elevated temperatures. However, *they are relatively uncommon in the traditional chemistry of aqueous solutions and in organic chemistry.* (Note: as discussed above, some organic polymer formulations exhibit solid solution characteristics and, as such, are known as *polymer blends* or *polymer “alloys.”*)

Immiscible alloys — alloys which contain an undissolved metallic element (lead brass and beryllium-copper alloys are examples). In such alloys, the immiscible metal may have been dissolved in the molten metal but then precipitated out upon cooling. The immiscible metal, depending upon its concentration in the alloy, is dispersed at grain boundaries (Cu-Be) or as globules (Pb-brass) within the body of the solid alloy. Lead brass and lead steel alloys are used commercially because the undissolved lead acts as a lubricant during the machining process. In the brass alloys, it also provides for pressure tightness in cast fittings for compressed air and for plumbing. Alloys based on immiscibility in the liquid state are relatively rare among alloys. There are many alloys based on immiscibility in the solid state, however. In addition to Cu-Be,

⁹ Reproduced from Flinn, R.A. and P. K. Trojan. 1981. *Engineering Materials and Their Applications*. Houghton Mifflin Co., Boston, USA. p. 49.

other examples include the silicon particles in many of the aluminum casting alloys, and graphite particles in the cast iron alloys as shown in Figures 2a and 2b.

An alloy, in the solid form, usually has more than one phase which can be identified by optical microscopy. These phases are the result of microsegregation of the phases of different composition during solidification and subsequent cooling of the alloy or specified heat treatments of the solid alloy. An alloy may contain as separate phases:

- **Component metal in substantially pure form** having negligible solid solubility in other phases present.
- **Solutions** where one or more elements, metallic or non-metallic, have dissolved in a dominant metal without major changes to the crystal structure of the latter.
- **Intermediate phases or compounds** with a different crystal structure from the component metals. The latter will probably have some solid solubility in the intermediate phase.
- **Compounds of metals and non-metals**, such as oxygen, nitrogen, carbon, phosphorous and sulphur. These would be oxides, nitrides, carbides, phosphides and sulphides, respectively.

In many alloy systems, there appear metallic phases other than primary solid solutions. These are commonly known as intermediate phases. Such phases essentially constitute a compound or substance that is separate and distinct from any of the components and have physical and chemical properties that are different from any of the components. The following might be considered a logical transitional sequence between a primary solid solution and an intermediate phase:

1. Primary solid solution with short-range order (α -solid solution of zinc in copper).
2. Primary solid solution with long-range order (copper-gold and iron-aluminum systems).
3. Ordered phase with a crystal structure different from the α -solution (e.g., the β -phase in copper-zinc alloys with more than 40% Zn).

The third step represents an intermediate phase. β -brass is distinguishable from α -brass not only crystallographically (it is body-centred cubic, whereas copper and α -brass are face-centred cubic) but also by microscopy and by a variety of physical properties including a freezing point of 1083°C for pure copper and of 900 to 1083°C for α -brass depending on the percentage of zinc dissolved in the copper. *Thus, β -brass represents a separate compound from either the copper or the zinc from which it was derived.*

