

PRINCIPLES OF  
**BRAZING**



David M. Jacobson  
Giles Humpston



# Principles of Brazing

David M. Jacobson

Giles Humpston



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# Preface

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*Principles of Brazing* primarily aims at presenting the subject in a form that is readily accessible to practitioners of this joining technology, while at the same time offering a scientific perspective of brazing. It focuses on fundamental principles rather than providing recipes for producing brazed joints. Based on *Principles of Soldering and Brazing*, published in 1993, this volume includes much new material on brazing, covering progress over the past decade.

The largely artificial distinctions between brazing and soldering are preserved because, despite the many commonalities, it has been found that practicing engineers are concerned with either soldering or brazing and seldom are involved with both simultaneously. The companion volume, *Principles of Soldering*, addresses this complementary need. A large proportion of the literature on brazing and soldering may be charged with being heavy on description and light on critical analysis. We have endeavored to redress the balance, while striving to avoid being unduly simplistic or overly mathematical in our approach. Admittedly, we may not always have succeeded in this aim.

As in *Principles of Soldering and Brazing*, we have striven to maintain the focus on the fundamental aspects of brazing and have deliberately avoided entering into specific joining technologies in detail. Therefore, it is inevitable that some topics are not accorded due consideration, although it is hoped that sufficient references are provided to enable the reader to pursue these further.

The authors recognize that the range and extent of the knowledge base of metal joining is not immediately obvious, and mastery of the subject requires a fairly deep understanding of materials. This point is particularly apposite to the wetting of ceramics by metals, discussed in Chapter 7. The behavior of self-fluxing copper-phosphorus brazes and the poor mechanical integrity of joints made with these brazes to steel unless nickel is present represents another example of the interplay of factors that need to be considered and understood (see Chapter 3).

Two areas of brazing that have benefited from significant research efforts in recent years are active brazing and diffusion brazing. These are also areas in which the authors have been directly involved, and accordingly, individual chapters are devoted to each of these topics in this new edition (Chapters 6 and 7).

No attempt has been made to gather a comprehensive list of publications in our bibliography. Those that are included have been selected because they are useful basic texts, cover important subject matter, or relate to exemplary pieces of work, whether in respect of methodology, technique, or other noteworthy feature. It was felt that if the value of the book depended on its bibliography, it would rapidly become dated. The advent of computer search facilities and databases of scientific journal and conference abstracts should enable the reader who wishes to chase up references on specific topics to obtain further information without too much difficulty.

The reader should note that all compositions given in this book are expressed in weight percentage in accordance with the standard industrial practice, and these have, for the most part, been rounded to the nearest integer. The ratio of elements in intermetallic compounds, again by convention, refers to the atomic weight of the respective constituents. The general convention used for referring to braze alloy families is that adopted by the alloy phase diagram community, namely, in the alphabetical order of the elements, by chemical symbol. However, when referring to specific braze compositions, for the most part we have listed the elements in order of concentration. The alternative, which is widely accepted in the metal joining literature, is to express compositions in alphabetical order of the chemical symbols of the major constituents, followed by the minor constituents. The authors



prefer the system based on concentration because, otherwise, lesser ingredients can punctuate the composition order, which would be illogical and avoids debate as to whether a constituent is a major or minor element. Thus, for example, we refer to an alloy of composition Ag-22Zn-21Cu-2Sn-0.01Ce as a silver-copper-zinc braze.

Specific references are given with each chapter. For those wishing to read more generally on particular topics, the authors recommend the texts listed as Selected References at the end of this preface.

Many phase diagrams are subject to ongoing research, resulting in continued improvement in the accuracy and detail of the information. The most recent version of a diagram may be identified by consulting the latest cumulative index of phase diagrams, published in the Cumulative Index of the periodical *Journal of Phase Equilibria* (ASM International). This index refers to the source of the thermodynamically assessed diagram of interest. The reader is advised that the four compendia of binary phase diagrams published in the 1960s, 1970s, and 1980s (colloquially referred to as Hansen, Elliott, and Shunk) are now known to contain many errors and omissions.

