

SOLDERING HANDBOOK

3rd Edition



American Welding Society



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Soldering Handbook

3rd Edition

by

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American Welding Society

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Preface

The perception of soldering as a mature technology has been replaced over the past several years with an increased appreciation for the science and engineering principles that underlie the *successful* implementation of this joining technique. Recent efforts to understand soldering technology have come about largely on the heels of the electronics revolution, since soldering remains as the primary assembly technique for electronic component packaging and printed circuit board products. However, the narrow spotlight on electronics applications has expanded as technologists consider soldering processes for a wider range of structural applications.

At present, several excellent textbooks are available on the topic of soldering. However, those references have targeted primarily electronics applications. It became apparent to the American Welding Society and, in particular, the AWS C3 Committee on Brazing and Soldering, that there is a growing need for a more generalized resource on soldering technology. It was also recognized that such a text should be written so as to be readily understood by individuals having a wide range of backgrounds; from the field assemblers and furnace operators to the engineering staff and technical managers. The opportunity to create such a text coincided with plans to revise the AWS *Soldering Manual*. The result of this effort is the *Soldering Handbook*.

The *Soldering Handbook* is constructed with the following eight general topics:

1. Fundamentals of Soldering Technology; 2. Solder Materials; 3. Substrate Materials; 4. Fluxes; 5. Solder Pastes; 6. Assembly Processes; 7. Inspection Techniques for Product Acceptance and Process Optimization; and 8. Environmental, Safety, and Health. Thorough discussions are provided in each of the major topical areas, including important principles on materials and processing as well as handy access to tabulated properties data. The text is formatted to serve as a reference book; therefore, some information is duplicated in order to assure a clarity of discussion within each section. The handbook also provides a substantial reference section at the end of the text which lists sources of information for those individuals wishing additional details on specific topics.

It is the author's goal that the information provided in this handbook will allow soldering technology to be more fully utilized in advanced structural joining applications, as well as to enhance its continued use as a critical assembly technology for the electronics industry.

I wish to thank the volunteers of the AWS Technical Activities Committee and the AWS C3 Committee on Brazing and Soldering who reviewed the manuscript of this handbook. I also wish to thank Dr. Robert Messler, Jr. of Rensselaer Polytechnic Institute, for his critical and detailed examination of the manuscript and Howard Woodward of AWS for his efforts in editing of the handbook. Finally, I wish to thank Mr. Jerome Rejent and Ms. Alice Kilgo of Sandia National Laboratories for their efforts in compiling the metallographic data used in the text. This work was supported in part by Sandia, a multiprogram laboratory operated by Sandia Corp., a Lockheed Martin Company, for the United States Dept. of Energy under Contract DE-AC04-94AL85000.

This book is dedicated to my wife Karen and daughters Maria and Sara.

Paul T. Vianco, Ph.D.

Chair, AWS C3B Subcommittee on Soldering

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AWS Soldering Handbook

1. Fundamentals of Soldering Technology

1.1 Introduction

Joining processes, which attach two or more substrates or base materials together, be they metals, ceramics, or plastics, can be considered as coming under one of two generalized methodologies: *filler material joining*, or *fusion joining*.

Filler material joining refers to the use of a third material to form a bond between the two base materials, and includes the processes of *soldering*, *brazing*, and *adhesive bonding*. The filler material must adhere to both base materials in order to effect an adequate bond. Although the bonding mechanism in such cases may cause chemical changes at the substrate material surfaces in order to promote adhesion, *at no time does the temperature of the substrates exceed their respective melting points*.

When the melting temperature of the substrate material is exceeded, the bond is formed by a *fusion joining* process, e.g., welding. In welding, the two substrates are joined by the intermixing of their mutually molten segments. A third material, also referred to as a filler material, may be simultaneously melted and added to the molten base materials.

Because metals have been an integral part of engineered structures since the dawn of civilization, filler material joining processes have a long history of use with these base materials. However, filler metal joining methodologies have also been applied to the other materials subsets, including ceramics and plastics.

Soldering and brazing are high-temperature filler metal processes that are used in many engineering applications. The difference between soldering and brazing is defined by the melting temperature of the filler metal. A filler metal which has a liquidus temperature below 450°C/842°F is referred to as a *solder material*, or simply a “solder”; a filler metal with a liquidus temperature exceeding 450°C/842°F is a *brazing filler metal*. Although the distinction between the two processes is

determined solely by a melting property of the filler metals, the different temperature ranges have numerous attributes as well as drawbacks for the manufacturing processes that use either methodology. Some timely comparisons will be made throughout the text.

Lastly, it should be noted that the joining of two metals can also be realized by the use of adhesive materials, or “glues.” Generally, issues that need to be resolved with the use of adhesives are:

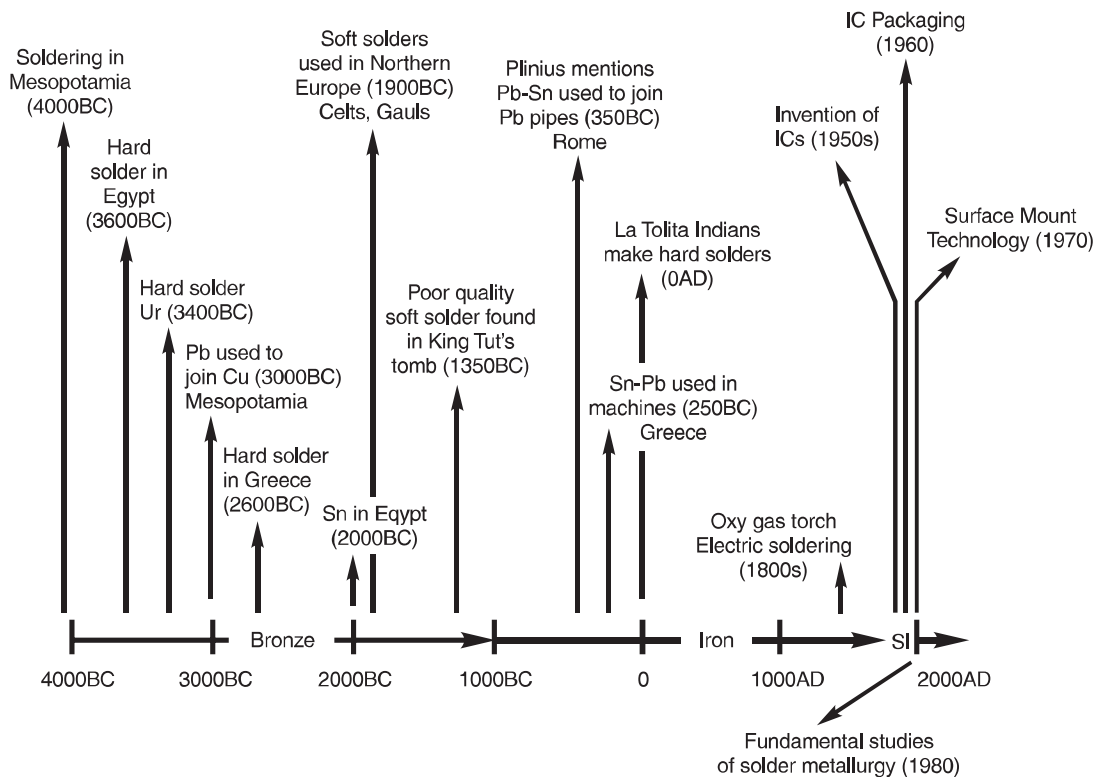
- (1) bulk strength levels to accommodate design loads;
- (2) adhesion strength; and
- (3) property stability (aging) over the service lifetime of the joint.

Although adhesives will certainly not replace the filler metal joining methodologies of brazing and soldering, they are finding many niche applications.

Soldering is a relatively old technology. Shown in Figure 1.1 is a time line which illustrates the 6000-year history of soldering [1]¹. Written details of the earliest uses of soldering are rare, since the art was generally practiced by slaves and considered unimportant to historians who, generally, belonged to society’s upper class. Archeological evidence of soldering from the earliest periods (4000 to 2000 BCE) is limited to artifacts, primarily jewelry and adornments, constructed with gold (Au)-based solders, since these materials were very resistant to corrosive deterioration. Artifacts having tin (Sn) based solders, the foundation of today’s soldering technology, are less prevalent, since Sn and Sn-based alloys more readily succumbed to corrosion by rainwater and naturally occurring chemicals in the ground.

The earliest practices with nonprecious metal solders were evidenced through the use of pure lead (Pb) by the

1. The numbers in brackets correspond to those in the references in Annex E.



(Reprinted by permission, The Metallurgical Society, TMS. Journal of Metals, Vol. 45, No. 7, "Issues in the Replacement of Lead-Bearing Solders," P. Vianco and D. Frear, p. 14, Fig. 1.)

Figure 1.1—Historical time line of soldering technology.

Mesopotamians in c. 3000 BCE to join copper (Cu) pieces. Pure Pb has a melting temperature of 327°C/ 621°F. Tin was not readily available to the Mediterranean cultures at that time. Tin and Sn-Pb solders were developed by the Celtic and Gaul cultures of Northern Europe in c. 1900 BCE, owing to the rich Sn ore deposits of that region. At that time, Sn-Pb solders were used to assemble tools and cooking utensils that were made largely of Cu and Cu-based alloys. The Romans used Sn-Pb solders to seal the Pb liners of their aqueducts.

As with the rest of Western Civilization during the Middle Ages, soldering experienced little progress, being limited to the making of jewelry and common household implements. However, the Industrial Revolution quickly expanded the use of soldering technology, particularly with the availability of portable heat sources, i.e., compressed gas for torches and electricity for the resistive heaters in soldering irons. Plumbing, including conduit and radiators, food and water containers, as well as light-duty tools and sheet-metal construction for automobile fenders and panels were some of the many uses to which soldering was applied. However, it was the advent of electronics in the early 20th century, and its continuing

evolution to the present day, which has quickly become the hallmark application of soldering technology.

Today, soldering technology can be categorized into two general fields based upon application:

- (1) *electronics soldering*, which describes the assembly of silicon microchip devices, printed circuit boards, motherboards, and connectors for the purpose of electrical signal transmission; and
- (2) *structural soldering*, which pertains to the role that is primarily that of mechanical fastening, i.e., non-electronic applications.

Clearly, many of the advances in soldering technology over the past half-century, both in the development of materials as well as new processes, have taken place in the electronics arena. However, these new materials and processes as well as an enhanced understanding of electronic solder joint properties can be applied equally to structural soldering applications. Failure to incorporate this increased understanding of solder joint behavior into larger scale, structural applications will only result in higher-than-necessary manufacturing costs, and an increased likelihood of poor product reliability. Irrespective of the source of innovation, all of soldering

technology will benefit from these and future advancements in the field. Those advancements include the development of new materials, such as higher-strength alloys; new processing concepts that include laser heating and the resurgence in ultrasonic soldering; as well as predicting joint performance and reliability by computer modeling and advanced inspection techniques. Electronics soldering will remain the leading proving grounds for many of these new concepts, simply because of the intensity of effort in that area. Fortunately, most of those innovations can be readily adapted to structural applications. Newer concepts that more strictly pertain to structural applications will also develop as soldering finds increased uses outside of the electronics community.

The future roadmap of soldering technology, from alloys and fluxes to preassembly and postassembly cleaning processes, will be required to meet stricter worker safety and environmental regulations. While a large number of these rules and guidelines will continue to come from the federal government, similar statutes are also being established by state and municipal governments, primarily with regard to environmental pollution. Many rules address local environmental problems, such as urban centers placing limits on the release of volatile organic compounds (VOCs) so as to reduce smog levels in the air. Therefore, the technologist must not only stay abreast of the current advancements in soldering technology, but must also remain aware of new or changing regulations dealing with worker health and safety as well as those statutes that were established to protect the environment.

The text begins with a look at the physical and mechanical metallurgy of solder alloys and solder joints. This section helps to establish the microstructure-properties relationship that is critical toward predicting the service performance of solder joints. Next, an understanding of the wetting and spreading of molten metals (solders) on substrates is presented. At the moment that a solder joint is made, a synergism exists between the properties of the solder, the flux chemistry, the substrate material compositions, and the heat cycle, which all determine the quality of the solder joint. Although liquid wetting is clearly a complex subject, even a rudimentary understanding of wetting-spreading principles provides an important advantage to the process engineer and assembler who may be tasked with the manufacture of solder joints. Measurement techniques to determine these and other relevant properties of alloys and solder joints complete this section. Solder joint design practices are examined in the next section. The performance of the solder joint in service is not solely a function of the solder alloy properties, but must necessarily consider the properties of the substrate materials, geometry of the joint, and potential service conditions. The next sections

deal specifically with solder alloy compositions, substrate materials, fluxes, and assembly processes. The text winds up with a discussion of inspection techniques, rework and repair procedures, and an all-important section on environmental safety and health issues in soldering technology.

1.2 Physical Metallurgy

1.2.1 Metals and Alloys. An understanding of soldering technology requires the user to appreciate some of the fundamental principles and properties of metals and alloys. The background summary presented below is not intended to be exhaustive. The reader is referred to a number of excellent textbooks for details. A representative list is provided in the reference section [2, 3, 4].