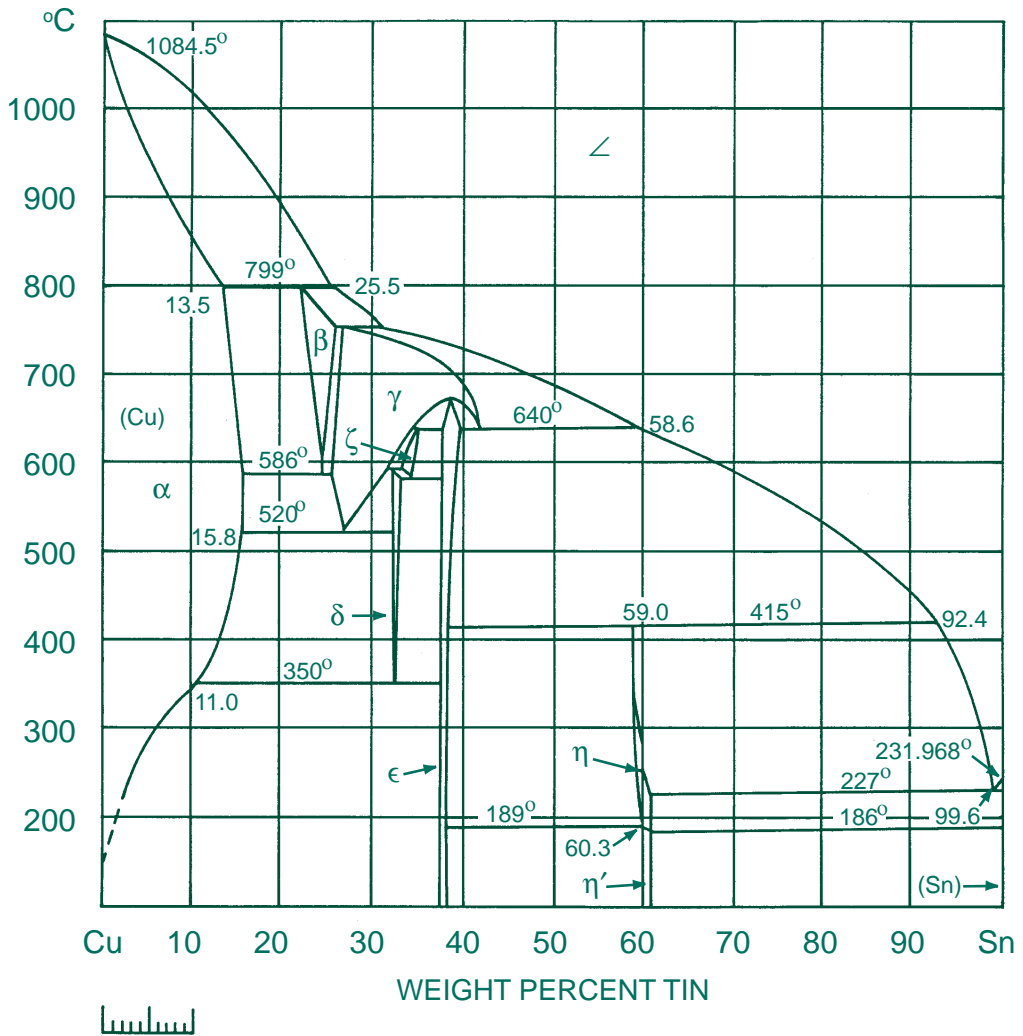


FIGURE 4.
The Copper-Tin System¹⁰

¹⁰ Hultgren, R.W. and P. Dasai. 1971. *Selected Thermodynamic Values and Phase Diagrams for Copper and Some of its Binary Alloys. INCRA Monograph I.* International Copper Research Association, Inc., New York, NY, USA.

Equilibrium Diagrams

Equilibrium diagrams, also called phase diagrams, are a graphic representation of the stability ranges for phases in metal and alloy systems. Stability regions (phase fields) are depicted as functions of composition, temperature, pressure or, in the case electrochemical systems, pH and Eh. A phase may simply entail a physical state (gaseous, liquid, solid) or, as in the case of metals and other solids, a homogeneous and crystallographically distinct structure. Phase diagrams are very useful tools for understanding alloy compositions and heat treatments.

Of the several types of phase diagrams that can be constructed for metallic systems, the most common are those that define regions of phase stability in terms of composition and temperature with pressure assumed to be at one standard atmosphere. These are most often constructed for two-element systems. An example of this type of diagram is shown in Figure 4 for the system Cu-Sn representing the several alloy compositions for the tin-bronze series of alloys. Other conventions are used to depict additional components of an alloy system.

Figure 4 indicates the various phases that are formed in the copper-tin system and their transformations with temperature. The copper-tin binary equilibrium diagram is complex, containing a peritectic¹¹ reaction and a series of eutectoid¹² reactions, each forming phases that are stable within specific composition ranges and temperature ranges. At true equilibrium, an 8% Sn alloy solidifies entirely as α (Cu with Sn in solid solution); however, in practice the wide freezing range causes extensive segregation to occur and, the last liquid to solidify is generally so enriched in tin that it undergoes a peritectic reaction at 799°C to form β . On cooling, the β -phase transforms via a eutectoid reaction into α and γ and ultimately into α and δ and finally into α and ϵ . In practice, the phase generally seen in the microstructure is the $\alpha + \delta$ eutectoid, because the δ to $\alpha + \epsilon$ reaction only takes place with prolonged low-temperature heat treatment.

High temperature phases, such as β , γ , and ζ , shown in Figure 4, do not exist in equilibrium at room temperature. However, by controlling the cooling rate of the alloy, i.e., quenching, these phases can be “frozen in” at room temperature and can exist under non-equilibrium conditions. By careful control of the heating and cooling of an alloy, the physical, mechanical and chemical properties can be controlled. *Thus, the properties of an alloy are as much a function of the heating and cooling treatment it has received as they*

11 Peritectic — having incongruent melting; i.e., the liquid formed at melting has a composition other than that of the solid — from Greek meaning “melt nearby.”