Information on new developments in soldering and brazing is scattered throughout a wide range of periodicals, as reflected in the sources cited in the references appended to the individual chapters. To keep abreast of the literature, the authors have found especially useful the following abstract publications: *Metals Abstracts* and *Science Abstracts*. Technical libraries can provide automated searches against specified key words as a monthly service.

We wish to thank our many colleagues and ex-colleagues for their helpful advice and encouragement, particularly Chris Corti of the World Gold Council for sharing his insights into the brazing of jewelry.

David M. Jacobson  
Giles Humpston

#### SELECTED REFERENCES

- Brandon, D.G., and Kaplan, W.D., 1997. *Joining Processes: An Introduction*, John Wiley & Sons
- Eustathopoulos, N., Nicholas, M.G., and Drevet, B., 1999. *Wettability at High Temperatures*, Pergamon Press
- International Organization for Standardization (IOS), 1990. *Welding, Brazing and Soldering Processes: Vocabulary*, (IOS/DIS 857-2) ISO (currently under revision)
- Liebermann, E., 1988. *Modern Soldering and Brazing Techniques*, Business News
- Nicholas, M.G., 1990. *Joining of Ceramics*, The Institute of Ceramics/Chapman and Hall
- Olson, D.L. et al., Eds., 1993. *Welding, Brazing and Soldering*, Vol 6, *ASM Handbook*, ASM International
- Schwartz, M.M., 2003. *Brazing*, 2nd ed., ASM International
- Schwartz, M.M., 1990. *Ceramic Joining*, American Society for Materials
- Thwaites, C.J., 1983. *Capillary Joining: Brazing and Soft-Soldering*, Books Demand UMI

## About the Authors

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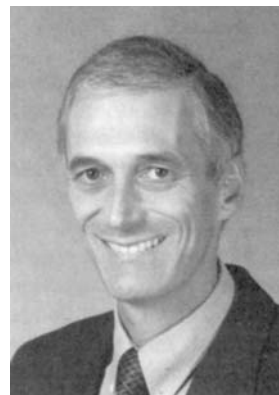


**David M. Jacobson** graduated in physics from the University of Sussex in 1967 and obtained his doctorate in materials science there in 1972. Between 1972 and 1975 he lectured in materials engineering at the Ben Gurion University, Beer-Sheva, Israel, returning as Visiting Senior Lecturer in 1979–1980. Having gained experience in brazing development with Johnson Matthey Ltd., he extended his range of expertise to soldering at the Hirst Research Centre, GEC-Marconi Ltd., which he joined in 1980. Currently, he holds the position of Professor of Manufacturing Technology at the Centre for Rapid Design and Manufacture, Buckinghamshire Chilterns University College, in High Wycombe. He is the author of more than 80 scientific and technical publications in materials science and technology and more than a dozen patents. He has been awarded three prestigious awards for his work on brazing.

Professor Jacobson's principal outside interests are archaeology and architectural history, focusing on the Near East in the Graeco-Roman period. He has published extensively in these fields, which extend to the numismatics and early metallurgy of that region. He recently completed a Ph.D. thesis on Herodian architecture at King's College, London, and teaches part-time in this subject area at University College, London. Professor Jacobson is married with two grown-up children and lives in Wembley, England, close to the internationally famous football stadium.

**Giles Humpston** took a first degree in metallurgy at Brunel University in 1982, followed by a Ph.D. on the constitution of solder alloys in 1985. He has since been employed by several leading industrial companies, where he has been involved with determining alloy phase diagrams and developing processes and procedures for producing precise and high-integrity soldered, brazed, and diffusion-bonded joints to a wide variety of metallic and nonmetallic materials. His expertise extends to fine-pitch flip-chip; new materials development; and packaging and interconnection for electronics, radio frequency, and optical products. He is a cited inventor on over 75 patents, the author of more than 60 papers, and the recipient of six international awards for his work on soldering and brazing.

