

ALLOYING

UNDERSTANDING THE BASICS



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UNDERSTANDING THE BASICS

Edited by
J.R. Davis
Davis & Associates



**The Materials
Information Society**

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Preface

Alloying may be defined as “the process of adding one or more elements or compounds to interact with a base metal in order to obtain beneficial changes in its mechanical, physical, or chemical properties or manufacturing/processing characteristics.” For the purposes of this publication, the definition has been limited to those alloying processes that affect the *bulk* of the material; therefore, surface alloying processes such as carburizing, nitriding, ion implantation, and hot dip galvanizing are not covered. However, elements or compounds that lead to a preferential microstructure and subsequent improved properties are covered. Examples of these are grain refiners (grain refining results in better forming or higher strength), inoculants added to molten cast irons to produce changes in graphite distribution and improvements in mechanical properties, magnesium-containing nodulizing (or spheroidizing) additions in ductile irons for high strength and ductility (up to 18% elongation), and the addition of certain elements, such as calcium, sodium, strontium, and antimony, to refine the structure of aluminum-silicon casting alloys as well as improve their tensile properties and ductility. Also included are discussions of some powder metallurgy (P/M) materials that technically may fall outside the definition of alloying given above. An example is copper-base dispersion strengthened materials. Copper can be strengthened by using fine dispersed particles of aluminum oxide. Because this oxide is not immiscible in liquid copper (i.e., it does not “interact”), dispersion-strengthened copper cannot be made by conventional ingot metallurgy and alloying techniques; P/M techniques must be used. Dispersion-strengthened superalloys made by “mechanical alloying” are also described.

Although emphasis has been placed on deliberate alloying additions (minor or major alloying elements), the effects of trace or tramp elements are also summarized. Such impurities can have a profound affect on processing and properties of metals and their alloys. For example, impurity levels in the parts per million range can significantly lower the electrical conductivity of copper.

I wish to thank a number of people who provided invaluable assistance throughout this project. The introductory article, "Principles of Alloying," was authored by Hugh Baker, consulting editor to ASM and a longtime contributor to the ASM Handbook and Phase Diagram programs. I have had the privilege of working with Hugh for some twenty years. Thanks are also extended to Larry Korb (Rockwell International), an ASM Fellow and past Chairman of the ASM Handbook Committee. Larry was instrumental in defining the scope of the book and supplied material for several articles, including those on carbon and low-alloy steels and aluminum alloys. Finally, the helpful comments and assistance from the ASM Editorial staff are acknowledged. In particular, I would like to thank Steve Lampman from Technical Publications for his involvement in the early stages of the project.

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Principles of Alloying*

Introduction and Overview

Metals are seldom used in commercial applications in their pure (un-alloyed) condition. Instead, one or more chemical element is normally alloyed with the base metal to alter its characteristics to make it easier to fabricate and/or perform better in the application. Although in the broad sense, alloying covers changing the chemical composition of the surface of a part by such processes as plating, cladding, nitriding, ion implantation, carburizing, and hot dip galvanizing, this book is limited to only those alloying processes that affect the bulk of the material, while surface modification is discussed in other ASM publications. This book, however, does cover the addition of inoculant materials to the melt to alter the microstructure of the solid part. Some of the characteristics that are affected by alloying (or inoculating) are listed in Table 1.

Alloying for Mechanical Properties

Room-Temperature Strength. The most common reason for alloying is probably to improve room-temperature strength. The strength of a metal part is determined by its resistance to plastic (permanent) deformation when loaded beyond its elastic limit. Because this plastic deformation occurs by the mechanism of *slip* along the crystallographic planes in the grains of the metal (Fig. 1), the object of alloying to improve strength is that of increasing resistance to crystallographic slip. There are several ways to accomplish this increase in resistance, but before these are discussed, the internal structure (microstructure) of the metal should be examined.

*This article is written by Hugh Baker, Consulting Editor, ASM International.

Table 1 Metal characteristics affected by alloying

Mechanical properties	Processing properties
Room-temperature strength	Castability
Hardenability	Weldability, brazeability, and solderability
Fatigue resistance	Formability
Creep resistance	Machinability
Service properties	Physical properties
Heat resistance	Elastic modulus
Toughness and cold resistance	Density
Corrosion/oxidation resistance	Magnetic properties
Hardness and wear resistance	Electrical properties
	Thermal expansion properties
	Color

The atoms in each metal part are normally arranged into many different individual crystals (*grains*). The configuration *structure* of the crystal lattice and the distance between the atoms in the crystal (*effective atom diameter*) are those that result in the lowest energy state for the atoms in the crystal and are unique to each metallic element and temperature being considered. (Some metals have different unique crystal structures and atomic diameters at different temperatures; that is, they form different *phases* at different temperatures.) The planes of the crystals in a metal part are usually oriented in a great many different directions, many of which