12 Eutectic — having congruent melting; i.e., the liquid formed at melting has the same composition as the solid — the eutectic composition will be the lowest melting point formed by the two constituents — from Greek meaning “easily melted.”

are of the elemental composition. In addition, as mentioned above, for many alloys, useful mechanical properties are further developed by mechanically working (rolling, hammering, etc.) the alloy form.

Metallic Mixtures

There are two types of *mixture* in metallic systems.

On the one hand, a metallic mixture is a simple physical mixture of two or more metals that are unreacted and undissolved. Such mixtures are heterogeneous, in that there is no solution of one metal in the other nor are there any chemical compounds formed by the simple act of mixing. *Each component exists in its original state and can be physically separated one from the other. Each component retains the physical and chemical properties of the unmixed metal.* An example of such a physical mixture is the blend of iron and copper powders that is sintered at elevated temperatures to form alloys. Before sintering, the copper and iron powders are a physical mixture and the powders can be re-segregated by physical means.

On the other hand, as mentioned in the definition for alloy, mixtures can and do exist in alloys. These are different from the simple mixtures described above. Two or more phases often coexist in an alloy and are each a reaction product of the alloying process. Each phase represents a unique chemical entity. While these alloys appear homogeneous to the naked eye, when viewed with the aid of either an optical microscope or an electron microscope, it can be seen that the phases are distinguishable as unique micro-constituents separated by interfaces. Using x-ray diffraction techniques, each phase of the alloy can be seen to have its own unique crystal structure. Being separate entities, these individual phases do not display the physical and chemical properties of their parent elements. Rather, they have their own unique physical and chemical properties. The properties of the mixture as a whole also depend on the relative amounts of the phases, the morphologies of the phases and the arrangement of atoms at the interfaces between the phases. However, unlike unalloyed mixtures, *mixtures, as they exist in alloys, cannot be separated into the individual phases or elemental components by ordinary physical means.* Once the iron and copper powders, mentioned above, are sintered (alloyed) the iron-copper alloy cannot be separated into elemental iron and copper by simple physical means as can the unsintered blend of iron and copper powders. The graphite flakes in the graphite-iron mixture and the silicon particles in the silicon-aluminum mixture of the alloys depicted in Figures 2a and 2b cannot be separated by simple physical means either.

CHAPTER 4

Transformation of Metals and Alloys to a Bioavailable State

For a substance to have an impact on the environment, it must be either soluble in water (the natural environment of biological systems) or sufficiently volatile or finely divided as dust to be transported by air. *Metals, categorically, are not soluble in water.* Solubility can only be achieved by ionization — the result of a chemical process known as *corrosion*. Metals cannot be dissolved in water and then be precipitated or crystallized out again without a change in their chemical composition. Substances such as sugar and table salt are soluble in that they can be dissolved into solution and can be recovered again with exactly the same chemical composition that they had upon dissolution. Metals, on the other hand, must undergo a chemical reaction with one or more components of the environment (oxygen, chlorine, etc.) to dissolve in water. In this case, the metal is not in solution as the elemental metal but rather as an ion of the metal. If these ions are recovered from solution by precipitation or crystallization, they will have the chemical composition of the ionic compound formed, not that of the original metal. The only way that the metal itself can be recovered from solution is by the application of a reduction process, such as electrolysis, hydrogen reduction or cementation, which reverses the oxidation process that led to the ion formation.

Corrosion is the deterioration of a material resulting from chemical attack by substances in the environment. The tarnishing of silver (reaction with oxygen or hydrogen sulphide) and the rusting of iron (reaction with oxygen and water) are corrosion processes which lead to the formation of chemical compounds on the surface of the metals or alloys. The compounds thus formed may be either soluble or insoluble in aqueous media. As with all chemical reactions, the rate of corrosion depends on the temperature and the concentration of reactants and products. The concentration of corrosion products in solution is controlled by the rate of the corrosion reaction and the solubility of the chemical compounds thus formed. In aqueous solution, the metal atom appears as a metallic ion (cation) which has a non-metallic ionic counterpart (anion).

As stated earlier, one of the reasons alloys are produced is to provide a metallic material with improved corrosion resistance. This is usually achieved by the addition of components that aid in the development of a protective film on the surface. The stainless steels are important examples of such alloys. Stainless steel is corrosion-resistant because of the formation of an iron-chromium oxide film on its surface. For this to

occur, at least 4 wt% chromium (Alloy S50100) and as much as 26% chromium (Alloy S31000) in some alloys must be present. The austenitic stainless steels are the most resistant to corrosion. In these alloys, nickel serves to stabilize the γ -phase (i.e., austenite) at room temperature. Otherwise, the austenite is stable at relatively high temperatures only. In this case, nickel is present in substitutional solid solution, substituting for iron in the face-centred cubic crystals.