Metals are a class of materials comprised of one *element* such as copper (Cu), tin (Sn), lead (Pb), aluminum (Al), iron (Fe), and zinc (Zn). *Alloys* are materials comprised of two or more (elemental) metals; including, brass (Cu + Zn), bronze (Cu + Sn), Monel (Ni + Cu + Si), stainless steel (Fe + Ni + Cr + Mn + Si), and numerous superalloys having upward of ten or more metallic constituents. The reason for developing alloys, whether for soldering or other applications, is to have a material with properties which cannot be realized by any one elemental metal. The targeted properties may include melting temperature(s), corrosion resistance, strength, hardness, or ductility, to name only a few.

The properties of alloys can not always be predicted from the properties of the individual metal constituents. For example, combining a metal A of high strength with the metal B of low strength does not necessarily produce an alloy (A + B) of medium strength. The atomic interactions which take place when metal A is combined with metal B can be very complex.² Besides strength and other mechanical properties (e.g., ductility, fatigue resistance, etc.), the alloy (A+B) may display physical properties, i.e., melting temperature, electrical conductivity, color, etc., that are far different from those of the individual, elemental metals. For example, in the case of alloys used as solders, a relatively low melting temperature has often been a primary objective.

A primary consideration by design and manufacturing engineers when selecting a solder for a particular application is its melting and solidification (freezing) properties. As the temperature of a solid material is increased, a critical temperature is reached at which the solid begins to

2. Presently, powerful computers and theoretical models which describe the structure of the atom, have been combined in the field of "molecular dynamics" and used to predict bulk material properties (at least to a first-order).

change into a liquid; this process is referred to as *melting*. The cooling of a liquid causes the reverse transformation to occur; this is the process of *solidification*. Although, theoretically, the melting temperature and the solidification temperature should be equal, this may not necessarily appear to be so, due to the effects of heating or cooling rate as well as the presence of impurities in the material. Rapid heating rates or cooling rates will delay the respective transformation events, resulting in a *melting temperature that appears to be higher*, and a *solidification temperature that is lower*, than the presumed value.

Purity of the solder will also affect the melting and solidification behavior, even when the contaminating species has no intrinsic interaction with the basis metal(s). The presence of impurities results in the melting and solidification temperatures being *reduced*; this phenomenon is referred to as *melting point depression*. Probably one of the most common examples of melting point depression is the action of rock salt on roadways covered with ice or snow. The salt dissolves in the water, causing a reduction in its melting or freezing temperature. As a result, the water-salt mixture remains in a liquid state at temperatures below $0^{\circ}\text{C}/32^{\circ}\text{F}$, thereby delaying the formation of ice on the road surface. Generally, the larger

the amount of impurity that is present, greater is the decrease in the melting temperature, until the base material becomes saturated with the contaminant.

All elemental metals, e.g., Pb, Sn, Ni, etc., melt/solidify at a single temperature, referred to as the *melting temperature*, T_m , or *freezing temperature*. However, in the case of alloys which have more than one elemental metal, the melting (or solidification process) does not necessarily occur at a single temperature. Rather, the process of melting (or solidification) may take place over a temperature *range*. That range is defined by two temperature limits: the *solidus temperature*, which establishes the lower limit; and the *liquidus temperature*, which forms the upper limit. These temperatures are abbreviated as T_s and T_l , respectively. This point is illustrated in Figure 1.2, using the solidification process as the example. At temperatures above the liquidus point, the metal alloy is completely liquid. As heat is lost from the molten alloy, the alloy temperature drops, reaching the liquidus temperature, T_l . Here, solidification begins by the formation of solid particles in the liquid. As the alloy temperature drops through the range below T_l but remains above the solidus temperature T_s , the number and size of the solid particles grow as the alloy transforms from a liquid

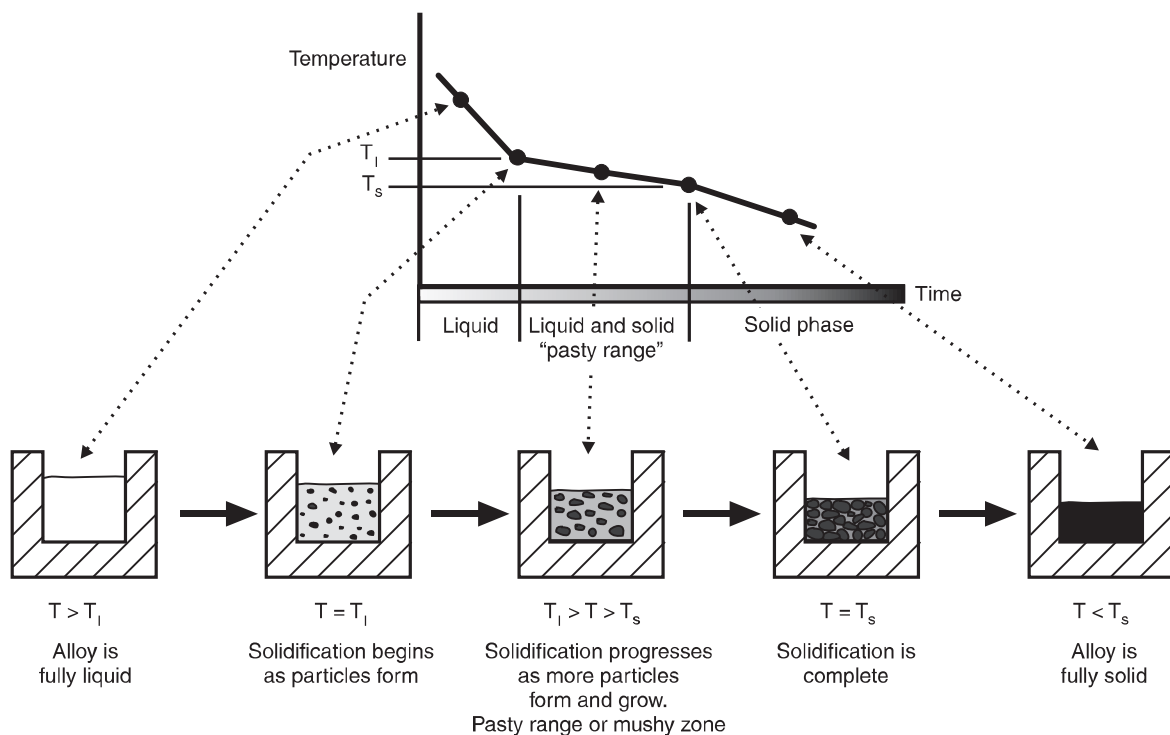


Figure 1.2—The material consistency of an alloy undergoing solidification which does take place over the temperature range $T_s < T < T_l$.

to a solid. The alloy has the consistency of a paste or mush due to the presence of both solid particles and liquid; hence, the temperature range between T_l and T_s , ($\Delta T = T_l - T_s$) is called the *pasty range* or *mushy zone*. At T_s , the alloy has fully solidified, and remains so at temperatures below the value of T_s . Exactly the reverse progression takes place upon heating this same material through T_s and T_l until a fully liquid material is realized once again.

The temperature span between the solidus and liquidus temperatures, i.e., the pasty range, can be from zero to as much as a hundred Celsius degrees. Alloys having a zero pasty range, that is, those with equal liquidus and solidus temperatures, melt and solidify at a single temperature, just like the elemental metals. These alloys are referred to as *eutectic alloys* or *eutectic compositions*. The single transformation temperature is called the *eutectic temperature*, T_{eut} .

It is important to know the solder alloy's liquidus temperature, T_l , above which it is completely liquid; the solidus temperature, T_s , below which the alloy is solid; and the pasty range or mush zone defined as $\Delta T = T_l - T_s$. From an applications point of view, the liquidus and solidus temperatures are used to: (1) develop an appropriate process to fabricate a joint; and (2) define the maximum service temperature of the finished joint, respectively. The process used to make the joint typically uses temperatures above T_l in order for the solder to flow. On the other hand, when the completed joint is placed into service as part of a product or assembly, the service temperatures must remain below T_s ; otherwise, the joint will begin to melt and lose its integrity as a mechanical fastener.

A useful tool for describing the melting properties of metal alloys over a range of compositions and temperatures is the *phase diagram*. The phase diagram identifies the various phases of a particular alloy *composition* that would be present at equilibrium, given the *temperature* to which that composition is exposed. An example of the phase diagrams for the Sn-Pb binary (or two elemental) system is shown in Figure 1.3 [5]. The x-axis is alloy composition, from 100% Pb, 0% Sn (the "Pb" end) to 0% Pb, 100% Sn (the "Sn" end). The y-axis is temperature. The various areas or "fields" in the diagram represent the different phase structures that can be present in the material, given the alloy composition (x-axis) and the temperature (y-axis).

A more detailed explanation of the phase diagram follows shortly. First, some summary points are in order. Phase diagrams have been developed for nearly every practical binary alloy combination that can be permuted from elements in the Periodic Table. An extensive compilation also exists for many of the more commonly used *ternary* alloys, i.e., those alloys having *three* ele-

ments) and even a few *quaternary* alloys (four elements). Phase diagrams can be developed through experimental techniques such as Differential Scanning Calorimeter (DSC) or Differential Thermal Analysis (DTA). These techniques are described in more detail in later section (1.4.3). Recently, the advent of computer simulation techniques that model atomic interactions have resulted in the ability of metallurgists to compute the phase diagrams of some higher-order ternary and quaternary systems.

It must be noted that the alloy properties described by the phase diagram represent a condition of thermodynamic *equilibrium* at the particular temperature. Such a condition would prevail when the alloy was allowed to cool at an infinitely slow rate so that the atoms had sufficient time to take up their lowest energy positions. Clearly, processing conditions that allow an infinitely slow cooling rate cannot be achieved, nor are they desired from the point of view of cost-effective manufacturing. Thus, this hypothetical condition is most closely approximated at the slowest cooling rate during solidification. The microstructure that is observed in actual solder joints will differ due to the variations in the *cooling rate* caused by differences in the base material structures and process parameters. The importance in realizing that there exists deviations from an equilibrium microstructure that is predicted by the phase diagram, is that the *observed* microstructure ultimately determines the solder joint mechanical properties. The phase diagram serves as an important predictive tool by providing an approximation of the anticipated microstructure.

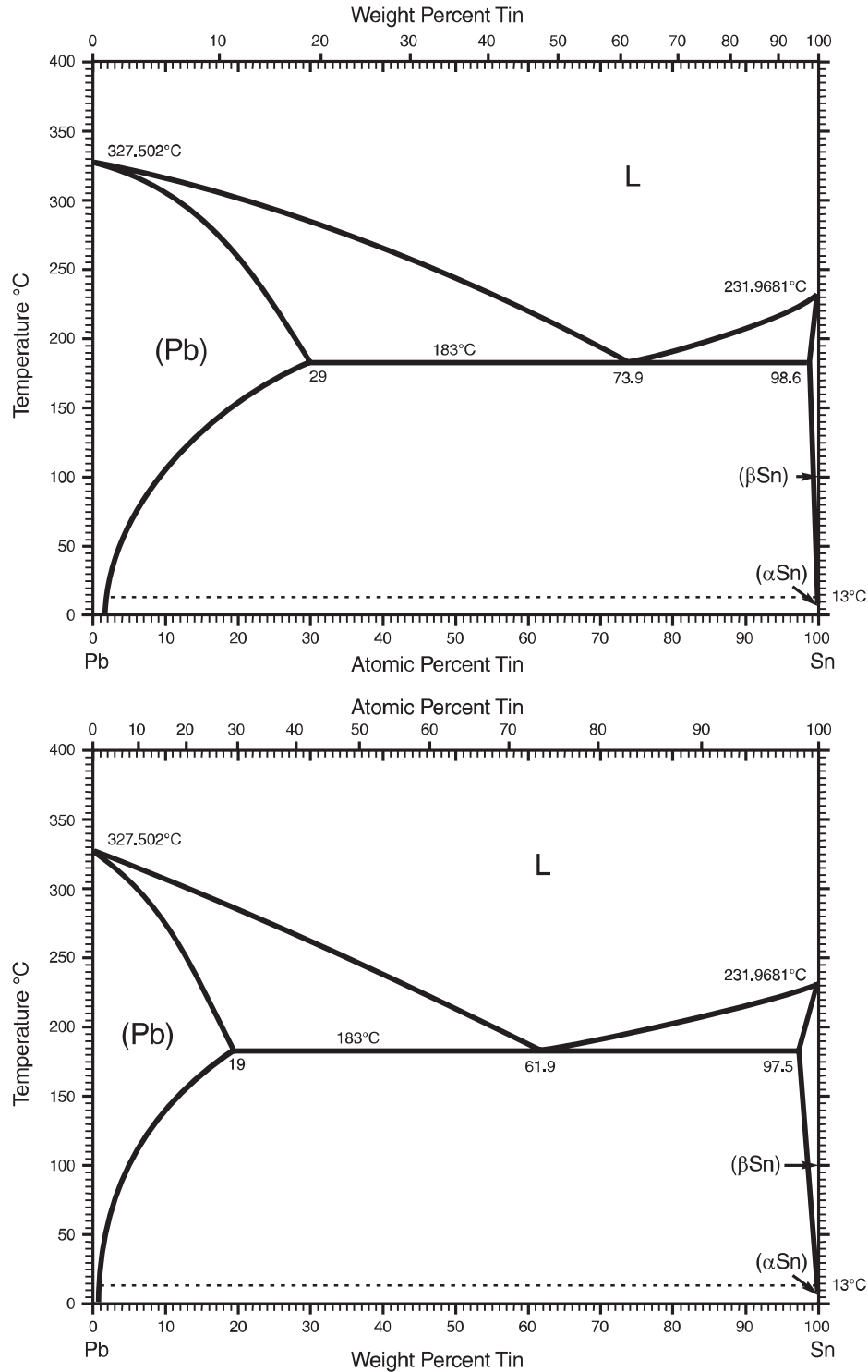
In the next section, a more detailed description of phase diagrams is presented. The discussion describes the properties of the diagram, as well as presents those tools that are necessary to interpret them. Even a very basic understanding of the phase diagram provides a powerful tool for: the design engineer at the conception stage of a product, and specifically its solder joints; the manufacturing engineer whose role is to develop the soldering process; and the failure analyst who must search for the source of a defective solder joint at the point of factory inspection or in fielded hardware.