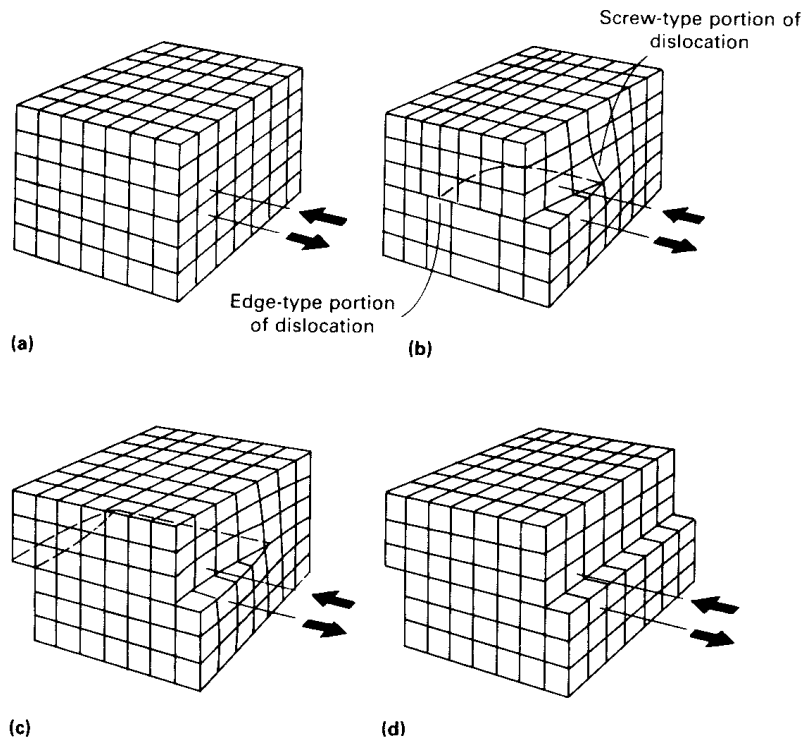


Fig. 1 Four stages of slip formation. (a) Crystal before displacement. (b) Crystal after some displacement. (c) Complete displacement across part of crystal. (d) Complete displacement across entire crystal

are not closely aligned with the direction of the external loading direction. As shown in Fig. 2, the atoms in the three-dimensional regions between the individually oriented crystals (the grain boundaries) are not aligned with either crystal and, therefore, are in a higher energy state than the crystals themselves.

All the various ways of increasing resistance to slip in a metal part are based on increasing the interference to the slip process. These include: grain refining, cold work, solid-solution hardening, age hardening, dispersion hardening, phase transformation, and duplex-structure strengthening. In multigranular parts, the orientation of the slip planes in adjoining grains is seldom aligned, and the slip path must change directions when traveling from one grain to another. Reducing grain size produces more changes in direction of the slip path and lengthens it, while the permanent deformation of the part caused by cold work results in distortion of the crystal structure, which makes slipping more difficult (*work hardening* or *strain hardening*). Vanadium, aluminum, tungsten, and nitrogen are examples of excellent grain refiners in steels, while titanium, vanadium, aluminum, and zirconium additions to carbon and low-alloy steels inhibit grain growth.

Atoms of a different element can be added to the base metal (up to the limit of solid solubility for the second element), but these new atoms will, of course, have a different effective diameter than those of the base metal. If the new atoms are quite small, they may be able to fit in the interstices between the host atoms in the crystal, but some distortion of the crystal lattice will probably result (Fig. 3a). If the difference in size of the atoms is fairly small, the new atoms can substitute for base metal atoms in the

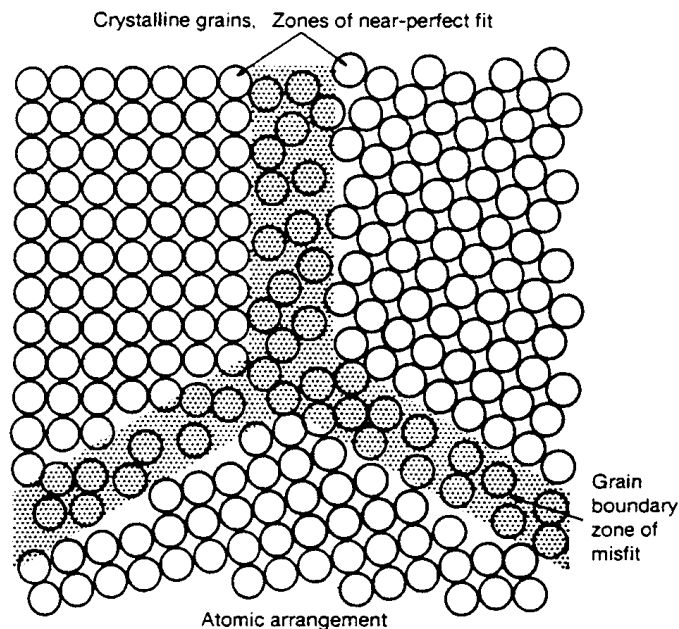


Fig. 2 Nature of grain boundaries

crystal lattice, but some distortion of the lattice will also result. In either case, the distortion caused by the *solid solution* will result in making slip more difficult (solid-solution hardening) (Fig. 3b).