There are two types of corrosion that are of concern to the environmental aspects of metals and alloys: oxidation by atmospheric attack; and, aqueous, or electrochemical, attack.

Atmospheric Oxidation

Atmospheric oxidation represents the direct chemical reaction between a metal or alloy and atmospheric oxygen which results in an oxide coating, or scale, on the metallic surface. There are various mechanisms for the corrosion, or building of scale, on metals. Each is distinguished by a specific type of diffusion through the scale. For some metals, the scale is tenacious and protective against further environmental attack. For others, the coating tends to be porous or to crack, and oxidation continues until the entire core of metal is consumed. There are four diffusion mechanisms commonly identified with metallic corrosion:

- diffusion of molecular oxygen through an *unprotective* porous oxide film to react at the metal-oxide interface;
- diffusion of metal ions (cations) through a non-porous oxide film, *that may be protective*, to react with the oxygen at the oxide-air interface;
- diffusion of oxygen ions (anions) through a non-porous oxide film to react with the metal at the metal-oxide interface; and,
- diffusion of both cations and anions through a non-porous oxide film to react within the oxide film rather than at the interface.

Each of these diffusion processes leads to a different rate of oxidation. It is this rate of oxidation that controls the rate at which a metal is made available to the environment.

Aqueous Corrosion

Aqueous corrosion is the dissolution of a metal (as an ion) into an aqueous environment. The metal atoms dissolve as ions which form as a result of a chemical reaction between the metal surface and the aqueous solution. Generally, such corrosion reactions are electrochemical in nature; i.e., generated by an electrical current. A similar set of mechanisms exists in aqueous corrosion as in atmospheric corrosion, in which the final reaction product is a film on the metal surface. This film may be protective (passive) or non-protective (active).

A common form of electrochemical corrosion reaction is the concentration cell, where in corrosion and the associated electrical current are due to slight differences in ionic concentrations in the aqueous solution in contact with the metallic surface. In concentration cells, the anode is the site on the metal surface where corrosion is occurring. The anode supplies electrons to the site where electrons are accepted (the cathode).

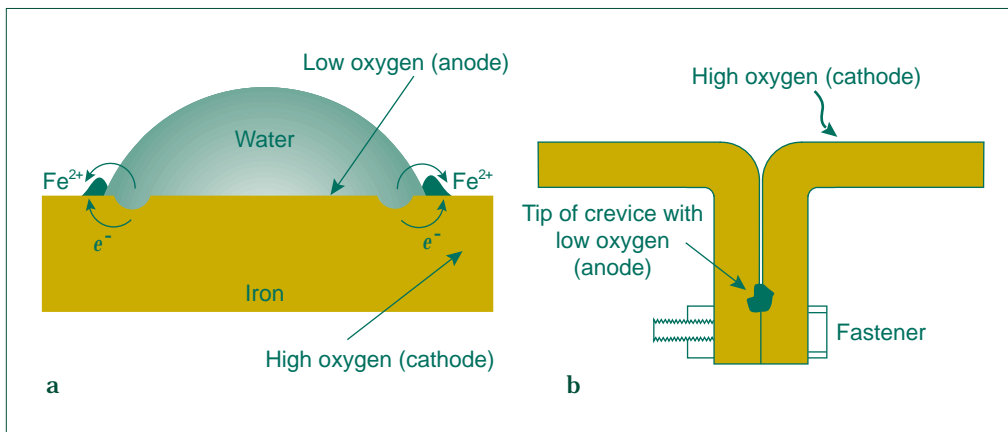


FIGURE 5.

Concentration cells: (a) Corrosion occurs beneath a water droplet on a steel plate due to low oxygen concentration in the water. (b) Corrosion occurs in the crevice because of limited access to oxygen dissolved in the water.¹³

¹³ Reproduced from: Askeland, D.R. 1994. *The Science and Engineering of Materials*. PWS Publishing Co., Boston, MA, USA, p. 134.

An electrolyte (i.e., aqueous solution) must be in contact with both the anode and the cathode, thus completing the electrical circuit, for corrosion to occur. The electrical circuit provides the means by which the metallic ions leave the anode and move to the cathode to accept the electrons.

In a concentration cell, corrosion can result even when the anode and the cathode are on the same piece of metal. Thus, the anode and cathode may be two separate items or two different sites on the surface of the same item. An example of corrosion of this type is shown in Figure 5b where a crevice creates the conditions for a differential concentration to occur.

In Figure 5b, the cathode and anode are both in water, but the concentration of oxygen dissolved in the water is lower at the anodic site in the crevice than it is outside of the crevice. It is this difference in oxygen concentration that drives the corrosion reaction. This demonstrates that it is not just the composition of the alloy that controls the possibility of corrosion and hence release to the environment but, in some cases, *the design of the structure in which the alloy is used*. However, if concentration corrosion is likely, alloy compositions are chosen that are less susceptible to such corrosion.