1.2.1.1 Phase Diagrams

1.2.1.1.1 Binary Alloy Phase Diagrams. A binary alloy, designated A-B, can be described as having four *degrees of freedom*, or variables, that completely describe that system:

- (1) the amount of element A;
- (2) the amount of element B;
- (3) temperature; and
- (4) pressure.

Most uses of metals and alloys take place under a constant, ambient atmospheric pressure so this parameter



(Binary Alloy Phase Diagrams, Vols. 1 and 2, edited by T. Massalski, 1986. ASM International, Materials Park, OH 44073-0002, Sn-Pb, p. 1848.)

Figure 1.3—The binary Sn-Pb alloy system phase diagram.

does not typically require consideration. However, when working with a material at elevated temperatures and under very high pressure conditions, then pressure *must* be accounted for in describing the alloy metallurgy. In a binary system, A-B, knowing the amount of A automatically determines the amount of B: $B(\%) = 100\% - A(\%)$; or $B = 1 - A$, if A and B are represented as fractional amounts. Therefore, the description of a binary alloy can be reduced to two parameters:

- (1) the content of either A or B; and
- (2) the temperature.

This descriptive tool is a two-axis plot, referred to as the *phase diagram*. As noted previously, phase diagrams of binary alloys have composition on the abscissa (x-axis) and temperature as the ordinate (y-axis). The case of the Sn-Pb binary system was shown in Figure 1.3. The composition axis (0 to 100%) can be represented as either the weight-percent (wt.%) or as the atomic-percent (at.%) of one of the elements. In Figure 1.3, that element is Sn. The Sn content increases from left to right. Therefore, the amount of Pb (%), being the quantity, $(100\% - \%Sn)$, increases from right to left. The conversion between weight-percent to atomic-percent is often necessary in the absence of having both scales being present on the phase diagram. The conversion calculation is illustrated below with the Sn-Pb case. Reversing the steps will allow the conversion of atomic-percents to weight-percents.

- (1) Sample composition: 63Sn-37Pb (wt.%)
- (2) Convert wt.% to mass quantities, assuming a total mass of 100 grams:

63 wt.% Sn = 63 grams Sn

37 wt.% Pb = 37 grams Pb

- (3) Divide the mass quantities by the respective atomic weights (or *gram-molecular weight*) designated as grams/mole. The gram-molecular weight, or *atomic weight* values can be obtained from a Periodic Table of the Elements provided in this text (Table 1.1).

Sn: $(63 \text{ grams}) / (118.7 \text{ grams/mole}) = 0.531 \text{ moles}$

Pb: $(37 \text{ grams}) / (207.2 \text{ grams/mole}) = 0.179 \text{ moles}$

- (4) Add together the number of moles of Sn and Pb to get a total number of moles:

$0.531 + 0.179 = 0.710$

- (5) Divide the mole amount of each component by the total number of moles in the alloy, to obtain the atomic, or mole, fraction of each component:

Sn: $0.531 / 0.710 = 0.748$

Pb: $0.179 / 0.710 = 0.252$

- (6) Multiply the atomic fractions by 100 to obtain the atomic percentages (to two significant figures):

Sn: $0.748 (100) = 75\%$

Pb: $0.252 (100) = 25\%$

Therefore, the composition 63Sn-37Pb (wt.%) is equivalent to: 75Sn-25Pb (at.%).

There are several protocols that are used in the expression of alloy compositions. Generally, metal alloys are represented by weight-percent composition, the respective percent of each element being a coefficient of the element symbol. This is precisely the manner in which the Sn-Pb solder was represented in Step (1) of the sample computation above: 63Sn-37Pb. A similar protocol is used with atomic percents; therefore, the use of either weight-percents or atomic percents should be clearly delineated in the text. As will be seen shortly, metal elements can also form *covalently* bonded phases in solder joint metallurgies. These materials are often referred to as “line compounds” or “intermetallic compounds”; they are traditionally represented by having their atomic percent compositions written as atomic ratios in the form of subscripts after the elemental symbol (without hyphenation). An example that is commonly encountered in solder systems is the intermetallic compound, Cu_6Sn_5 , which is a product of the metallurgical reaction between the Sn component of solder and Cu metal.

The phase diagram of the Sn-Pb system (Figure 1.3) is illustrative of one class of binary alloy phase diagrams commonly referred to as *simple eutectic* systems. A simple eutectic system is characterized by the presence of one *single phase-to-multiphase reaction* that is the eutectic point. The simple eutectic Sn-Pb system is used here to illustrate the fundamental principles of phase diagrams. More complex cases are illustrated later along with the appropriate discussion.

First, the composition of 85Sn-15Pb is examined in a reproduction of the phase diagram in Figure 1.3, now shown in Figure 1.4. A vertical line identifying this composition is drawn from the x-axis. At a temperature of $275^\circ\text{C}/527^\circ\text{F}$ (point A), the alloy is completely molten and has a single phase, that of the liquid, L. Decreasing the temperature, solidification begins to take place at a temperature of $210^\circ\text{C}/410^\circ\text{F}$ (point B). This temperature is the liquidus temperature, T_L . The initial particulates that form in the liquid, will have a composition represented by the point B', or 98.5Sn-1.5Pb—as projected down to the x-axis. The remaining liquid will have nearly the same composition as the starting material (point B). Now, there are two phases present in the solder: the liquid phase and the solid 98.5Sn-1.5Pb particle phase. The composition has entered a two-phase “field.” This phase field is represented on the diagram as the sum of a Greek letter for the solid phase and L, for the liquid phase. In this case, the representation $\beta + L$ is used. As the temperature is decreased further toward point C, four events occur:

- (1) more solid particles form in the liquid matrix so that the material takes on the consistency of an increasingly thicker paste;

Table 1.1
Table of the Elements, Giving Symbol, Atomic Number, and Atomic Mass*

GROUP IA		IIA		GROUP VIII														IIIB		IVB		VB		VIB		VIIB		IIB		IIIA		IVA		VA		VIA		VIIA		VIII																					
CODE (Crystal Structure)		Cubic, Face Centered Cubic, Body Centered Cubic		Diamond Hexagonal Rhombohedral		Orthorhombic Monoclinic Tetragonal																																																							
1	H 1.01 Hydrogen	3	Li 6.94 Lithium	4	Be 9.01 Beryllium	11	Na 22.99 Sodium	12	Mg 24.31 Magnesium	19	K 39 Potassium	20	Ca 40.08 Calcium	21	Sc 44.96 Scandium	22	Ti 47.9 Titanium	23	V 50.94 Vanadium	24	Cr 51.99 Chromium	25	Mn 54.94 Manganese	26	Fe 55.85 Iron	27	Co 58.93 Cobalt	28	Ni 58.71 Nickel	29	Cu 63.54 Copper	30	Zn 65.37 Zinc	31	Ga 69.72 Gallium	32	Ge 72.59 Germanium	33	As 74.92 Arsenic	34	Se 78.96 Selenium	35	Br 79.91 Bromine	36	Kr 83.8 Krypton	54	Xe 131.3 Xenon	86	Rn 222 Radon												
58	Ce 140.12 Cerium	59	Pr 140.91 Praseodymium	60	Nd 144.24 Neodymium	61	Pm 145 Promethium	62	Sm 150.35 Samarium	63	Eu 151.96 Europium	64	Gd 157.25 Gadolinium	65	Tb 158.92 Terbium	66	Dy 162.5 Dysprosium	67	Ho 164.93 Holmium	68	Er 167.26 Erbium	69	Tm 168.93 Thulium	70	Yb 173.04 Ytterbium	71	Lu 174.97 Lutetium	87	Fr 223 Francium	88	Ra 226.05 Radium	89	Ac 227.03 Actinium	90	Th 232.04 Thorium	91	Pa 231 Protactinium	92	U 238.03 Uranium	93	Np 237 Neptunium	94	Pu 239 Plutonium	95	Am 243 Americium	96	Cm 247 Curium	97	Bk 245 Berkelium	98	Cf 252 Californium	99	Es 254 Einsteinium	100	Fm 257 Fermium	101	Md 258 Mendelevium	102	No 259 Nobelium	103	Lr 260 Lawrencium

CODE (Crystal Structure)



*ATOMIC WEIGHTS BASED
UPON 12 AS THE EXACT
ATOMIC WEIGHT OF CARBON-12.

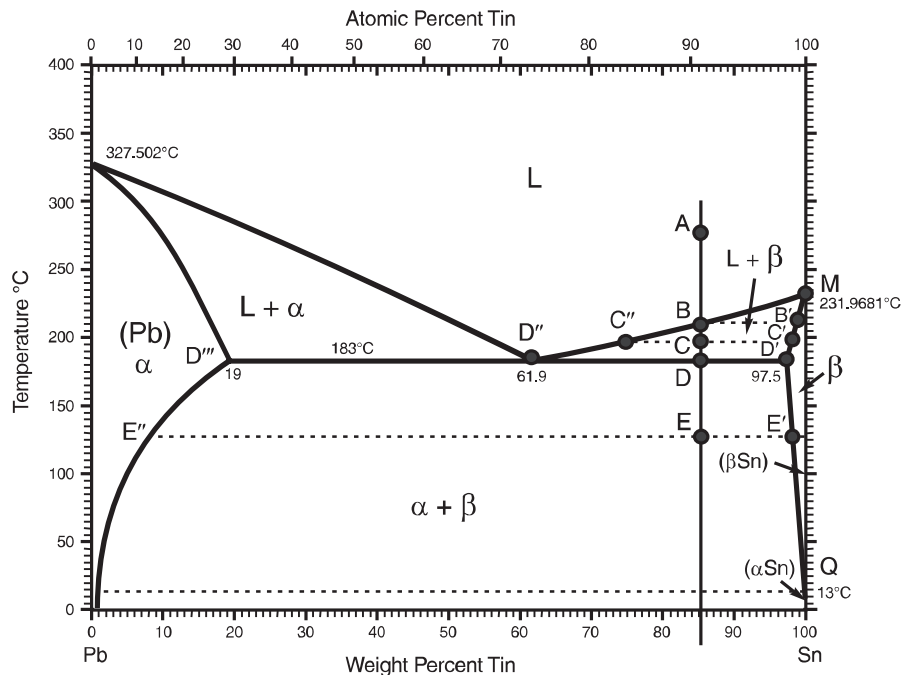


Figure 1.4—Sn-Pb alloy phase diagram to illustrate text discussion on 85Sn-15Pb.

(2) concurrently, a diminishing amount of liquid phase is present;

(3) the composition of the solid particles changes to C' and

(4) the composition of the remaining liquid phase changes to the value at point C".

The line connecting points C' and C" is referred to as the *tie line*. The tie line receives its name from the fact that it connects, or ties together, the compositions of the two phases that are present at that temperature value.

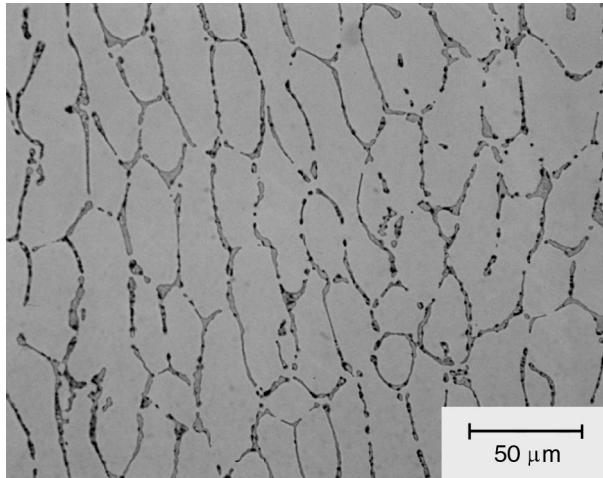
It is often desirable to know the weight fraction of the alloy that is solid and that fraction which is liquid at a temperature, such as at the temperature of C—195°C/383°F. This can be done using the so-called “lever rule.” This rule is stated as follows, and is illustrated with the help of Figure 1.4: The weight fraction of the alloy that is a solid is given by the length of line C-C" divided by the length of the tie line C'-C". Likewise, the weight fraction of the alloy that is a liquid at the temperature of point C is the length C'-C divided by total length C'-C". Or, it can be computed by subtracting the weight fraction of the solid from unity.

Next, a temperature that is a fraction of a degree higher than 183°C/367°F is reached (point D). At this point, the alloy is comprised of: (1) a liquid phase, L, of composition D", which constitutes $(D'-D)/(D'-D'')$ weight fraction of the alloy; and (2) a solid phase, β, of

composition D', and which makes up $(D''-D)/(D'-D'')$ weight fraction of the alloy specimen. It is noted that as the temperature dropped from 210°C/410°F to 183°C/361°F, the solid phase composition of the alloy traced the path B'D' along the line MD'. The entire path MD' is termed the *solidus line*. Likewise, the composition of the liquid phase traced the segment BD" along the line MD". The entire path MD" is termed the *liquidus line*.