When a metal solidifies from the molten state, crystal nuclei first form and then grow together to create grains, the last material to solidify forming the boundaries between the grains. When the amount of alloying atoms added exceeds the limit of solid solubility, the excess atoms of the alloying element will become trapped in the grain boundaries. Then, as the temperature is further decreased, the excess atoms try to unite with atoms of the base metal to form small regions of *intermetallic compound*. Although these regions have a different crystal structure than the base metal, the two crystal structures remain *coherent*, and the mismatch between the two lattice structures causes strain hardening of the part (Fig. 4a and 4b). At relatively low temperatures, the reaction between the base metal atoms and the excess alloying atoms is normally quite slow, and the strain-hardening phenomena is called *age hardening* (and sometimes called by the misnomer *precipitation hardening*). If the reaction is allowed to continue, the regions of intermetallic compound grow and actually precipitate out of solution (become *noncoherent*) and form discrete particles (Fig. 4c and 4d). When this happens, the mismatch straining is lost and the part becomes *overaged* and loses strength. There are many examples of alloying for age hardenability, including copper added to aluminum to form 2000-series alloys.

As stated previously, some metals have different unique crystal structures and atomic diameters at different temperatures; that is, they form different stable *phases* at different temperatures. Examples are alpha and beta titanium and alpha and gamma iron. Some metal phases are transitional rather than stable. An important example of a transitional phase is the martensite form of iron, which is a hard material that strengthens a part when it is formed (by *phase transformation* of quenched gamma iron).

If the second phase material that is finely dispersed throughout the matrix material of the alloy is a hard material, such as martensite in steel

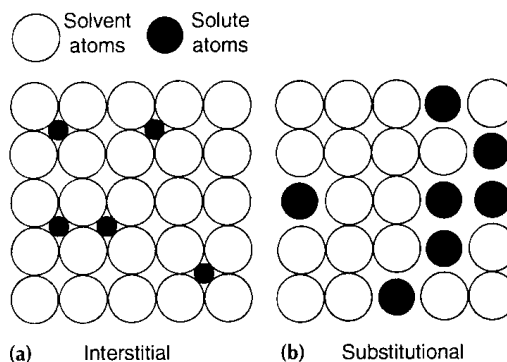


Fig. 3 Solid-solution mechanisms. (a) Interstitial. (b) Substitutional

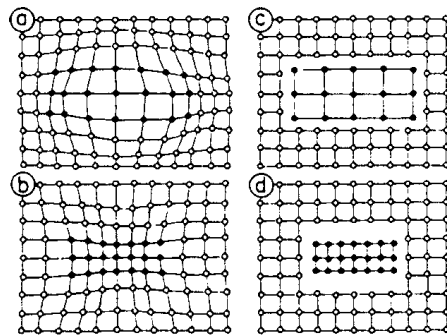


Fig. 4 Coherent (left) and noncoherent (right) precipitation. (a) and (b) A coherent or continuous structure forms when any precipitate is very small. (c) and (d) Coherency is lost after the particle reaches a certain size and forms its own crystal structure. Then a real grain boundary develops, and severe lattice stresses disappear.

or alumina (Al_2O_3) in aluminum, the alloy is strengthened by *dispersion hardening*. Another example of dispersion hardening is dispersion-strengthened copper produced by internal oxidation. These alloys, which feature a fine, uniform dispersion of aluminum oxide particles in the copper matrix, exhibit higher strength and stability at elevated temperature. Dispersion-strengthened nickel-base alloys are produced by high-energy ball milling yttria (Y_2O_3) powder and the nickel-base alloy powder together (*mechanical alloying*). The improved elevated-temperature strength of these alloys is due to a uniform dispersion of fine refractory oxide (yttria) particles in a superalloy matrix.

Austenitic stainless steels are produced by alloying with gamma-stabilizing elements, notably nickel and chromium. These alloys have been strengthened by a heat treating and working process by which a *duplex structure* containing a very intimately mixed conglomerate of alpha and gamma grains is formed that offers more resistance to slip than the gamma-only structure of standard austenitic stainless steel.

Hardenability is the relative ability of a ferrous alloy to form martensite when quenched from a temperature above the upper critical temperature. The hardenability of steel is increased by increasing the carbon content and by alloying with such elements as boron, chromium, and manganese. The hardenability of irons and steels is discussed in greater detail in the articles covering these materials. Quenching of steel in water to produce martensite, however, often results in severe cracking of the part. Adding sufficient alloying elements will allow parts to harden in room-temperature air, greatly minimizing this problem.