Dr. Humpston is a licensed amateur radio enthusiast and has published several articles and reviews on electronics, radio, and computing. His other interests include exploring vertical axis wind turbines, building grid-tie inverters, flying radio-controlled gliders, winemaking, and growing bonsai. He lives with his wife, Jacqueline, and their three children in a small village in Buckinghamshire, England and in San Jose (Silicon Valley), California.



**David Jacobson** and **Giles Humpston** are the coauthors of the companion volume, *Principles of Soldering*, and the predecessor to this two-volume set, *Principles of Soldering and Brazing*, which was published by ASM International in 1993, with more than 4000 copies sold.

# History

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## Origins of Brazes and Brazing

Brazing is not a modern invention. Archaeological evidence shows that it has been practiced continuously since ancient times. Because the earliest forms of metalwork often required joints, and the ingredients of common brazes were either of noble metals or base metals extracted from readily winnable ores, brazing appears to predate soldering heritage by 2 to 3 millennia, despite the higher temperatures involved.

Brazing of gold and silver using foils of copper or copper alloyed to the more precious metals has been practiced earlier than 3000 B.C. One of the oldest known applications of brazing is the fabrication of a gold chalice and other objects found in the tomb of Queen Shab-Ad of Ur in the Euphrates valley, dated to about 3200 B.C. [Maryon 1936]. A Proto-Elamite figurine of this vintage, in silver, was clearly assembled by brazing with copper [Lang and Hughes 1991]. From about 2800 B.C., we have the copper fittings on the canopy of the sarcophagus of the Egyptian Queen Hetep-heres, which were joined using a copper-silver braze [Brooker, Beatson, and Roberts 1975]. Brazing is documented as a clearly recognizable process in the 4th century A.D. Leiden Papyrus X, recipes 31 and 33 [Caley 1926]. Abundant direct evidence of brazing being used as a joining method has also been obtained from objects dated from the Roman Imperial period. Thus, brazing in its most traditional form takes advantage of the reduction of the melting point of copper on alloying with gold or silver to below that of all three individual metals. The 12th century writer on craftsmanship, Theophilus, describes a brazing alloy made of two parts of silver and one part of copper, which is not far from the silver-copper eutectic (Ag-28Cu) [Hawthorne and Smith 1963, p 107].

Pliny the Elder (1st century A.D.) mentions another version of the same brazing method, which was used in antiquity to join gold granules to gold sheet [Pliny, *Natural History*, xxxiii 29 (see Rackham, 1952); Wolters 1983]. A powdered copper-bearing ore, such as malachite, is heated with a flux in a reducing environment, generally provided by the organic gum, which is used to hold the granules in place. This operation yielded finely divided copper, which on alloying with the noble metal makes the brazed joint. The same author provides the first documented account of a copper-zinc braze. This involved the addition of one part of white copper (brass) to two parts of white lead (tin). A joint in a gold ewer dating from the 4th century was found to contain both copper and zinc [Lang and Hughes 1991]. At this point, brazing appears to have halted its development. We know that verb *braise* derives partly from the Old French, *braser*, meaning to burn. In the 16th century, the English verb *braise* denoted “expose to the action of fire.” By the late 17th century, it acquired the meaning “solder with an alloy of copper and zinc,” i.e., essentially its present connotation, including the original precious metal origins.

An early application of diffusion brazing, known as Sheffield plate, was developed by Thomas Bolsover in 1743 [Bradbury 1912]. Sheffield plate is produced by rolling together a plate of copper sandwiched between two thin sheets of silver. The pressed assembly is heated in air using a small amount of flux at the edges to prevent oxidation. Above the silver-copper eutectic temperature of 780 °C (1436 °F), diffusion during heating produces a liquid phase, which fuses the silver sheets to the copper plate. This material is then rolled down to a thinner sheet, and this was exploited by the industrial pioneer Matthew Boulton in the second half of the 18th century as a cheap substitute for solid silver in domestic wares.