The temperature 183°C/367°F is the eutectic temperature, T_{eut} , of the binary Sn-Pb system. At 183°C/367°F, complete solidification has taken place. At a temperature that is a fraction of a degree lower than 183°C/367°F, the solder is now comprised of two solid phases: a Sn-rich phase designated β and having a composition D' (97.5Sn-2.5Pb); and a Pb-rich phase, α, having a composition D" (19Sn-81Pb). These phases (compositions) are sometimes referred to as the *terminal phases (compositions)* because they are at the terminus or endpoints of the tie line D'-D". As the temperature is further decreased to 125°C/257°F (point E), the compositions of the two solid phases, α and β, have changed to 92Pb-8Sn (E") and 98.5Sn-1.5Pb (E'), respectively. The weight fraction of each phase can still be computed by the lever rule.

Shown in Figure 1.5 is an optical micrograph of the microstructure of the 85Sn-15Pb solder. The dark particles are the Pb-rich phase; the light regions are the predominating Sn-rich phase. The observed



(Courtesy of Sandia National Laboratories)

Figure 1.5—Optical micrograph of the microstructure of the 85Sn-15Pb solder. The dark areas are the Pb-rich phase; the light regions are the Sn-rich phase. The cooling rate was 10°C/18°F/min.

microstructure was produced under a cooling rate of 10°C/18°F/min.

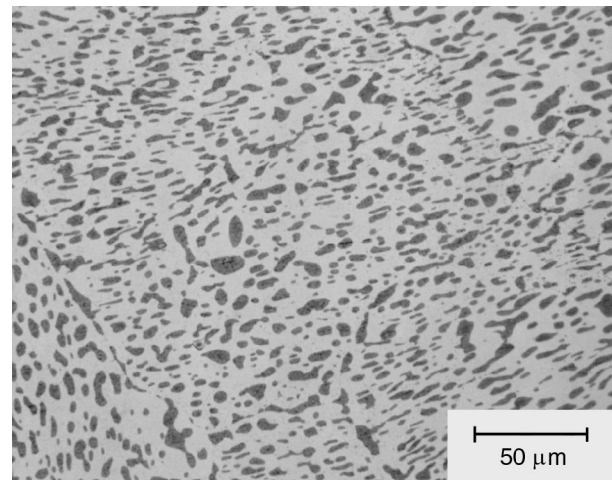
It is in the solid state that the actual compositions of the two phases will differ from those predicted by the phase diagram and its underlying *equilibrium* assumption. Compositional changes in the solid α and β phases require solid-state diffusion processes which are significantly slower than are diffusion processes in a liquid phase. Therefore, it is with increased difficulty that the solid alloy phases will reach the equilibrium compositions indicated by the phase diagram and particular temperature. Moreover, the diffusion kinetics slow even more as the temperature is further decreased. Along these lines, it can be expected that the compositions of the two solid-state phases will come closer to those predicted by the phase diagram when the slowest cooling rates are present following solidification. Conversely, fast cooling rates will “lock-in” composition profiles and microstructures at room temperature that are more representative of the higher-temperature regime.

Since the microstructure observed at room temperature does not necessarily represent the equilibrium state of the material, it can be expected that the microstructure will attempt to evolve so as to reach that equilibrium condition. That is, the microstructure is said to be *metastable*. This evolution is particularly important for solder alloys because room temperature is, relatively speaking, a “high” temperature for these materials. Thus, microstructural changes can readily take place at room temper-

ature, and at an increasingly quicker pace as the service temperature increases, through thermal activation of the solid-state diffusion processes. It is important to consider these microstructural changes because it is the alloy microstructure which determines the mechanical and physical properties of the solder. The phase diagram analysis provided above would apply equally as well to alloys with compositions that would lie between the points D" and D'" as projected on the x-(composition) axis (Figure 1.4).

The composition, 61.9Sn-38.1Pb, presents a unique circumstance in Figure 1.4. This composition solidifies at a single temperature, 183°C/361°F; that is, the solidus and liquidus temperatures are equal to 183°C/361°F. As noted above, 183°C/361°F is referred to as the eutectic temperature and the composition, 61.9Sn-38.1Pb is the eutectic composition. It will often be noted that 63Sn-37Pb is identified as the eutectic composition for the Sn-Pb system. The differences in these two compositions has a negligible effect on performance. As in the case of the 85Sn-15Pb composition described above, the eutectic alloy has two terminal phases upon solidification, the Pb-rich α phase and the Sn-rich β phase. The weight fraction of each of the α and β phases can be determined by the lever rule as previously discussed, and will change slightly as the temperature decreases as per the equilibrium condition reflected in the phase diagram.

Shown in Figure 1.6 is the microstructure of 63Sn-37Pb solder. The sample had been aged at 70°C/158°F for 400 days, and therefore, exemplifies an equilibrium



(Courtesy of Sandia National Laboratories)

Figure 1.6—Optical micrograph of 63Sn-37Pb solder microstructure following aging at 70°C/158°F for 400 days in order to realize an equilibrium condition.

microstructure for this composition. The light matrix is the Sn-rich phase; the darker particulates are the Pb-rich phase. The white spots in the Pb-rich phase are dissolved Sn which had since precipitated out of solution as the equilibrium concentration was reached for Sn in Pb (at 70°C/158°F): 1–2 wt.%. It is noted that there is no observable Pb in the Sn-rich phase, confirming the small amount (< 1 wt.%) that is predicted by the phase diagram, Figure 1.4.

A slightly different composition-temperature history is developed for an alloy composition of 95Pb-5Sn, Figure 1.7. Beginning at 350°C/662°F (point Z), the temperature is decreased and the alloy remains entirely liquid until point Y is reached at a temperature of approximately 315°C/599°F. At 315°C/599°F, solidification begins to take place with the first solid phase having the composition represented by point Y' (97.5Pb-2.5Sn). Much as was the case of the 85Sn-15Pb composition, passing from point Y (315°C/599°F) to point X (307°C/585°F) results in an increase in the amount of solid phase and concurrently, a decrease in the amount of remaining liquid. The composition of the solid phase changes from Y' to that represented by point X (the starting composition) along the solidus line, N-D''; the liquid phase composition changes from that at point Y to that of point X'

(92Pb-8Sn) along the liquidus line N-D''. The lever rule still applies for determining the relative amounts of the solid and liquid phases. At point X, solidification is complete and the material (composition) is located in the α phase field as the temperature drops further. That is to say, the alloy has a single phase comprised of Pb with some Sn dissolved in it.

The single-phase solid state will persist at the original, overall composition of 95Pb-5Sn until the temperature has decreased to that of point W (95°C/203°F). At that point, *phase separation* will take place in which the Sn precipitates out of the Pb; the solder now exhibits two-phases, a Pb-rich phase of the composition represented by W, and a Sn-rich phase having the composition represented by point W'. As the temperature drops further, the equilibrium microstructure will be comprised of a Pb-rich phase having a composition determined by the temperature along line segment W-P, and a Sn-rich composition represented by points on line segment W'-Q, as per the specific temperature value. This case is exemplified by the point V (60°C/140°F) with the Pb-rich phase having the composition represented by point V'' (98Pb-2Sn), and the Sn-rich phase represented by point V' (99Sn-1Pb). Again, as was noted earlier, after the alloy has become fully solid, in this case at the temperature of

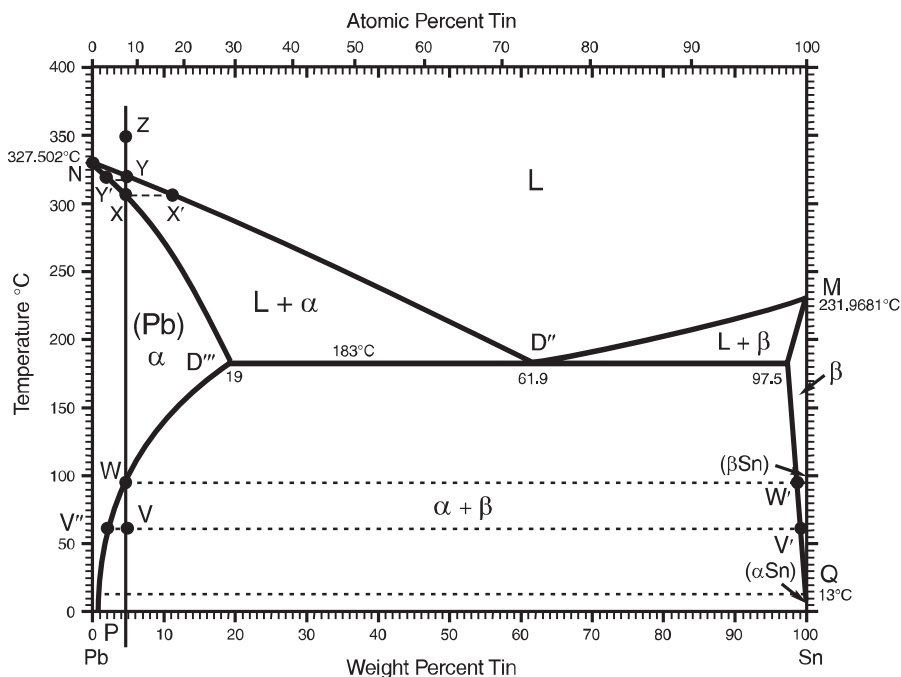
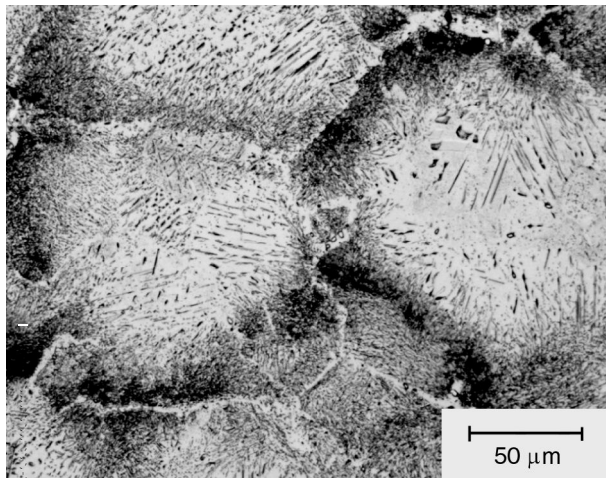


Figure 1.7—Sn-Pb Alloy phase diagram to illustrate the text discussion on the 95Pb-5Sn starting composition.

307°C/585°F (point X), microstructural changes accompanying further decreases in temperature become very sluggish due to the slower solid-state diffusion processes; therefore, the equilibrium microstructures may not fully evolve. A micrograph of the 95Pb-5Sn solder is shown in Figure 1.8; the cooling rate was 10°C/18°F/min.

In each of the composition scenarios described above: 85Sn-15Pb, 61.9Sn-38.1Pb, and 95Pb-5Sn; the sequence of melting from the solidified material to a fully liquid alloy would proceed in the opposite sequence as was described for the solidification process.

The nonequilibrium, or metastable, microstructure can change under the influence of service temperature and solder joint lifetime. However, the metastable condition will have minimal effect on the melting properties of the solder. There may only be a small shift in the solidus and liquidus temperatures, but generally of a magnitude that has little consequence on the processing parameters or procedures used to rework a solder joint. The binary alloy phase diagram of the Sn-Pb alloy system represents a simple eutectic. Several binary systems with practical importance to soldering technology are also simple eutectics [6]. Examples include the Sn-Bi binary system having 57Bi-43Sn (or 58Bi-42Sn) as the eutectic composition ($T_{\text{eut}} = 139^\circ\text{C}/282^\circ\text{F}$); and the Sn-Zn alloys with 91.2Sn-8.8Zn as the eutectic composition ($T_{\text{eut}} = 199^\circ\text{C}/389^\circ\text{F}$). Other binary alloy systems that are of particular pertinence to soldering technology have rather complex phase diagrams, but may include a eutectic composition that has engineering application, for example, the Sn-Ag



(Courtesy of Sandia National Laboratories)

Figure 1.8—Optical micrograph of the microstructure of the 95Pb-5Sn solder. The cooling rate was 10°C/18°F/min.

system with 96.5Sn-3.5Ag as the eutectic composition ($T_{\text{eut}} = 221^\circ\text{C}/430^\circ\text{F}$). Each of these systems are discussed in relevant detail in section 2.4.