Fatigue Resistance. Fatigue, the damage caused to a material by cyclic stressing, results from the fact that the material is not ideally homogeneous. Therefore, in each half cycle of stressing, minute strains are produced that are not completely reversible. These strains cause incremental

slip and local strain hardening, which gradually lead to the formation of minute cracks that grow and coalesce until failure eventually occurs. While manufacturing conditions, such as cold forming, welding and brazing, plating, and surface conditions, significantly affect fatigue resistance, it is usually also directly related to the hardness and tensile strength of the material. Therefore, alloying to produce good hardness and tensile strength usually results in good fatigue resistance. In addition, reducing unwanted trace elements and inclusions to increase tensile strength also helps to increase fatigue strength.

Creep Resistance. Creep, time-dependent extension under stress, occurs by the movements of *dislocations* through the metal grains (see Fig. 1). Because their movement at lower temperatures is impeded by grain boundaries and second-phase particles, chemical compositions that help produce fine grain size and microstructures that result in “grain-boundary pinning” particles improve creep resistance. At higher temperatures, creep occurs primarily by grain-boundary sliding. Therefore, increasing grain size improves creep resistance at these temperatures.

Alloying for Service Properties

Heat Resistance. Metals for high-temperature service must be alloyed to promote improved tensile strength and/or creep strength (see previous paragraph). Steels are a good example. While at room temperature or slightly above, carbon serves admirably to increase the tensile strength of steel; at higher temperatures, carbon is less effective. For temperatures of about 350 to 550 °C (700 to 1000 °F), additions of molybdenum, tungsten, or niobium are effective in increasing the strength of chromium steels. For still higher-temperature service, it is necessary to use steels of an austenitic type, which are formed by adding sufficient nickel.

Toughness and Cold Resistance. Plain carbon and low-alloy steels, like many metals that have a body-centered cubic lattice structure at room temperature, are susceptible to a lowering of absorbed impact energy with decreasing temperature. This change is accompanied by a transition in the appearance of the fracture surface from a ductile one to a brittle one. This *ductile-to-brittle transition* occurs over a relatively narrow subfreezing temperature range (the DBTT). The composition of the steel, as well as its microstructure, significantly affects both the transition temperature and the energy absorbed during fracture at any particular temperature. For example, to avoid low-temperature brittle fracture, carbon and phosphorus should be kept low, while boron and manganese additions are helpful. Nickel additions to steel in the range of 2.25 to 9% improve low-temperature toughness and strength, because they lower the DBTT of steels.

Corrosion/Oxidation Resistance. Corrosion of metals takes several different forms, including environmental, galvanic, and stress corrosion. Environmental and stress corrosion can both be influenced by the chemical composition and microstructure of the material. For example, as stated earlier, austenitic stainless steels are produced by alloying with gamma-stabilizing elements, notably nickel and chromium. The excellent corrosion resistance of stainless steels relies mainly on the *passivity* of its surface. As such, environments that tend to break down this passivity are more detrimental to stainless steel, while environments that tend to maintain this passivity do not damage stainless steel. Chromium atoms are similar in size to iron atoms, so when chromium is alloyed in iron at a level of no more than 11% Cr, the chromium atoms replace some of the iron atoms, thus forming a substitutional solid solution (see Fig. 3b), and this iron-chromium material has much-improved corrosion resistance over iron alone. Unalloyed titanium also develops a passive surface, which allows it to be used in severely corrosive environments, but if its surface passivation is disturbed, corrosion proceeds at a high rate. Many nickel-base alloys also have long been noted for their corrosion resistance.

The most common type of environmental corrosion is oxidation, which is an electrochemical process that requires the presence of moisture (liquid) in the environment. When environmental corrosion occurs, metal atoms go into solution in the liquid as ions, which releases the excess electrons. The production of the ions and excess electrons creates an electrical potential, called an *electrode potential*, which differs from metal to metal. One of the most effective ways of countering the corrosive effects of the presence in a part of atoms of a metal having a high electrode potential is to alloy with a metal that will tie up the undesirable atoms as relatively inert compounds, for example, adding magnesium to aluminum alloys that contain iron as an impurity. Because aluminum has a relatively high electrode potential, its surface rapidly loses its shiny appearance and develops a gray oxide coating, but alloying with magnesium helps to keep it bright.

Stress-corrosion cracking (SCC) results from the combination of static tensile stress (externally applied or residual) and a particular environment. Some alloys and microstructures are more susceptible to this type of cracking than others. For example, magnesium alloys that contain more than about 1.5% Al are susceptible to SCC, and the presence of zinc in the magnesium-aluminum alloy increases this susceptibility. Stress-corrosion cracking in aluminum-magnesium alloys can be minimized by limiting the magnesium content to 3%, while SCC in brasses can be minimized by decreasing the zinc content to less than 15%.