In the early 20th century, brazing alloys and techniques underwent further evolution with the development of low-temperature silver brazing alloys, which have found widespread application in industry.

## CHAPTER 1

# Introduction

---

### 1.1 Joining Methods

BRAZING AND SOLDERING jointly represent one of several methods for joining solid materials. These methods may be classified as:

- Mechanical fastening
- Adhesive bonding
- Brazing and soldering
- Welding
- Solid state joining

Other methods, such as glass/metal sealing, electrostatic welding, and so forth, are dealt with elsewhere [Messler 1999; Nicholas 1998; O'Brien 1991; Bever 1986].

Schematics of these joining methods are given in Fig. 1.1. These methods have a number of common features but also certain significant differences. For example, brazing and soldering are the only joining methods that can produce smooth and rounded fillets at the periphery of the joints. The joining methods just listed are in the order in which they lead to fusion of the joint surfaces and tend toward a “seamless” joint.

Because brazing and soldering lie in the middle of this sequence, they share several of the features of the other methods. For example, brazed and soldered joints often can be endowed with the advantageous mechanical properties of welded and diffusion-bonded joints; at the same time, in most cases they can be disassembled readily, without detriment to the components, like mechanically fastened joints. These features make brazing and soldering highly versatile.

The principal characteristics of the various joining methods are summarized in the paragraphs that follow.

#### 1.1.1 Mechanical Fastening

Mechanical fastening involves the clamping together of components without fusing the joint

surfaces. This method often, but not always, relies on the use of clamping members such as screws and rivets. In crimping, the components are keyed together by mechanical deformation.

Characteristic features of mechanical fastening include:

- A heating cycle is generally not applied to the components being joined. A notable exception is riveting, where the rivets used for clamping are heated immediately prior to the fastening operation. On subsequent cooling the rivets shrink, causing the components to be clamped tightly together. Historically, riveting has been used in shipbuilding because this joining method can achieve watertight joints between large plates of steel that make up the hull of a ship.
- The reliance on local stressing to effect joining requires thickening or some other means of reinforcement of the components in the joint region. This places a severe restriction on the joint geometries that may be used and imposes a weight penalty on the assembly. Another constraint on permissible joint configurations is the need for access to insert the clamping member.
- The method usually requires special mechanical preparation, such as drilling holes, machining screw threads, or perhaps chamfering of abutting surfaces, in the case of components to be crimped.
- The choice of suitable joint configurations is highly dependent on service conditions, for example, whether leak-tightness is required. Joints may be designed to accommodate thermal expansion mismatch between the components in the assembly. In the extreme case, joints can be made to permit complete freedom of movement in the plane perpendicular to the clamping member, as applied to the joint bars (fishplates) used to couple train rails.

## 2 / Principles of Brazing

- The electrical and thermal conductance across the joint is a function of the effective area that is in contact. This depends on many other parameters, such as the clamping force and the materials used; in service, the conductance is unlikely to be constant.