A second type of aqueous corrosion mechanism is *galvanic corrosion*. In a galvanic corrosion cell, there are two metals of different composition that provide the anode and the cathode. The driving force of this type of electrochemical cell is the relative tendencies of each metal to ionize. An example of this type of corrosion occurs when a copper surface is in contact with an iron surface. In this case, the iron corrodes in favour of the copper because iron has a stronger tendency to ionize than does copper. In this system a voltage of 0.777 volts is associated with the overall electrochemical process. Such electrochemical processes are the basis of batteries. Table 2 shows the electromotive force series (redox potential) for a number of pure metals relative to hydrogen.

The electromotive series is a useful guide to corrosion tendencies. The higher the metal is in the series, the more noble, or less chemically reactive, it is. The greater is the difference in the electrode potential between two metals, the greater is the degree of galvanic corrosion. However, the series is somewhat idealistic inasmuch as engineering designs seldom involve pure metals in standard concentrated solutions. Instead, they involve commercial alloys in various aqueous environments. The alloying of metals substantially changes the electrochemical potential and therefore their chemical reactivity. This is illustrated in Table 3 which shows the galvanic series of metals and alloys in sea water.

As shown in Table 3, iron and plain carbon steel are near the active end of the galvanic series; whereas, some passive stainless steel alloys are among the most noble (unreactive) of the metals and alloys, in spite of the fact that they are ferrous alloys.

TABLE 2.
Electromotive Force Series for Selected Metals

Electrode	Metal-metal ion equilibrium (unit activity)	Electrode potential relative to hydrogen (Volts)
Cathode - Most noble	Au-Au ³⁺	+1.498
	Pt-Pt ²⁺	+1.2
	Pd-Pd ²⁺	+0.987
	Ag-Ag ⁺	+0.799
	Hg-Hg ²⁺	+0.788
	Cu-Cu ²⁺	+0.337
	H ₂ -H ⁺	0.000
	Pb-Pb ²⁺	-0.126
	Sn-Sn ²⁺	-0.136
	Ni-Ni ²⁺	-0.250
	Co-Co ²⁺	-0.277
	Cd-Cd ²⁺	-0.403
	Fe-Fe ²⁺	-0.440
	Cr-Cr ³⁺	-0.744
	Zn-Zn ²⁺	-0.733
Al-Al ³⁺	-1.662	
Mg-Mg ²⁺	-2.363	
Na-Na ⁺	-2.714	
Anode - Most active	K-K ⁺	-2.925

Source: After A. J. de Bethune and N.A.S. Lord, as summarized in M.G. Fontana and N.D. Greene. 1978. *Corrosion Engineering*. 2nd ed. John Wiley & Sons, Inc. New York, NY, USA.

In Table 3, (active) and (passive) designations indicate whether an active or passive oxide film has developed on the surface of the alloy being measured. Passivity is caused by the formation of a surface film of hydrated metal oxide that interferes with the anode reaction and drastically lowers the corrosion rate. The surface of a metal or alloy first exposed to the aqueous environment is usually active. The passive state is developed after prolonged exposure of that surface to oxygen in the environment — either in water or air. Thus, the potential for a metallic ion from an alloy to enter the environment can

TABLE 3.
Galvanic Series in Sea Water

Electrode	Metal or alloy
Cathode - Most noble	Platinum
	Gold
	Graphite
	Titanium
	Silver
	Chlorimet 3 (62 Ni, 18 Cr, 18 Mo)
	Hastelloy C (62 Ni, 17 Cr, 15 Mo)
	18-8 Mo stainless steel (passive)
	18-8 stainless steel (passive)
	Chromium stainless steel 11-30% Cr (passive)
	Inconel (passive)(80 Ni, 13 Cr, 7 Fe)
	Nickel (passive)
	Silver solder
	Monel (70 Ni, 30 Cu)
	Cupronickels (60-90 Cu, 40-10 Ni)
	Bronzes (Cu-Sn)
	Copper
	Brasses (Cu-Zn)
	Chlorimet 2 (66 Ni, 32 Mo, 1 Fe)
	Hastelloy B (60 Ni, 30 Mo, 1 Mn)
	Inconel (active)
	Nickel (active)
	Tin
	Lead
	Lead-tin solders
	18-8 Mo stainless steel (active)
	18-8 stainless steel (active)
	Ni-resist (high nickel cast iron)
	Chromium stainless steel, 13% Cr (active)
	Cast Iron
Steel or unalloyed iron	
2024 aluminum (4.5 Cu, 1.5 Mg, 0.6 Mn)	
Cadmium	
Pure aluminum	
Zinc	
Anode - Most active	Magnesium and magnesium alloys

Source: LeQue, F.L. 1970. *Introduction to Corrosion*. National Association of Corrosion Engineers, Houston, TX, USA. p. 27.

change with time; i.e., as an initially active surface is converted to a passive one by exposure to the conditions of the environment itself.