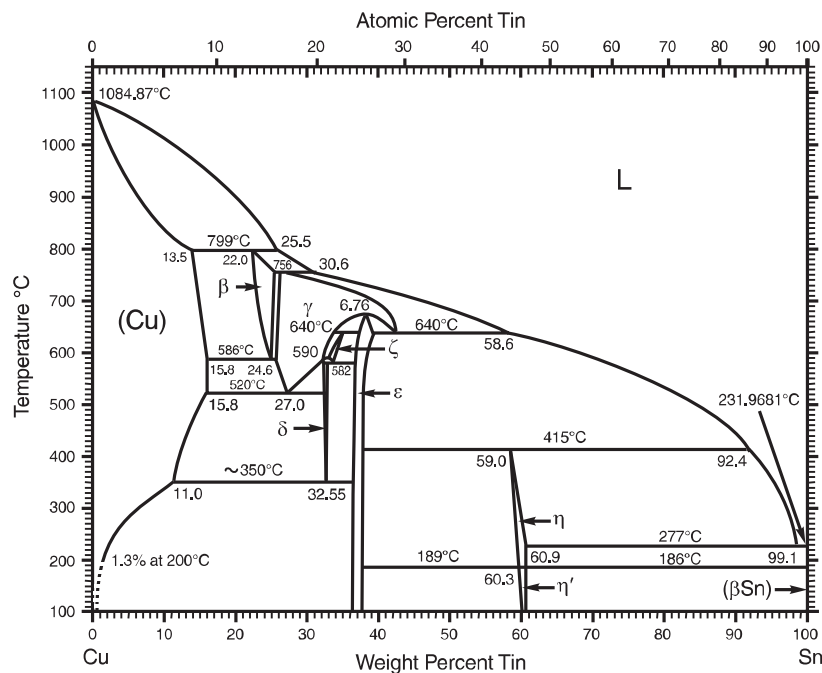
Three binary alloys of importance to soldering technology, and which have particularly complex phase diagrams, are the Cu-Sn, Au-Sn, and Ni-Sn systems. The binary alloy phase diagrams of these systems are shown in Figures 1.9, 1.10, and 1.11, respectively [7]. The Cu-Sn system will be used as an example. It is instructive to identify the potential phases that can form per specific amounts of Cu and Sn, at a given temperature, (Figure 1.9). For example, at 150°C/302°F, those phases are, from left-to-right or decreasing Cu and increasing Sn:

- (1) (Cu), the parenthesis denoting a slight solid solution content of Sn at approximately 0.6 wt.%;
- (2) Cu + ϵ -phases;
- (3) the ϵ -phase (Cu_3Sn);
- (4) ϵ + η' phases;
- (5) η' -phase (Cu_6Sn_5);
- (6) η' + Sn phases; and
- (7) β - or pure Sn.

The single phases ϵ and η' are often referred to as line compounds or intermetallic compounds and are identified by singular compositions, Cu_3Sn and Cu_6Sn_5 , respectively. However, the phase diagram shows a field (area) of finite width for either phase, indicating a small compositional variation is theoretically possible. Such a composition spread has rarely been observed experimentally so that the stoichiometric formulas are used to represent these phases. As was noted in the simple eutectic case, and as is *always* the case in phase diagrams, the single phase fields (solid solution of Cu and a little Sn, ϵ -phase, η' -phase, and pure Sn) are separated by fields of two-phase compositions, made up of the two phases indicated by the borders (or terminuses) of the two adjoining, single phase fields.

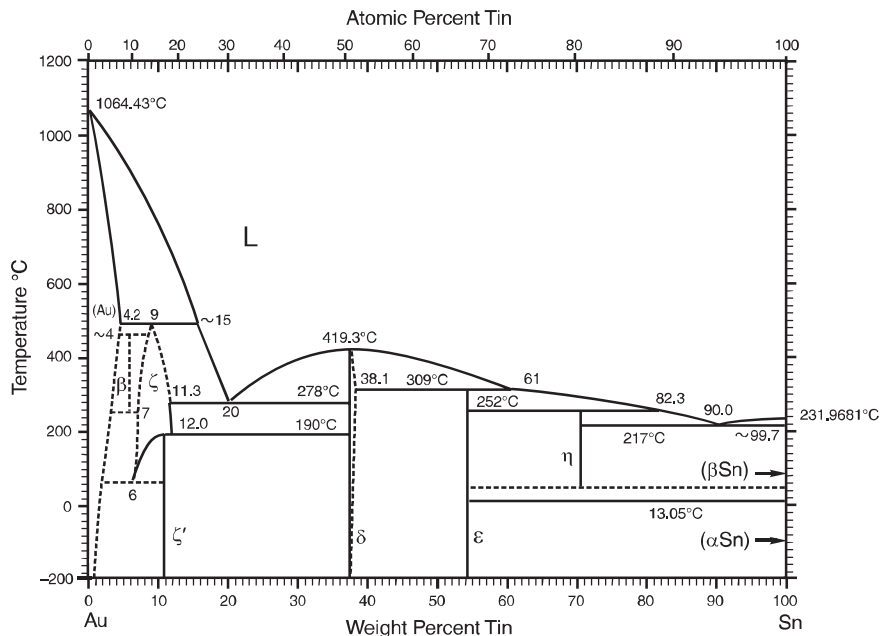
The same principles used in the analysis of the Sn-Pb simple eutectic system are applicable for the Cu-Sn system. This point is illustrated for case of 50Cu-50Sn composition in Figure 1.12. Starting at point A (760°C/1400°F) in Figure 1.12, the alloy is completely molten (single phase). Cooling progresses, and at point B (680°C/1256°F), solidification begins to take place. At point C (660°C/1220°F), a two-phase pasty structure is observed, comprised of solid γ phase particles with the composition of point C' (58Cu-42Sn) and liquid having a composition of point C'' (44Cu-56Sn). The lever rule still applies for determining the relative amounts of each phase that is present in the material.

Cooling further brings the alloy to point D. Point D is still a two-phase, solid-liquid composition. However, aside from the composition change of the liquid to 41.4Cu-58.6Sn, the solid phase particles transform from the γ phase to the ϵ phase, which has a phase diagram



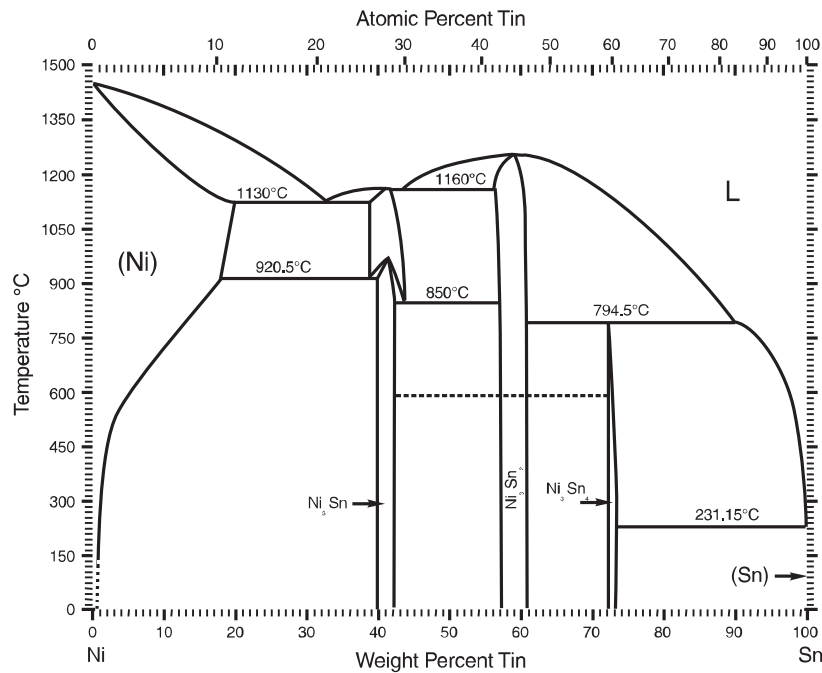
(Binary Alloy Phase Diagrams, Vols. 1 and 2, edited by T. Massalski, 1986. ASM International, Materials Park, OH 44073-0002, Cu-Sn, p. 965.)

Figure 1.9—Binary alloy phase diagram for the Cu-Sn system.



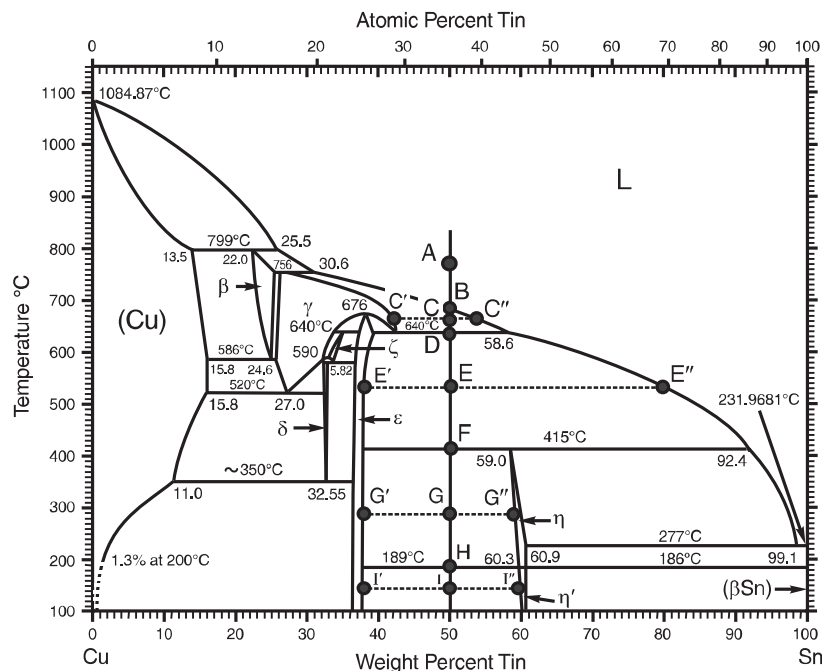
(Binary Alloy Phase Diagrams, Vols. 1 and 2, edited by T. Massalski, 1986. ASM International, Materials Park, OH 44073-0002, Au-Sn, p. 316.)

Figure 1.10—Binary alloy phase diagram for the Au-Sn system.



(Binary Alloy Phase Diagrams, Vols. 1 and 2, edited by T. Massalski, 1986. ASM International, Materials Park, OH 44073-0002, Ni-Sn, p. 1759.)

Figure 1.11—Binary alloy phase diagram for the Ni-Sn system.



(Binary Alloy Phase Diagrams, Vols. 1 and 2, edited by T. Massalski, 1986. ASM International, Materials Park, OH 44073-0002, Cu-Sn, p. 965.)

Figure 1.12—Binary alloy phase diagram of the Cu-Sn system with instructive markers per the text.

composition of 61Cu-39Sn (wt.%), but is usually observed having a nominal composition of 63Cu-37Pb. This composition in wt.% can also be written in atomic percent or atomic fractions in subscript form, $\text{Cu}_{75}\text{Sn}_{25}$, which is simplified to Cu_3Sn_1 , or simply Cu_3Sn . At point E ($530^\circ\text{C}/986^\circ\text{F}$), the two-phase composition of ϵ (Cu_3Sn) and liquid (18Cu-82Sn) is observed. As more of the ϵ phase is created upon cooling, the concentration of Cu in the remaining liquid phase is observed to have decreased.

At point F ($415^\circ\text{C}/779^\circ\text{F}$), the alloy completely solidifies into a two-phase solid, one phase is the ϵ phase (Cu_3Sn), and the second phase is the η phase. The diagram shows the η phase at $415^\circ\text{C}/779^\circ\text{F}$ to be 41Cu-59Sn. The alloy is still two-phase, comprised of the two intermetallic compounds Cu_3Sn (ϵ) and η . The relative amounts of the two phases can be determined from the lever rule.

Point H, $189^\circ\text{C}/372^\circ\text{F}$, represents a solid-state transformation. At this temperature, the η phase has undergone a transition represented by a slight shuffling of the atoms that results in a small change to the atomic structure. The change is so slight that it is noted simply by adding an apostrophe to the phase designation, η' . The η' phase is identified by the stoichiometry, Cu_6Sn_5 . The two-phase structure of ϵ and η' is retained upon further temperature decreases below $189^\circ\text{C}/372^\circ\text{F}$, e.g., point I.

Similar analyses can be made of the Au-Sn and Ni-Sn systems in Figures 1.10 and 1.11, respectively. In the case of the Au-Sn system, Figure 1.10, the single phases: ζ' , δ , and ϵ , are truly line compounds as they do not allow a variation in composition way from the singular value. It will also be noted that the Au-Sn system has two eutectic reactions, one at the 80Au-20Sn composition and a second at the 10Au-90Sn composition. The eutectic temperatures are $278^\circ\text{C}/532^\circ\text{F}$ and $217^\circ\text{C}/423^\circ\text{F}$, respectively. The Ni-Sn phase diagram, and specifically the single-phase (stoichiometric) compounds of the Ni-Sn system, closely resemble those of the Cu-Sn binary alloy in that they have a finite composition range.

While it is important to understand the solidification sequence of phases as predicted by the phase diagram for the Cu-Sn, Au-Sn, and Ni-Sn systems, it will be observed in discussions on solder/base metal interface reactions that engineering interest in the evolution of phases in these systems does not always pertain to solidification sequences, per se; but rather, liquid-state and solid-state reactions at the solder/base metal interface. An effectively infinite supply of both solder and base metal components will lead to the appearance of phases in a manner that is not readily predicted by the phase diagram. The phase diagrams, in general, are good at determining *which phases* can potentially be present at the interface. However, they are less successful at determining the relative amounts of the phases that may be present, as well as

predicting the appearance of “additional phases” that are metastable, or temporary. That is because the dissimilar metals (base metal versus solder alloy) in contact at that interface represent a *nonequilibrium* situation. A phase diagram, whether binary, ternary, or of higher order, is limited by its capacity to predict phases present *at equilibrium, at the designated temperature, and with specific quantities of the constituent metals*.