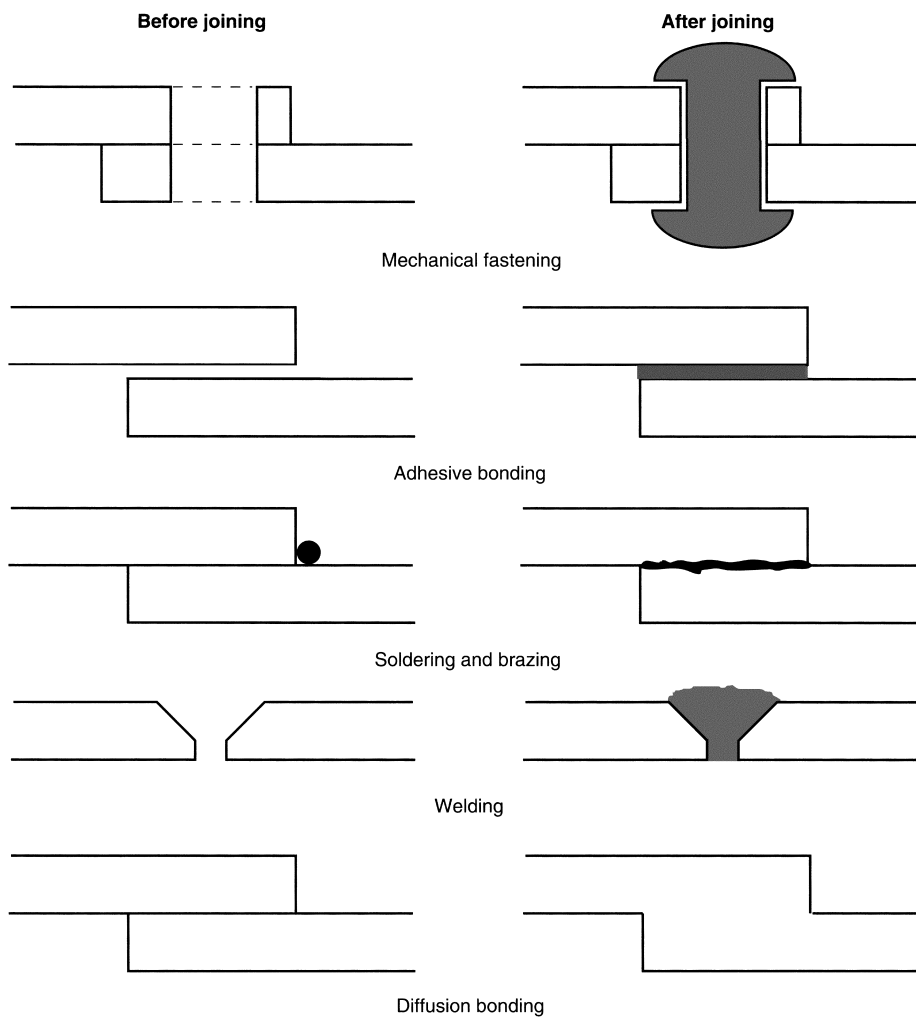
Mechanical fastening is used widely in conjunction with brazing processes, particularly as a method of holding preforms of brazing alloy in place during the heating cycle. Figure 1.2 shows one such application where multiple strips of brazing foil are held in place by twist-tag fasteners. In the assembly of aircraft structures made of light aluminum alloys, riveted joints are complemented and reinforced by adhesive bonding.

### 1.1.2 Adhesive Bonding

Adhesive bonding involves the use of a polymeric material, often containing various additives, to “stick” the components together. The process involves a chemical reaction, which may simply occur through exposure of the adhesive to air, leading to the formation of a hydrogen-type bond between the cured adhesive and the respective components. The original interfaces of the joint are preserved in this type of bonding process.

Characteristic features of adhesive bonding include:

- It is inherently a low-stress joining method because it is carried out at relatively low



**Fig. 1.1** Principal methods for joining engineering materials

temperatures, and most adhesives have high compliance.

- A diverse range of methods is available for curing adhesives.
- The geometry of the components tends not to be critical.
- Constraints apply to the geometry of the actual joint; in particular, large areas and very narrow gaps are necessary to ensure mechanical integrity.
- Joints tend to be weak when subject to forces that cause peeling. For this reason, adhesive joints are used frequently in combination with mechanical fastening, for example, in air-frame assemblies.
- Joint integrity tends to be sensitive to the state of cleanliness of the mating surfaces and to the atmosphere of the service environment.
- The service temperature range of adhesively bonded joints is usually limited, owing to the restricted temperature range over which they are stable, as is their compatibility with organic and aqueous media.
- Joints usually possess poor electrical and thermal conductance, although by loading the organic adhesive with metal particles, moderate conductance can be achieved, which approaches that of some brazing alloys. Such loading, however, is often at the expense of adhesive strength.