Galvanic corrosion, which results from the contact of two dissimilar metals (alloys) in an electrically conductive liquid, is best dealt with by mechanical means (eliminating the liquid by proper design for good drainage, inserting a nonconductor between the metal parts, and/or plating

one of the contact surfaces with a more compatible metal) rather than by alloying.

Hardness and Wear Resistance. Gold is very soft and easily deformed in its pure (unalloyed) form. Therefore, when used in electrical contacts, coins, jewelry, dentistry, and other commercial applications, it is usually alloyed with harder metals, such as silver, copper, palladium, and platinum, to increase its hardness and wear resistance without an appreciable loss in oxidation resistance. The basic hardness of steel is increased by increasing the carbon content, while the *hardenability* of steel (the ability to form martensite upon quenching from above the upper critical temperature) is increased by increasing the carbon content and by alloying with such elements as boron, chromium, and manganese. The abrasion and wear resistance of steel is increased by additions of such elements as chromium, nickel, molybdenum, and tungsten. Cast iron engine parts have long been made more wear resistant by alloying with silicon. Silicon additions also increase wear resistance of aluminum alloys. High-alloy white irons have improved wear resistance due to the presence of massive chromium carbides. Austenitic manganese (Hadfield) steel has long been used in railroad “frogs” (points) and jaw-crushers because of its exceptionally high wear resistance. Lubricity of bronzes used for sleeve bearings is increased by alloying with 10% Sn.

Alloying for Processing Properties

Castability. Molten metal begins to cool as soon as it leaves the pouring ladle, and because some time is required for the metal to reach and completely fill a mold, a reasonable freezing range is necessary for a metal (alloy) to have good castability. As seen in Fig. 5, pure (unalloyed) metals and intermetallic compounds melt and freeze at a single temperature. Therefore, they are very difficult to cast into an involved shape. Alloying, however, not only decreases the melting/freezing temperature, but also extends the temperature range over which solidification occurs (see Fig. 5). Both of these effects increase castability. *Fluidity*, the ease with which the molten metal flows and fills the mold, is also increased by suitable alloying. For example, the fluidity of cast iron increases with increasing carbon content until the eutectic concentration (4.3%) is reached, and then decreases at higher carbon contents. The fluidity of aluminum is increased by additions of silicon and/or copper and magnesium and decreased by additions of nickel and/or manganese. The fluidity of brass is increased by additions of antimony.

Weldability, Brazeability, and Solderability. Although the weldability of a material depends on the welding conditions used, the composition of