As indicated above, the concept of an electromotive series for metals is somewhat abstract when it comes to practical systems, particularly alloys. This is because there are other material properties that have a more obvious effect on corrosion. In alloys, and even singular metals with impurities, many metallurgical factors can affect corrosion:¹⁴

- chemical segregation;
- presence of multiple phases;
- inclusions;
- cold work (introduction of defects); and,
- non-uniform stresses.

There are others, but the reason why these metallurgical factors affect corrosion is the same: they create anodic areas. If one area of a casting chills much faster than the bulk of the casting, it may be purer (through chemical segregation). When immersed in a corrosive solution, the pure area coupled with the less pure area provides a cell action. The same is true for multiphase alloys. If an alloy has a large area of a less corrosion-resistant phase, it behaves as an anode in a corrosion cell. This is true with austenitic stainless steel castings. A second phase (ferrite) occurs in what is supposed to be a single-phase (austenite) alloy, and corrosion tendencies are increased. If inclusions in alloys are metallic, they can lead to galvanic reactions; if they are non-metallic, they can sometimes inhibit corrosion. Wrought iron, which does not corrode (rust) as readily as many steel alloys, contains about 3% slag (silicates).

As mentioned above, many alloys derive their corrosion resistance from a surface condition that inhibits electrochemical action between the metal and its aqueous environment. This surface condition is known as *passivity*. In its simplest form, passivity is said to have occurred when a metal does not corrode in an environment that is known to be capable of causing corrosion of that particular metal. Passivity occurs by the formation of a protective film on the surface of the metal. There are various theories as to how passive films are formed. One theory is that a simple oxide film is formed on the metal surface with oxygen from the electrolyte (aqueous environment). Another is that the film consists of a gas that has been absorbed onto the surface of the metal and acts as a barrier to diffusion of metal ions from the substrate to the surface. Some of the metals that have a tendency to form passive surfaces are chromium, nickel, cobalt, iron and molybdenum. Consequently, alloys are tailored for corrosion resistance by the addition of one or more of these metals.

¹⁴ Budinski, K.G., loc. cit., p. 385.

Non-Uniform Corrosion

The very nature of alloys suggests that they do not necessarily corrode in a uniform manner and therefore the composition of elements entering the environment is not necessarily the same as the composition of elements in the alloy. There are two forms of non-uniform corrosion in alloys — intergranular attack and dealloying.¹⁵

Intergranular attack is simply a preferential corrosion at the grain boundaries of a metal or an alloy. The grain boundaries, being somewhat amorphous and of varying composition relative to the grains (phases) that they encompass, are higher-energy areas and, in uniform corrosion, may be negatively charged (anodic) relative to the grains. In this form of corrosion, with the dissolution of the material between the grains, the grains simply fall away from the metal surface relatively unattacked. Thus, the composition of material entering the aqueous environment will be that of the grain boundaries, and will not necessarily reflect the bulk composition of the alloy itself.

An example of intergranular attack is the sensitization of some stainless steel alloys. Any time that an austenitic stainless steel is heated to temperatures in the range of 400 to 850°C, a temperature range quite common to welding practices, chromium carbides tend to form at the grain boundaries. The carbides are formed from chromium and carbon that were in solid solution in the alloy. When chromium diffuses through the matrix to the grain boundary, it depletes the matrix material next to the grain boundary, and this region essentially becomes a low-alloy steel. Many environments will then readily attack the chromium-depleted grain boundary region. In this case, since chromium was depleted from the sensitive area, the material entering the aqueous environment will be deficient in chromium relative to the bulk composition of the alloy. Metallurgists avoid this problem either by minimizing the alloy's carbon content or by including carbide-forming elements, such as niobium or tantalum, so that chromium carbides cannot form. Intergranular attack also occurs in some high-strength aluminum alloys and in some copper alloys.

The most classic case of dealloying is in the *dezincification* of yellow brass (Cu-Zn). Dezincification occurs in some brass alloys under certain environmental conditions; namely, in sea water, in water of neutral pH at elevated temperatures or when stagnant water conditions occur. Dezincification is a problem that commonly occurs in valves and faucets in households. Brasses with less than 15% zinc do not dezincify. Their corrosion characteristics follow that of copper, which is relatively corrosion-resistant. However, brasses with greater than 15% zinc are prone to dezincification, and β and α -

¹⁵ Budinski, K.G., *loc. cit.*, p. 396.