Polymer chemistry is a rapidly evolving science and some very advanced adhesives have

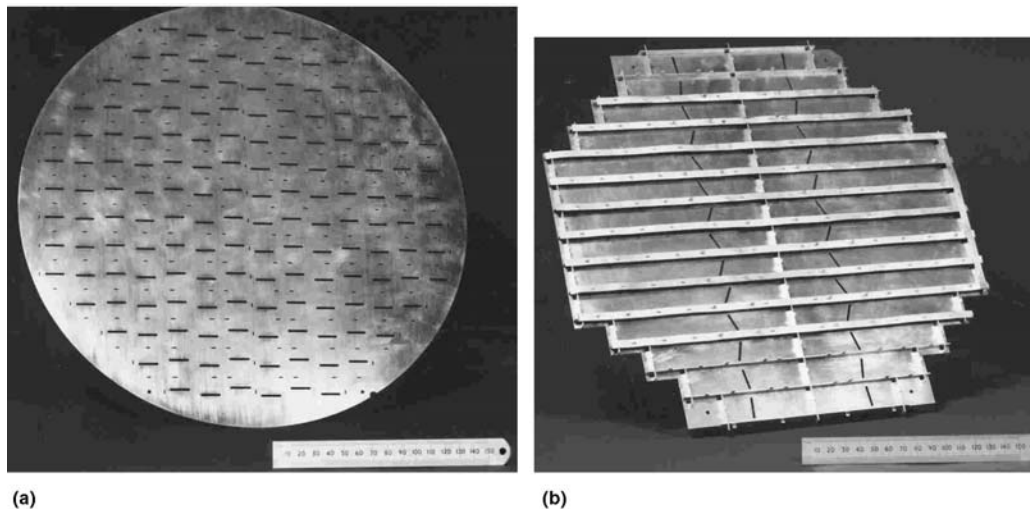
appeared on the market with properties highly tailored for particular functions. However, as adhesives do not have high temperature stability, they are never used in combination with brazes.

### 1.1.3 Brazing and Soldering

Brazing and soldering use a molten filler metal to wet the mating surfaces of a joint, with or without the aid of a fluxing agent, leading to the formation of metallurgical bonds between the filler and the respective components. In these processes, the original surfaces of the components are “eroded” by virtue of the reaction occurring between the molten filler metal and the solid components, but the extent of this “erosion” is usually at the microscopic level ( $<100\ \mu\text{m}$ , or  $4000\ \mu\text{in.}$ ). Joining processes of this type, by convention, are defined as brazing if the filler melts above  $450\ ^\circ\text{C}$  ( $840\ ^\circ\text{F}$ ) and as soldering if it melts below this temperature.

Characteristic features of brazing and soldering include:

- All brazing operations and most soldering operations involve heating the filler metal and joint surfaces above ambient temperature.
- In most cases, the service temperature of the assembly must be lower than the melting temperature of the filler metal.
- It is not always necessary to clean the surfaces of components prior to the joining operation because fluxes that are capable of



**Fig. 1.2** A phased array radar antenna prepared for brazing. The (a) front face and (b) interior show strips of brazing foil held in place by twist-tag mechanical fasteners. Courtesy of BAE Systems Ltd.

## 4 / Principles of Brazing

removing common oxides and organic films are available. However, there are penalties associated with the use of fluxes; for example, they leave behind residues, which are often corrosive and can be difficult to remove.