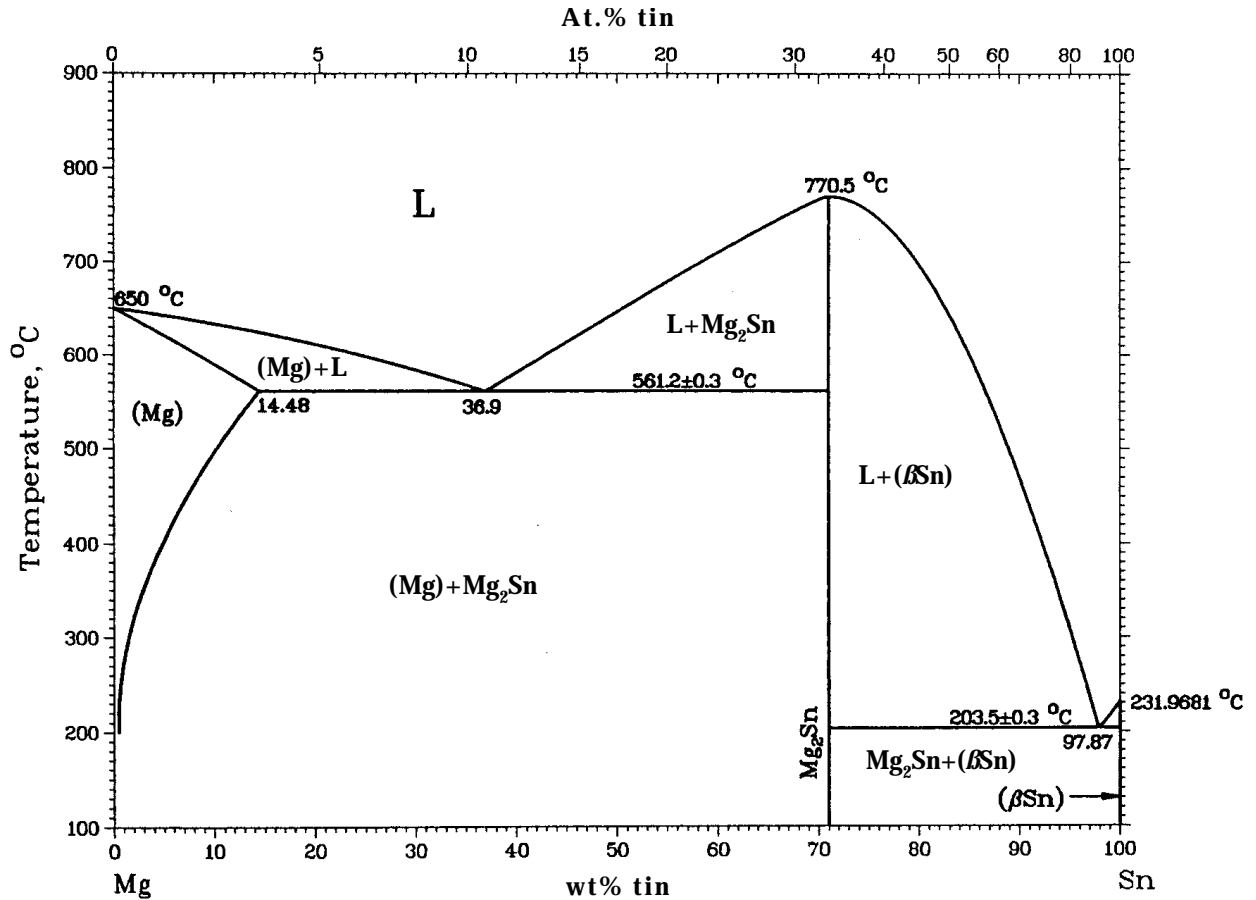


Fig. 5 Phase diagram for the magnesium-tin system, which exhibits a high-melting intermetallic compound. Source: A.A. Nayeb-Hashemi and J.B. Clark, 1988

the material is always a significant factor, as well as the composition of the filler material. Because welding is a type of casting process, the same alloy factors must be considered. For example, silicon is added to aluminum weld wire to increase its fluidity and to ensure production of sound welds. Another factor that must be considered, however, is the mechanical constraint on the freezing metal that the weld joint produces. If there are any low-melting second-phase materials in the grain boundaries, *hot tears* can form in these regions as the weld metal shrinks during cooling. High-temperature brazing fillers can be produced from alloys containing silver and other precious metals with nickel and copper, while low-temperature solder alloys are made from lead, tin, silver, indium, antimony, cadmium, and zinc.

Formability. Good formability requires that the material to be bent, drawn, stretched, ironed, or otherwise permanently deformed into a usable shape have a chemical composition that offers a combination of good ductility and strength. Low ductility and low strength both limit the amount of forming that the material can endure before tearing occurs. The

composition should also be such that there is a low tendency for formation of second-phase particles, such as sulfides in steel, which can lead to cracking or splitting during forming. The addition of 8% Ni to austenitic stainless steel lowers its rate of strain hardening, permitting deep drawing of stainless parts. Alloying, in conjunction with thermal/mechanical processing, can result in alloys that have more than 100% elongation (are *superplastic*) and that can be formed into intricate shapes.

Machinability is increased by alloying inclusions that lubricate the machine tool and break up the formed chip into small pieces. For example, lead, nitrogen, calcium, manganese, or phosphorus can be added to carbon and low-alloy steel to improve machinability, while selenium or sulfur are added to stainless steel to achieve improved machinability. Free-machining copper alloys are produced by additions of such elements as lead, sulfur, phosphorus, and tellurium.

Alloying for Physical Properties

Elastic Modulus. Several attempts have been made to take advantage of the high value of elastic modulus of beryllium in an alloy. One was an aluminum-matrix material for aerospace, called Lockalloy, after Lockheed Aircraft Company. The age-hardenable beryllium-copper alloys also have good values of elastic modulus, which are combined with high strength.

Density of an alloy is usually close to the value determined by the relative amount of the main constituents and their densities. A good estimate of the resulting value of density for an alloy can be obtained from the rule of mixtures. The addition of lithium to aluminum and magnesium is an example of producing light-weight aerospace alloys.

Magnetic Properties. All metals have magnetic properties of one type or another. *Ferromagnetic* materials are those that are strongly attracted to a magnet. Elements that are naturally ferromagnetic at room temperature include iron, nickel, and cobalt. These metals, however, lose their ferromagnetic properties when the temperature is raised above the *Curie* temperature for the metal (or alloy) in question and become *paramagnetic*, which means that they are much less strongly attracted to a magnet.

Magnetically soft materials are ferromagnetic materials that retain little or no magnetism when removed from a magnetic field. These materials are often produced by adding silicon, aluminum, or nickel to iron to increase its electrical resistivity and thereby reduce eddy-current losses and make it more suitable for alternating current motors, generators, and transformers. Cobalt additions to iron can be used to promote high permeability, while silicon additions can increase the temperature at which

grain growth occurs, allowing for more preferential grain orientation in the core material.