β brasses with over 37% zinc are very prone to dezincification, especially in sea water. Normally such alloys would not be used under conditions that induce dezincification. However, the situation can be corrected by the addition of trace amounts of arsenic and/or antimony to the alloy. Thus, Arsenical Admiralty Brass (30% Zn), Alloy C44300, and Arsenical Naval Brass (40% Zn), Alloy C46500 each contain 0.02 – 0.06% arsenic; Antimonial Admiralty Brass (30% Zn), Alloy C44400, contains 0.02 – 0.10% antimony.

Other examples of dealloying include selective leaching of aluminum from aluminum-bronzes, selective leaching of nickel from copper-nickel alloys and graphitization — the dissolution of iron from grey cast iron alloys leaving only the graphite. The aluminum-bronze problem is solved by adding about 4% nickel to the alloy; nickel dealloying is reduced by control of the environment and the solution velocity; however, graphitization is extremely difficult to control and is probably the most costly form of dealloying since it commonly affects underground municipal water mains.

Nature of the Environment

In considering the transformation of a metal or an alloy to a bioavailable state, the chemical nature of the environment to which it is exposed is as important as the composition of the metal or alloy. Some of the major types of environment that engineering materials may be subjected to are:

- acids (oxidizing or reducing);
- bases;
- salts (acid, neutral, alkaline);
- gases; and,
- solvents.

In addition to these, corrosion processes are influenced by:

- temperature;
- velocity of the flow of solution past the surface of the metallic object;
- amount and nature of dissolved gases in the solution; and,
- nature and concentration of anions in the solution.

On Bioavailability

While we have said that in order for metals or the components of an alloy to become bioavailable, they must be made soluble (ionized) by chemical reaction, *solubility itself does not necessarily make the metal species bioavailable*. Bioavailability is further complicated by the nature of the metal ion species, the half-life of the species once it is in solution¹⁶ and the presence of other components in solution that may react with or absorb the metal species. Bioavailability refers to the amount of a chemical compound that can be absorbed by an organism.¹⁷ The amount that can be absorbed is determined by conditions within the solution as well as within the organism itself. For example, it has been shown that the effect of copper on the growth of algae is a function of the amount of Cu^{2+} that is present. However, the toxicity of this copper species is affected by natural processes, particularly complexation/chelation and sorption/desorption.¹⁸ Thus, there are a number of parameters associated with the environment itself that control the bioavailability of metals once they have been solubilized — hardness, pH, oxidation/reduction potential, and the composition of and concentration of ions, particulate matter and organic carbon present in the environment.¹⁹

For further discussion of the bioavailability of metals, see the ICME publication *Persistence, Bioaccumulation and Toxicity of Metals and Metal Compounds*.²⁰

16 I.e., the time for half the metal ions in solution to be converted back to an insoluble/non-bioavailable form by the action of substances — usually organic — in the aqueous medium.

17 Parametrix, Inc., *loc. cit.* p. 17.

18 Harrison, F.L. 1985. Effects of physiochemical form on copper availability to aquatic organisms. In R.D. Cardwell, R. Purdy, and R.C. Bahner (editors). *Aquatic Toxicology and Hazard Assessment*. Seventh Symposium. pp. 469-484. ASTM. *Special Technical Publication Number 854*. Amer. Soc. Test. Mat., Philadelphia, PA, USA. 587 p.

19 Parametrix, Inc., *loc. cit.* p. 18.

20 Parametrix, Inc., *loc. cit.*

CHAPTER 5

Summary and Conclusions

- An alloy is a metallic material, homogeneous in outward appearance, consisting of two or more elements that have been combined so that these elements cannot be readily separated by physical means.
- A mixture is a physical blend of solids and is heterogeneous in appearance. It may be comprised of pure components, compounds or solid solutions which can be separated by physical means.
- An alloy must be regarded as a separate substance, different from any of its components. The physical and chemical properties of an alloy are different from those of any of its components.
- In addition to its elemental composition, the physical and chemical properties of an alloy can be modified by heat treatment and by mechanical working. Thus, in addition to its elemental composition, the treatment that it has received and the entire processing history of an alloy must be described in order to define it adequately.
- Metals and alloys, *per se*, are insoluble in aqueous media and therefore cannot be considered bioavailable. In order to become soluble, and thus eligible for bioavailability, they must be ionized as the result of a chemical reaction called corrosion.
- One of the principal reasons why alloys, rather than pure metals, are used is to reduce corrosion which means that less metallic (soluble) ions are available to the environment. While commercial alloy design is primarily aimed at reducing corrosion in order to improve the durability of a metal part or structure, in filling this mission, it also serves to limit the availability of metallic ions to the environment.
- Corrosion is both a chemical and physical process in which diffusion of reacting species through films formed on the metallic surface can be the rate-controlling factor. Such films can be protective, thereby inhibiting further chemical reaction, or they can be non-protective. Many alloys are intentionally designed to have protective films in order to prevent or limit corrosion.