The use of the binary phase diagram to estimate interface reactions is first illustrated by the hypothetical case in Figure 1.13a. The simple eutectic was selected for illustration purposes only. The following procedure would apply to more complex phase diagrams as well. The first scenario, and typically the most often encountered, is that in which it is assumed that there is an infinite amount of both metals comprising the couple. At the temperature, T_0 , all phases are in the solid state. Pure component A is on the left side; pure component B is on the right side. *The line drawn from the pure-A side to the pure-B side on the phase diagram maps out the potential phases that can be expected across the interface of the couple*. From left-to-right, the interface structure begins with pure A and changes to the α solid-solution phase. The α solid solution would contain a concentration gradient of A and B that becomes richer in B toward the right. The next region would be that of the two phases, $\alpha + \beta$. Note that the two-phase composition would have only an infinitely small thickness at the interface. Finally, the β solid-solution phase would be present, leading into the pure-B field on the other side of the couple. Again, the schematic in Figure 1.13a by no means represents the relative amounts of each of the potential phase fields that may be present; those amounts are determined by the (nonequilibrium) reaction and diffusion kinetics. In fact, these kinetics may not allow a perceptible amount of some phases to be observed.

Should the temperature be raised to a value of T_1 , then again, a line is drawn across the phase diagram at that temperature. In this second case, because the L, L + α , and L + β phase fields are crossed; some melting can be expected.

The Cu-Sn phase diagram can be used to illustrate Sn-based solders on Cu. The Cu-Sn binary phase diagram is shown in Figure 1.9. First, the case of liquid Sn in contact with solid Cu is examined. Interfacial reaction layer thickness is dependent upon the time duration during which the molten solder is in contact with the base metal, given that this is a nonequilibrium situation. Shown in Figure 1.13b is an optical micrograph of the Sn-Cu interface following the exposure of Cu to liquid Sn for 300 s. The Sn was at $260^\circ\text{C}/500^\circ\text{F}$ [8]. A thicker structure developed after the same time duration, 300 s, but with a higher, molten Sn temperature of $340^\circ\text{C}/644^\circ\text{F}$ (Figure 1.13c). As would be indicated by drawing horizontal

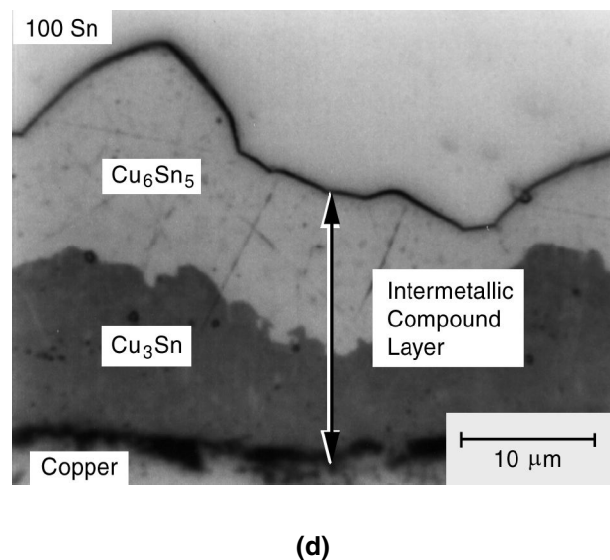
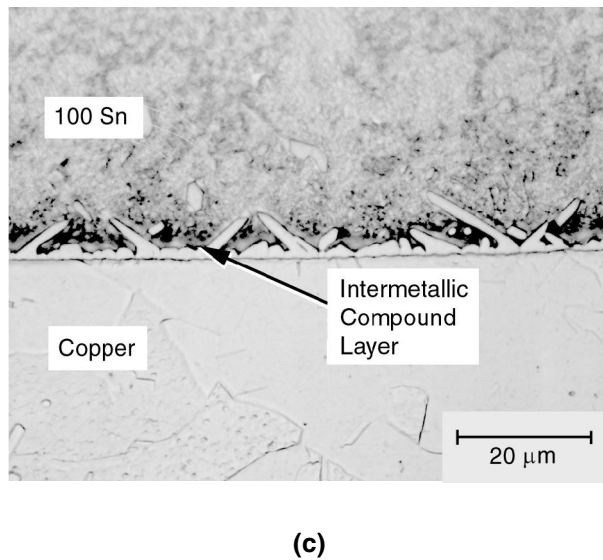
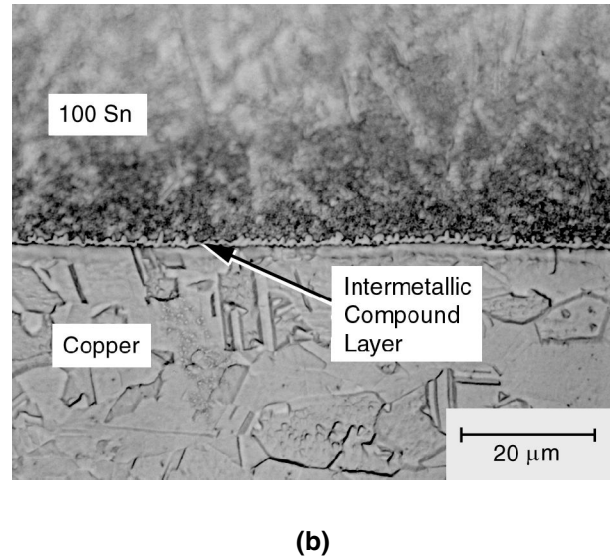
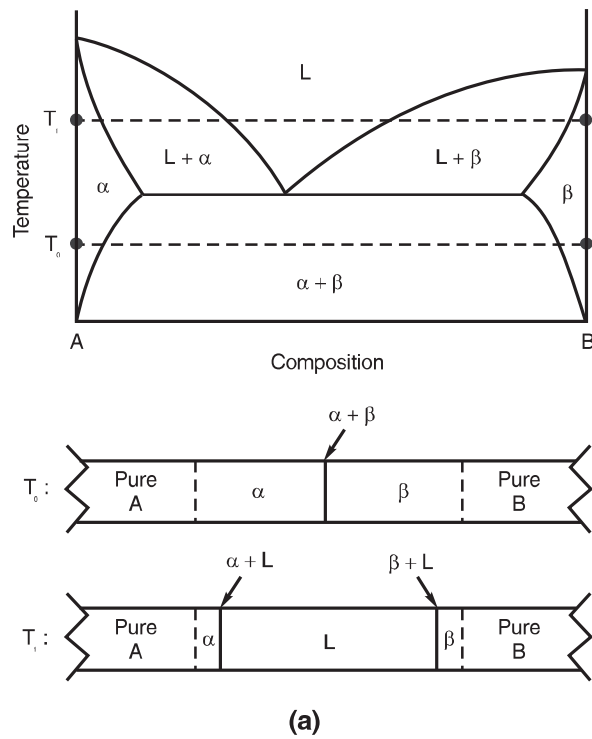


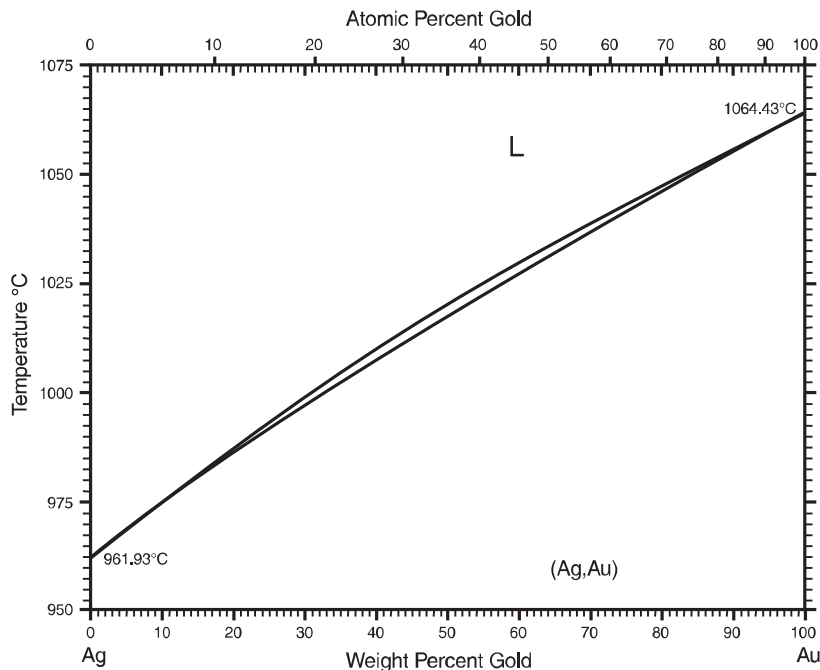
Figure 1.13—Reaction product development at solder/substrate interfaces through the use of the binary alloy phase diagrams: (a) Schematic diagram of phase identification in bimetal couples for a simple (AB) eutectic diagram. (b) Optical micrograph of the interface region between molten 100Sn and Cu after 300 s at 260°C (500°F). (c) Optical micrograph of the molten Sn/Cu interface after 300 s at 340°C (644°F). (d) Interfacial layer development from solid-state aging at 170°C (338°F) for 402 days.

lines across Figure 1.9 at temperatures of 260° and 340°C, there is no significant difference in the potential phases that can form at the Sn-Cu interface (right-to-left): L, L + η , η , η + ϵ , ϵ , (Cu) solid solution, and Cu. However, phases containing ϵ stoichiometry are not generally observed, thereby substantiating the prevailing nonequilibrium conditions.

Following solidification of the joint, the interface reactions can continue and intermetallic compound layers further develop by solid-state diffusion processes. The rate of solid-state growth increases with higher temperatures, since diffusion is a thermally activated process. Referring to Figure 1.9, the possible phase fields that can be present after aging at 170°C/338°F are determined by the intersection of the 170°C isotherm with the phase fields. Those phases are, right-to-left: Sn, Sn + η , η , ϵ + η' , ϵ , (Cu) + ϵ , and the solid solution of (Cu). The case of a 100Sn/Cu solder joint aged at 170°C for 402 days is shown in the optical micrograph in Figure 1.13d, which illustrates the intermetallic compound layer growth under elevated-temperature, solid-state diffusion [9]. The uncertainty of reaction kinetics under the *nonequilibrium* condition does not allow for a prediction of the relative thicknesses of the Cu_6Sn_5 (η') and Cu_3Sn (ϵ) layers. As a reminder, the two-phase fields do not have observable, corresponding layers at the interface.

In summary, binary phase diagrams can be applied to the physical metallurgy of soldering per the traditional solidification/melting processes involving solder alloys. However, in the case of the all-important interface reactions that can take place between the solder (molten or solid) and the substrate material, use of the phase diagram to predict reaction products is limited to only identifying the potential reaction product chemistries that *may* appear at the solder-substrate interface. Because the phase diagram can give no indication of the process kinetics which determine the growth rates of the interfacial reaction products, the relative amounts of those phases that may be present, cannot be predicted.

Up to this point, the simple eutectic phase diagram exemplified by the Sn-Pb binary system; and the more complex phase diagrams illustrated by the Cu-Sn, Au-Sn, and Ni-Sn binary systems have been examined. A third format of binary alloy phase diagram involves phases having considerable mutual solubility. An example of a complete, solid-solution binary alloy is illustrated by the Ag-Au phase diagram shown in Figure 1.14 [10]. For all combinations of Au and silver (Ag), cooling from the liquid state results in passage through a very small pasty range followed by solidification into a single-phase microstructure of Au and Ag dissolved into one another.



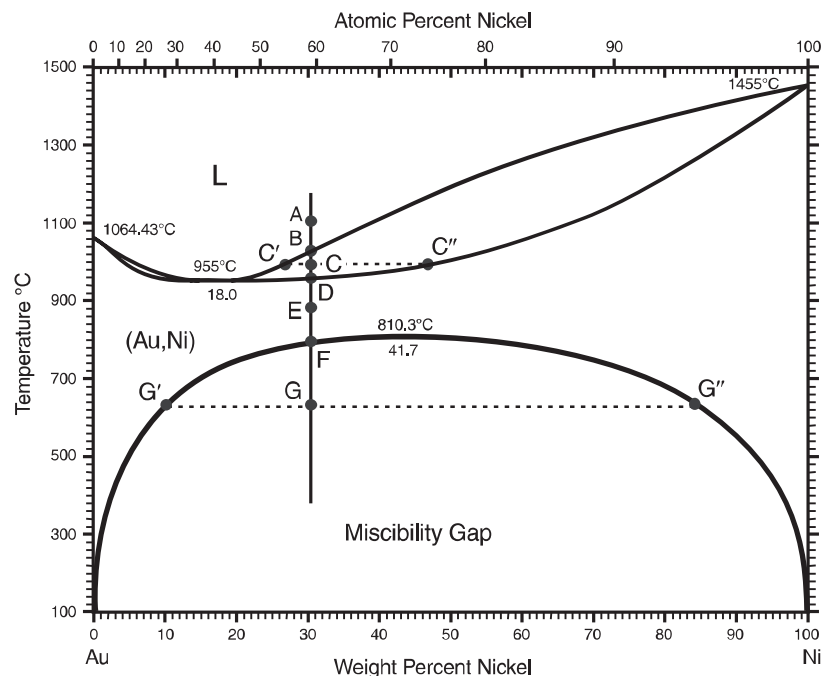
(Binary Alloy Phase Diagrams, Vols. 1 and 2, edited by T. Massalski, 1986. ASM International, Materials Park, OH 44073-0002., Au-Ag, p. 7.)

Figure 1.14—Binary alloy phase diagram of the Au-Ag system.