Magnetically hard materials for use as permanent magnets are also ferromagnetic materials, but are those that are capable by themselves of producing and maintaining relatively high magnetic induction without the aid of external magnetic fields. Permanent magnet materials are based on the cooperation of atomic and molecular moments within a magnetic body to produce a high level of retained magnetic induction. These materials are commonly hardened steels produced by phase-transformation hardening of plain (carbon) and alloyed (chromium, tungsten, or cobalt) steels, or by dispersion or precipitation agents (aluminum in iron-nickel or molybdenum in iron-cobalt). Other permanent magnet materials are alloys based on cobalt (platinum-cobalt and cobalt-rare earth) and ceramics based on hard iron oxides (ferrites).

Electrical Properties. One of the most important characteristics of a metal is the ease with which it transmits electrical current. The outer (valance) electrons in metal crystals are not tied to any specific atom and are, therefore, free to migrate in response to an electric field. However, any impediment to this free movement increases the resistance to the flow of the electrical current. These impediments include grain boundaries, second-phase particles, and lattice distortions caused by cold work, age hardening, and second elements in solid solution.

In some applications, such as electrical transmission wires, low electrical resistance coupled with adequate strength is desired. Oxygen-free copper, sometimes alloyed with minimal amounts of hardening agents (such as chromium, tellurium, beryllium, cadmium, or zirconium), is an important electric wire material. Some aluminum conductors are alloyed with silicon and magnesium to increase their strength without greatly decreasing their electrical conductivity.

In other applications, such as the magnetically soft materials described previously, greater electrical resistance is desired. In still others, such as electrical-resistance heating devices, high, uniform electrical resistance is required. Resistance-heating materials include nickel-chromium, nickel-chromium-iron, and iron-chromium-aluminum alloys.

Thermal Expansion Properties. Iron-nickel alloys have many anomalous properties, depending on the relative proportions of the two metals. For example, the coefficients of linear thermal expansion at room temperature range from a small negative value ($-0.5 \mu\text{m}/\text{m} \cdot \text{K}$) to a large positive value ($20 \mu\text{m}/\text{m} \cdot \text{K}$). One alloy, containing 36% Ni with small quantities of manganese, silicon, and carbon amounting to a total of less than 1%, has a coefficient so low that its length remains almost invariant (constant) for ordinary changes in room temperature. For this reason, the alloy, named Invar, has found many uses ranging from compensating

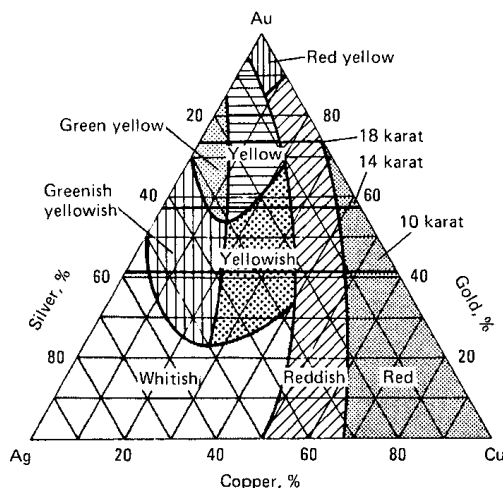


Fig. 6 Color chart for gold-silver-copper alloys for jewelry and dental applications

pendulums and balance wheels for clocks and watches to components for radios and other electronic devices.

Color. Most of the commercially important colored alloys for jewelry and dental applications are based on the gold-silver-copper system, which takes advantage of the different basic colors of these three elements to offer a wide range of color blends to suit the user (Fig. 6). Copper alloys are also available in a wide variety of colors (see the article on these alloys).

Effect of Properties on Alloying

The various techniques used for alloying and inoculation of metals have been developed to overcome physical, mechanical, and chemical problems caused by the fact that the base metal and the alloying or inoculate material have dissimilar properties. Some of these properties are discussed subsequently.

Melting Temperature. Producing a lead-tin solder alloy is fairly easy. Pieces of solid lead and tin can be melted together without much trouble, because their melting temperatures are fairly close (328 and 232 °C or 622 and 450 °F, respectively). Producing an alloy of aluminum and silicon, however, would appear to be more difficult due to the wide disparity in melting temperatures between the two constituents. Pure silicon melts at 1410 °C (2750 °F), while the melting temperature of aluminum is only 660 °C (1220 °F). If the temperature of the molten aluminum is raised to

that of molten silicon, much of the aluminum could be lost to oxidation and vaporization. However, examination of the aluminum-silicon binary phase diagram shows that a low-melting eutectic (577 °C, or 1071 °F) is formed at 12.6 wt% Si. Therefore, successful alloying of aluminum-silicon alloys is achieved by using master alloys or prealloyed ingots containing silicon contents at or near the eutectic point.