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- Often metallic elements that are considered to be toxic are added to alloys in order to increase their resistance to corrosion. Once alloyed, these toxic elements are not necessarily available to the environment.
 - The ecotoxicity of an alloy cannot be predicted based on its components. The products of corrosion entering the environment from an alloy do not necessarily have the same elemental composition as that of the bulk alloy.
 - Solubility itself does not constitute bioavailability. Bioavailability refers to the amount of a chemical compound that can be absorbed by an organism. The amount that can be absorbed is controlled by factors within the solution, such as the species of metal ion, and the presence of factors within the organism itself. A potentially toxic species can become detoxified by chemical reaction or complexation with other substances dissolved in the media.

APPENDIX

Metals of the Periodic Table

Ac - actinium	Nd - neodymium
Ag - silver	Ni - nickel
Al - aluminium	Os - osmium
As - arsenic	Pa - protactinium
Au - gold	Pb - lead
Ba - barium	Pd - palladium
Be - beryllium	Pm - promethium
Bi - bismuth	Po - polonium
Ca - calcium	Pr - praseodymium
Cd - cadmium	Pt - platinum
Ce - cerium	Ra - radium
Co - cobalt	Rb - rubidium
Cr - chromium	Re - rhenium
Cs - cesium	Rh - rhodium
Cu - copper	Ru - ruthenium
Dy - dysprosium	Sb - antimony
Er - erbium	Sc - scandium
Eu - europium	Se - selenium
Fe - iron	Si - silicon
Fr - francium	Sm - samarium
Ga - gallium	Sn - tin
Gd - gadolinium	Sr - strontium
Ge - germanium	Ta - tantalum
Hf - hafnium	Tb - terbium
Hg - mercury	Tc - technetium
Ho - holmium	Te - tellurium
In - indium	Th - thorium
Ir - iridium	Ti - titanium
K - potassium	Tl - thallium
La - lanthanum	Tm - thulium
Li - lithium	U - uranium
Lu - lutetium	V - vanadium
Mg - magnesium	W - tungsten
Mn - manganese	Yb - ytterbium
Mo - molybdenum	Yt - yttrium
Na - sodium	Zn - zinc
Nb - niobium	Zr - zirconium

NOTES

About the Authors

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William H. Dresher is a chemical engineer with a PhD in extractive metallurgy. He has over 30 years of research and development experience, at both the corporate and academic levels, in the fields of: extractive metallurgy of base and refractory metals; ceramics and high performance alloys; and, copper processing, products and marketing. He is an expert on the environmental aspects of copper in health and ecotoxicity. During his career, he has held the positions of Assistant Director of Research for the Mining and Metals Division of Union Carbide Corporation, Dean of the College of Mines of the University of Arizona, President of the International Copper Research Association, and most recently, Vice President of Technology of the International Copper Association. An internationally recognized expert on the processing, products and environmental aspects of copper, Dr. Dresher has focused on bringing good science and technology to these subjects.

Dr. Dresher is past president of the Mining and Metallurgical Society of America and a past member of the Board of Directors of the Society of the Minerals, Metals and Materials Society (TMS). He represented the field of materials on a special scientific exchange between the USA and Chile operated by the American Association for the Advancement of Science and the Chilean Academy of Sciences. He also served for ten years on the American Management Association's (AMA) Research and Development Council - an advisory body of corporate research and development executives that advises the AMA on its programming in the area of research and development management training.

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David R. Poirier

David R. Poirier is an educator and researcher with more than thirty years experience in the fields of materials science and engineering, and metallurgy and manufacturing engineering. Dr. Poirier is currently Professor of Materials Science and Engineering at the University of Arizona where he has been on the faculty since 1978. His research interest is in materials processing, mostly as it applies to the solidification of alloys. His work on macrosegregation in cast alloys earned him the John Chapman Award of ISS-AIME in 1980 and the NASDA Technology Utilization Program Award in 1983.

Dr. Poirier has published over ninety papers, and has given numerous presentations of his research work at major conferences and universities, and at industrial and governmental laboratories. He has coauthored three books: *Transport Phenomena in Materials Processing* (1994), *Transport Phenomena in Metallurgy* (1973) and *Heat Transfer Fundamentals for Metal Casting* (1994).

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