A variation to the case of complete, mutual solubility is that in which the complete, solid solution exists at higher temperatures. However, at lower temperatures, the process of *phase separation* or *spinodal decomposition* takes place. This phenomenon is illustrated by the Au-Ni phase diagram shown in Figure 1.15 [11]. A large two-phase mushy zone is observed to separate the liquid phase field, L, from the (Au, Ni) single-phase field (mutual solubility). Moreover, a eutectic point is observed at 18 wt.% Ni and 955°C/1751°F. The dome-shaped field at lower temperatures is termed the *miscibility gap*; it indicates the region of phase separation. The solidification process was illustrated with a composition of 70Au-30Ni, beginning with the liquid (single phase) at point A. Cooling causes the temperature to reach the start of solidification at point B (1040°C/ 1904°F). Continuing to lower temperatures causes the alloy to enter the two-phase (solid + liquid) mushy zone, and solidification continues much like previous cases. At point C, a solid phase of composition C'' (53Au-47Ni) and liquid of composition C' (74Au-26Ni) are observed. Solidification is complete at point D (970°C/1778°F), resulting in a single-phase solid of Au and Ni dissolved into one another (point E). At point F (800°C/1472°F), phase separation begins as the miscibility gap is encountered. In phase separation, a spatial

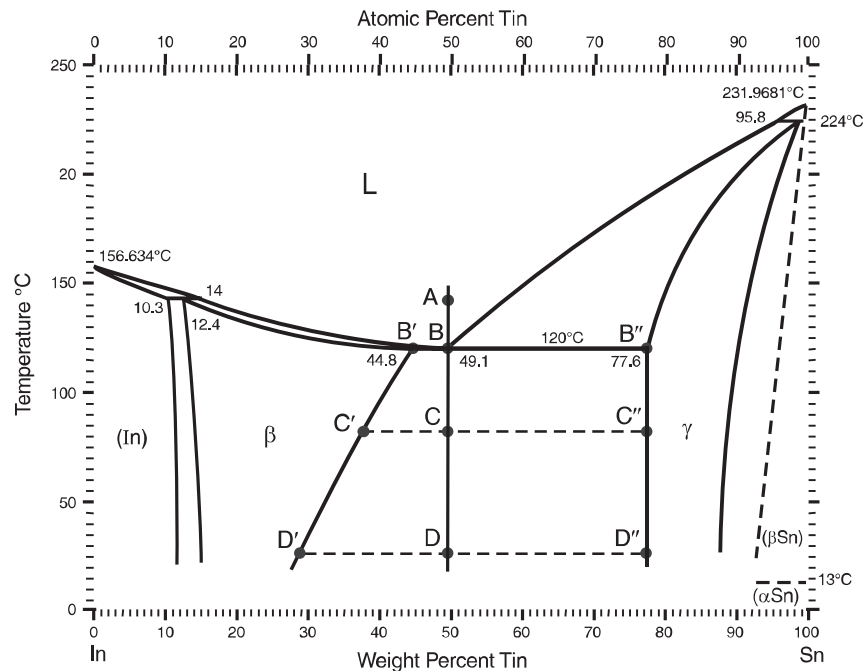
segregation takes place in which separate regions of one of two differing compositions can be identified; both compositions are solid solutions. For the case of point G (630°C/1166°F), regions of composition G' (90Au-10Ni, solid solution) and G'' (16Au-84Ni, solid solution) will form by solid-state diffusion processes. A further lowering of the temperature causes the equilibrium compositions to change slightly; however, as with all cases that require solid-state diffusion processes to realize equilibrium concentrations, nonequilibrium microstructures representing the higher-temperature regimes may prevail due to sluggish diffusion kinetics.

Several In-Sn solder compositions are used in a number of soldering applications, including low-temperature-service conditions. The In-Sn system is a binary alloy having an assortment of solid-solution phases. The phase diagram is shown in Figure 1.16 [12]. Observe that the binary system has a eutectic composition of 49.1In-50.9Sn and eutectic temperature of 120°C/248°F. The eutectic composition is often cited as simply 50In-50Sn. The interpretation of the diagram uses the same principles as discussed above. In Figure 1.16, the single-phase regions have been noted; between each of them are the two-phase regions, comprised of the two phases represented by either of the left and right border lines. The eu-



(Binary Alloy Phase Diagrams, Vols. 1 and 2, edited by T. Massalski, 1986. ASM International, Materials Park, OH 44073-0002, Au-Ni, p. 289.)

Figure 1.15—Binary alloy phase diagram of the Au-Ni system.



(Binary Alloy Phase Diagrams, Vols. 1 and 2, edited by T. Massalski, 1986. ASM International, Materials Park, OH 44073-0002, In-Sn, p. 1401.)

Figure 1.16—Binary alloy phase diagram of the In-Sn system.

itectic composition will be used to exemplify this system. Starting from the liquid (point A, 150°C/302°F), complete solidification takes place at once upon cooling to a temperature of 120°C/248°F at point B. The two-phase structure is comprised of the β phase with In and Sn in solution with one another, at a composition of 55.2In-44.8Sn (point B'). The second phase, the γ phase, again comprised of In and Sn in solid solution, would have a composition of 22.4In-77.6Sn (point B''). As always, the lever rule still holds for determining the relative amounts of each phase that are present in the overall microstructure of the solidified solder.

Further cooling to point C (85°C/185°F) results in retention of the two-phase microstructure of β and γ phases; however, each of these phases has changed composition to those represented by points C' (62In-38Sn) and C'' (23In-77Sn), respectively. The compositions continue to change upon a further drop to room temperature (point D: 25°C/77°F); the compositions of the β and γ phases are represented by points D' (71In-29Sn) and D'' (22In-78Sn), respectively. The compositions of the two phases predicted by the temperatures of points C (C' and C'') and D (D' and D''), respectively, are based upon assumed equilibrium conditions. The inherent slowness of solid-state diffusion process, particularly as the temperature decreases, can delay the achievement of those equi-

librium microstructures, sometimes indefinitely when at very low temperatures. Note that the β and γ phases are not intermetallic (line) compounds having a single composition. Rather, they are solid-solution chemistries that can have a range of compositions, depending upon the starting chemistry of the particular material at hand. Should the starting composition have been 80In-20Sn, then upon conclusion of all solidification, the alloy would be a single-phase material (β -phase) having the nominal (starting) composition of the molten alloy. This microstructure would persist for the remainder of the cooling segment.

Complete solid-solution binary alloys, or the variations noted above, are not commonly encountered in soldering technology. Generally, systems such as the simple eutectics and the more complex binary systems comprised of one-or-more line compounds, e.g., Cu-Sn, Au-Sn, etc., are encountered in a majority of soldering applications. Irrespective of the frequency favoring one type of binary alloy system over another, it cannot be over-emphasized that it is important for the soldering technologist to have a firm understanding of interpreting the various types of binary alloy phase diagrams, and their limitations based upon the underlying equilibrium assumption.

1.2.1.1.2 Ternary Alloy Phase Diagrams. As noted above, a majority of the commonly used solders are, in fact, binary alloys. Their melting properties and equilibrium microstructures are described by the binary alloy phase diagram. Even many of the metallurgical reactions that take place between the solder alloy, molten or solid, and the base material, can be aptly approximated by one or more binary interactions. However, the number of soldering applications involving solder alloys or solder-substrate systems having more than two elements that actively participate in the joint metallurgy is steadily growing. These higher-order interactions have become more prevalent with the development of new solders engineered to have properties optimized for particular manufacturing advantages and/or to meet stringent service environments. The solder metallurgist has been forced to look beyond the traditional binary alloys and to investigate *ternary alloys* (three elements), *quaternary alloys* (four elements), and higher-order alloy systems [13–15]. As a consequence, there is the need to predict and analyze the microstructure of higher-order solder alloys, and to interpret complex solder-substrate interactions that cannot be effectively described by binary alloy phase diagrams.

The next level of phase diagram tool is the *ternary phase diagram*. Several criteria are required to construct and interpret the ternary alloy phase diagram, simply because there are more degrees-of-freedom (variables) than in the case for the binary system. Recall from the earlier discussion that binary phase diagrams showed three of four possible degrees-of-freedom: the amount of A; the amount B; and the temperature. The fourth variable, pressure, was assumed constant. Also recall that the binary alloy phase diagram was a two-dimensional construct that describes the “temperature-composition” relationship. Only two dimensions were required because the amount of one element, e.g., B, was determined by the amount of the other element, A, as $1 - A$, assuming fractional quantities.

In a ternary system, a third component, C, requires the addition of a third dimension to the descriptive methodology, because now, two of the three components, A, B, and C, must be designated. The third component, e.g., C, is determined by $1 - (A + B)$, assuming the fractional representation of the component quantities. A simple, three dimensional phase diagram is constructed in Figure 1.17; the axes are shown in Figure 1.17a. The horizontal axes are the concentrations A and B; the amount of C would then be implicitly determined by $1 - (A + B)$. In the instance in which either A or B is zero, then the other axis, B or A, respectively, would represent the binary alloy cases of B-C or A-C, respectively. The vertical axis is temperature. The phase transitions that were represented by the liquidus and solidus lines in the binary phase diagram, become *surfaces* in the three-dimensional ternary phase dia-

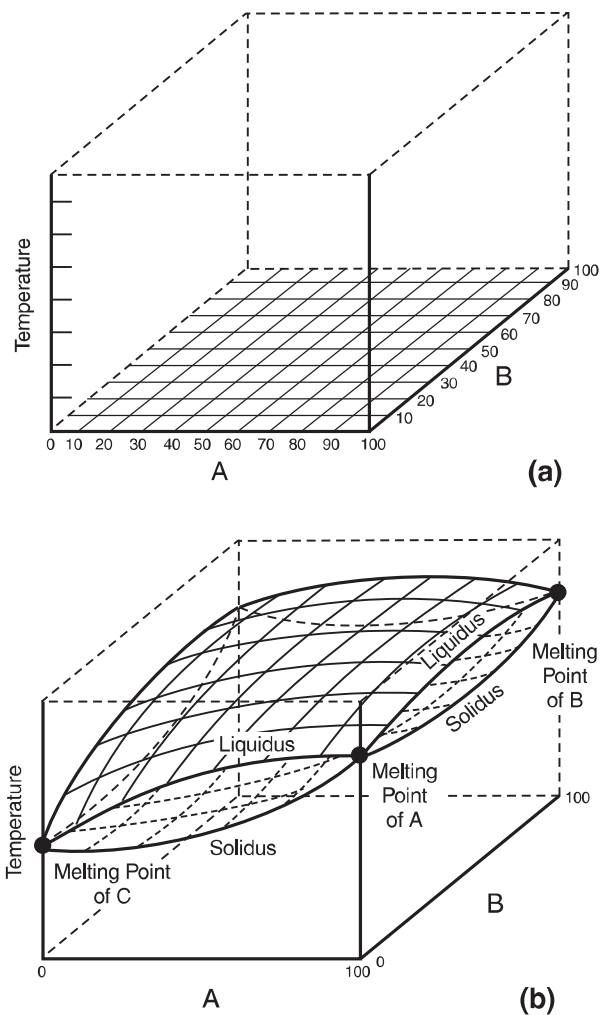


Figure 1.17—A “first cut” of a three-dimensional, ternary alloy phase diagram.

The graph of the axes is shown in (a). The horizontal axes are A and B; the vertical axis is temperature. The example of a solid solution alloy AB is illustrated in (b).

gram. This point is illustrated in Figure 1.17b using the simple case of a complete solid-solution ternary alloy A-B-C. Phase fields that were areas in the binary alloy phase diagram, become volumes of space in the three-dimensional ternary diagram.

Although today’s computer imagery can easily develop three-dimensional plots to describe ternary alloy systems, ternary systems have been described by two-dimensional constructs that accommodate the surface of a sheet of paper. Of course, reducing the three-dimensional ternary phase diagram, e.g., Figure 1.17b, into a two-dimensional representation must necessarily

occur at the price of losing some information. The lost information is caused by one of the parameters necessarily being kept constant. The following discussion will use very simple alloy systems to describe the features of the ternary alloy phase diagram. More intricate alloy systems having numerous phase or “volume fields” can be understood from these basic principles. The ternary systems are the highest-order alloys that can be represented visually in complete form; (e.g., Figure 1.17b). The use of visual constructs to describe higher-order alloy systems will require that greater amounts of information be compromised, typically by keeping additional variables constant.

The development of the two-dimensional, ternary phase diagram begins with a description of the *Gibbs triangle* [16]. The Gibbs triangle can be thought of as an outgrowth of the (ternary) axes diagram in Figure 1.17a, having been chosen to explicitly show the concentrations of all three elements. A Gibbs triangle for the three component system, A-B-C, is constructed in Figure 1.18, beginning with the initial outline in Figure 1.18a. It is an equilateral triangle with the three components at each of the apexes. A grid of lines is built-up in the triangle interior for each component A, B, and C. Figure 1.18b shows the concentration lines of component A in which the lines divide the distance between the A apex and its base on the opposite side, into fractional divisions. Parallel lines $a^{IX}-a^{IX}$, $a^{VIII}-a^{VIII}$, ..., a^I-a^I , and a^0-a^0 , describe the fractions, 0.9, 0.8, ..., 0.1, and 0.0, respectively, of the possible concentrations of A in the ternary system. That is, each line is a line of constant fraction of component A in the composition. A similar set of lines would be constructed for components B and C. The finished triangle is shown in Figure 1.18c. Each base or side of the triangle represents the binary compositions of the two components of the ending apex points; the third component is equal to zero. Therefore, the composition represented by point P (Figure 1.18c) is determined from the lines on which it is located: 0.2A, 0.7B, and 0.1C; that is, the composition is 0.2A-0.7B-0.1C. Interpolation between two parallel lines would provide values for compositions which do not lie directly on the grid lines. Of course, a check on the correct interpretation of the plot is that the fractional values must add up to 1; or 100% if percentages are used.