Density. If the specific weight of an alloying material is significantly different from that of the base metal, the alloying material will tend to either rise to the top or sink to the bottom of the melt, and vigorous stirring will be required to ensure a uniform chemical composition of the solid casting.

Solubility. Adding particles of inoculant material to a melt to refine the grains produced in the solid casting is often a problem. A fine grain size in the casting is produced when there are a great many grain-nucleation sites available in the melt. This usually is accomplished by use of an inoculating compound that is still solid at the temperature of the melt and that is relatively insoluble in the melt, thus remaining solid. Here again, vigorous stirring of the melt is required (to keep the solid particles from settling out).

Volatility. If the metal to be added to the melt has a high vapor pressure at the melting temperature of the base metal, much of the alloying or inoculating metal can be lost to the atmosphere. For example, special techniques must be used when adding magnesium to molten cast iron to nodulize the graphite.

Chemical Activity. Sometimes the alloying element used is quite chemically active and reacts with the atmosphere over the melt and/or with elements in it to form unwanted compounds. When this occurs, not only is some of the alloying effect lost, but the presence of the compounds formed may have an undesirable effect on the alloy if they are not removed.

Alloying Techniques

Several melting and casting techniques have been developed to overcome the problems caused by the base metal and the alloying or inoculate material having dissimilar properties.

Master Alloys, Hardeners, and Compounds. When alloying aluminum, metals having low melting temperatures, such as magnesium,

zinc, lead, bismuth, and tin, are commonly added directly to the melt and stirred in. Higher-melting metals, such as manganese, iron, titanium, and chromium, however, dissolve so slowly in the melt that they are introduced as rich (master) alloys or hardeners containing from 2 to 10% of the second metal in aluminum. When alloying magnesium, metals having low melting temperatures, such as aluminum and zinc, are once again commonly added directly to the melt and stirred in. Higher-melting metals such as manganese can be added in the metallic form, but it is usually added as manganese chloride to improve alloying efficiency.

Prealloyed Ingots. Many of the standard die casting alloys are available from suppliers already prealloyed and ready for melting and casting with little correction of chemical composition. However, in alloys containing constituents that tend to be lost during remelt, corrections must be made by adding the pure metal or a hardener having a fairly high content of the alloy element.

Mechanical Alloying. Elements that are incompatible in many ways can be alloyed through mechanical means, as described previously for the case of the dispersion-strengthened nickel-base alloys. Another example is alloying through the mixing of powdered metals. After the elements are brought together by mechanical means, they are allowed to further mingle by means of diffusion.

Surface Alloying

As stated earlier, although in the broad sense, alloying covers changing the chemical composition of the surface of a part by such processes as plating, cladding (by welding or spraying), nitriding, ion implantation, and carburizing; however, this book is limited to only those alloying processes that affect the bulk of the material, while surface modification is discussed in other ASM publications. Diffusion of the surface-alloying element into the base metal causes layers of different materials having different properties to form near the surface; these are alloys in the true sense of the word. The layers of hot dip galvanized steel are a good example. The outer surface is soft eta-phase pure zinc, next is a layer of hard, brittle zeta iron-zinc compound (FeZn_{13}), then a layer of ductile delta iron-zinc compound (FeZn_7), next a thin layer of hard, brittle gamma iron-zinc compound (FeZn_{10}) is formed, and finally the iron base metal. In electroplated parts, various chemical reactions occur between the plating element and the base metal that result in layers of varying composition in the plate thickness. This is also true for clad parts, such as trimetal bearings and heat exchangers. In both instances, the amount of time and temperature at which any diffusion can take place will determine the composition and

thickness of the layers. In carburizing by the pack, gas, vacuum, or plasma process, carbon is absorbed and diffused into a ferrous product to form a case capable of being subsequently hardened by quenching directly from the carburizing temperature or by cooling to room temperature and then re-austenitizing and quenching. The result is a hard case of high-carbon material surrounding a tough core of lower-carbon material. In nitriding by the gas, liquid, or plasma process, nitrogen is diffused into a ferrous product to produce a hard case with a tough core. Unlike carburizing, nitrogen is introduced at temperatures below the austenite-formation temperature for ferretic steels, and quenching is not required. As a result of not austenitizing and quenching, nitriding produces minimum distortion and results in excellent dimension control. The case of nitrided steel contains a diffusion zone with or without a zone of iron-nitrogen compounds, such as FeN and Fe₂₋₃N. Other surface-modification processes for ferrous products include carbonitriding, ferritic nitrocarburizing, aluminumizing, siliconizing, chromizing, and boriding. In ion implantation, medium- to high-energy atoms bombard a solid material, and this process offers the ability to alloy almost any element into the near-surface region of any substrate. The advantage of this process is that it produces improved product properties without the limitations of dimensional changes or delamination found in conventional coatings.

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