The imposition of a two-dimension limit on the ternary phase diagram means that the Gibbs triangle of compositions represents only a *single temperature*; that is, the ternary alloy phase diagram is typically an *isothermal section* passing through the three-dimensional phase space (volume) at a particular temperature of interest. Therefore, it is the temperature information that is compromised when describing a ternary alloy through a two-dimensional construct. In actuality, some visualizations

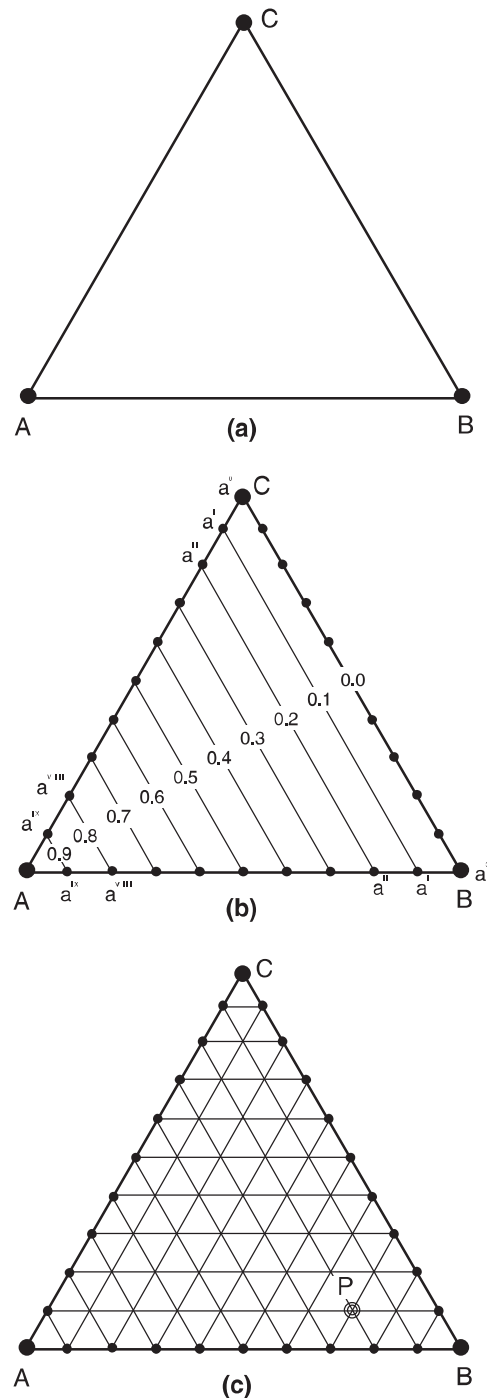


Figure 1.18—Construction of the Gibbs triangle for the ternary alloy comprised of A, B, and C. (a) Outline with each component at the apex of the equilateral construct. (b) The triangle with the lines of constant A component (as fractional quantity) in place. (c) The fully constructed Gibbs triangle for the A-B-C ternary system.

will be described below which illustrate a limited amount of temperature information, but not to the extent that is presented in the simpler binary alloy phase diagrams.

A two-dimensional, ternary phase diagram will now be developed for the simple solid solution composition represented by the three-dimensional, ternary alloy phase diagram in Figure 1.19a [17]. Specifically, the case in Figure 1.19a is that of the simple solid solution alloy, α , separated from the liquid phase, L, by the two-phase region, $\alpha + L$. The boundary *surfaces* between the two-phase region and the L phase, and the L phase and the α phase, are the *liquidus surface* and the *solidus surface*, respectively. The two-dimensional diagram is developed by taking an isothermal (horizontal) slice through the three-dimensional diagram. If the slice is taken at a low temperature so as to pass entirely through the α phase, then the two dimension representation will appear as in Figure 1.19b. An isothermal slice at a higher temperature passes through the solidus and liquidus surfaces resulting in the ternary diagram shown in Figure 1.19c. The intersection of the horizontal plane of constant temperature with the liquidus and solidus surfaces results in the formation of liquidus and solidus contour lines, respectively. An isothermal section at a higher temperature, shown in Figure 1.19d, illustrates the movement of the liquidus contour line, the solidus contour line, and the phase areas. Finally, at temperatures greater than that of the highest melting temperature component, the alloy is completely liquid; the ternary diagram would appear similar to that in Figure 1.19b, except that the liquid phase, L, would be present.

It was observed in the binary alloy phase diagrams that the tie lines in a two-phase region provided the compositions of the two (terminal) phases per the starting composition. The lever rule would be used to determine the amounts of each phase that were present in the microstructure. In the ternary phase diagram, the tie lines are not necessarily parallel to one another as shown in Figures 1.19c and 1.19d. The position and direction of the tie line between the liquidus and solidus lines are not obvious without experimental data. The criteria for tie lines in the ternary phase diagram are:

- (1) they are straight lines;
- (2) they run between the solidus and liquidus lines;
- and
- (3) they cannot cross along an isothermal cut.

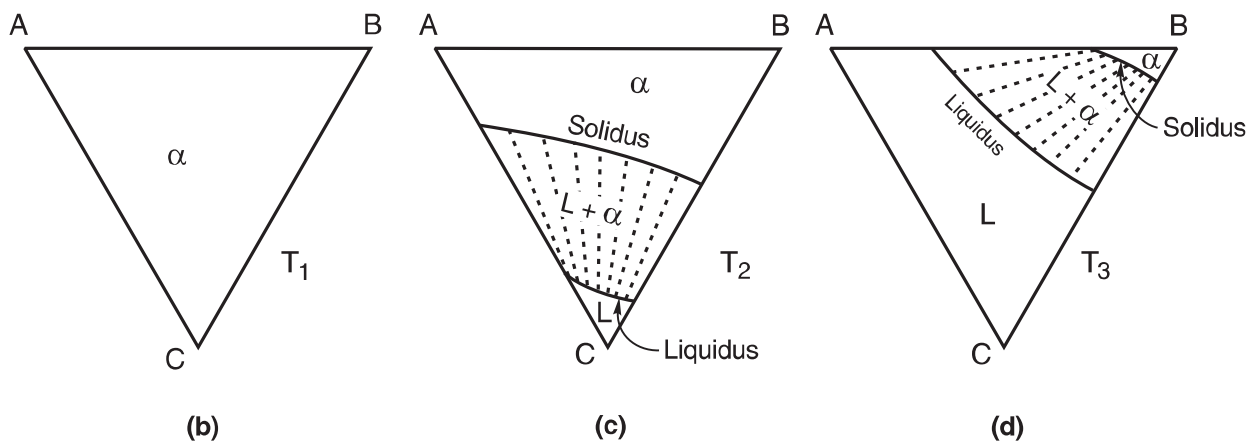
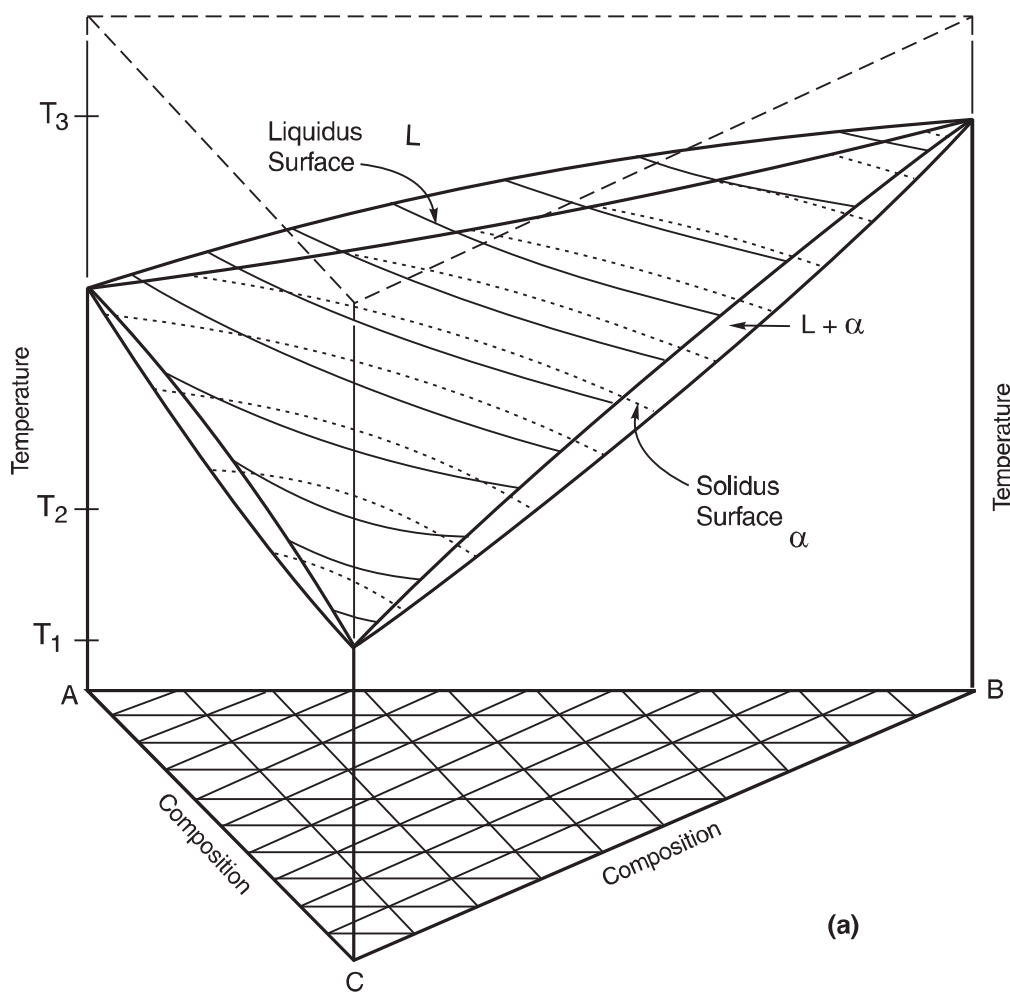
Since the overall alloy composition as well as the compositions of the liquid and solid phases all lie on the same tie line, the lever rule can still be applied in order to determine the relative amounts of each phase that are present in the alloy at the particular temperature.

The isothermal section, ternary phase diagram provides a description of the phase relationships at a particular temperature. When such diagrams are available for a

range of temperatures, then a more complete description of the equilibrium microstructure of the alloy can be constructed. Besides the traditional ternary phase diagram that shows the isothermal cut or section through the three-dimensional phase space, other variations to the ternary alloy phase diagram have been developed; these alternative constructs provide different formats of information. For example, should the liquidus surface of a ternary alloy be of interest for a particular application, then a graph is made in which the liquidus lines resulting from several temperature (isothermal) cuts are projected onto the Gibbs triangle. This plot is referred to as the *liquidus projection*. An example of the liquidus projection for the simple, solid-solution system is shown in Figure 1.20 [17]. Each liquidus line is denoted by the temperature isotherm from which it was created. The liquid phase would lie to the side of the particular liquidus line having the other, higher-temperature liquidus lines; to the lower-temperature, liquidus line side would be the two phase field (liquid plus solid). A similar construct can be performed with the solidus surface, thereby forming the *solidus projection* of solidus lines.

At this point, it is instructive to apply the above discussion to an actual ternary alloy system. This system is described as a *ternary, four-phase equilibrium*. This category of ternary phase diagram, and its slightly simpler sister category, the *ternary, three-phase equilibrium*, are commonly encountered with materials used in soldering applications. Nevertheless, both types of systems can be very complex to analyze; in fact, some of those complexities are beyond the scope of this text. The following example will familiarize the reader with basic features of the ternary alloy phase diagram. The case that is exemplified here is that of the Ag-Bi-Pb system, Figure 1.21 [18]. This case has particular pertinence to soldering technology due to frequently encountered interactions between Pb-Ag solders and Bi-containing materials or coatings as well as the use of low-temperature, so-called “fusible” solders that contain Bi. The liquidus projection is shown in Figure 1.21a. The liquidus lines are marked with the appropriate temperature values. The heavier lines designate “liquidus troughs.” As the term implies, the liquidus trough traces out the location of the intersection of two liquidus surfaces. The intersection of the two surfaces is a line. This construct is best understood by referring to the top schematic diagram in Figure 1.21b. The liquidus trough projection is not an isothermal contour line. In fact, the liquidus trough line is a collection of points of different temperatures. The liquidus troughs are added to the liquidus diagram to forewarn the reader of an artifact in the ternary system. The decrease in temperature along the trough is often indicated by arrows.

Referring to Figure 1.21a, three such troughs have intersected at point E_1 . Because the temperature trends



(Phase Diagrams in Metallurgy: Their Development and Application, by F. Rhines, 1956. Reproduced by permission of the McGraw-Hill Company, Fig. 12-4, p. 113; Fig. 12-6, p. 114.)

Figure 1.19—(a) Three-dimensional phase diagram (Gibbs triangle) for a simple solid-solution alloy. (b) Isothermal section through the phase diagram entirely in the solid solution phase α . (c) Isothermal section through the liquidus and solidus surfaces. (d) Isothermal section through the liquidus and solidus surfaces, but at a higher temperature than in (c).