- The appropriate joint and component geometries are governed by the filler/component material combination and by service requirements (need for hermeticity, stress loading, positional tolerances, and so forth). Complex geometries and combinations of thick and thin sections can usually be brazed or soldered together.
- Intricate assemblies can be produced with low distortion, high fatigue resistance, and good resistance to thermal shock.
- Joints tend to be strong if well filled, unless embrittling phases are produced by reaction between the filler metal and the components.
- Brazed and soldered joints can be endowed with physical and chemical properties that approximately match and, in some cases, even exceed those of the components, but solders and some brazes usually have limited elevated-temperature service capability and stability.
- Fillets are formed under favorable conditions. These fillets can act as stress reducers at the edges of joints that benefit the overall mechanical properties of the joined assembly.

Brazing and soldering can be applied to a wide variety of materials, including metals, glasses, ceramics, plastics, and composite materials. For many materials, and plastics in particular, it is necessary to apply a surface metalization prior to joining.

### 1.1.4 Welding

Welding involves the fusion of the joint surfaces by controlled melting through heat being directed specifically toward the joint. Commonly used heating sources are plasma arcs, electron beams, lasers, and electrical current that is passed through the components and across the joints (electrical resistance) [Messler 1999; O'Brien 1991]. Filler metals may be used to supplement the fusion process for components of similar composition, as, for example, when the joint gap is wide and, possibly, of variable width. In that situation, the filler is often chosen to have a marginally lower melting point than

the components in order to help ensure that it melts completely. The joining process then has many similarities with wide joint gap brazing.

Characteristic features of welding include:

- Welding invariably involves a heating cycle, which tends to be rapid. A very wide variety of welding processes are available.
- Welding cannot be used to join metals to nonmetals or materials of greatly differing melting points. There are exceptions, but these are generally limited to precise combinations of materials and highly specific welding methods.
- Joint geometries are limited by the requirement that all joint surfaces are accessible to the concentrated heat source.
- Welded joints may approach the physical integrity of the components but are often inferior in their mechanical properties, particularly fatigue resistance. This is due to stress concentrations produced by the high thermal gradients developed during joining and the relatively rough surface texture of welds.
- The heating cycle usually affects the microstructure and hence the properties of the components over a macroscopic region around the joint, called the *heat-affected zone* (HAZ). The HAZ is often influential in determining the properties of welded joints.
- Welding tends to distort the components in the region of the HAZ. This is associated with the thermal gradients developed through the use of a concentrated heat source to fuse the joint surfaces.

Where the brazing cycle is particularly rapid and conducted using a high-intensity heat source, as, for example, in brazing of refractory metals, the process has many similarities to welding. Likewise, there exist hybrid processes, such as braze welding. This joining method is of particular value for joining advanced multiphase materials such as metal matrix composites. Although the metal component of such materials can often be brazed readily, the nonmetal species can usually be wetted using only very different, and hence often incompatible, filler metals and processing conditions. Braze-welding overcomes these limitations. The method combines heating, usually achieved by the passage of electric current, combined with compression of the joint, and only a small quantity of additional, preplaced, filler metal. The heating cycle is so rapid that dewetting, porosity, and other phenomena associated with liquid phase



joining, which would normally be prevalent when attempting to braze such materials in a conventional manner, are suppressed. Advanced, ultralightweight bicycle frames have been formed from tubular members of long-fiber-reinforced aluminum-boron composites using this method [Schwartz 2003, Zvolinskii 1995].

### 1.1.5 Solid-State Joining

The term *solid-state joining* covers a wide range of joining processes, most notably pressure welding, friction welding, and diffusion bonding [Messler 1999; Nicholas 1998]. Pressure welding, at its simplest, involves deforming physically two abutting surfaces to disrupt any intervening surface films and enable direct metal-to-metal contact. This process can be performed either hot or cold. In friction welding, the heat and disruption of surface films needed to achieve a sound bond are achieved by subjecting the components to relative movement while applying a compressive force. The relative movement can be rotary or involve angular or linear reciprocation. Diffusion bonding, in its purest form, requires placing two faying surfaces in contact and heating the assembly until the voids at the interface have been removed by diffusion. Messler [1999] includes wet plating (electrolytic and electroless) and vapor deposition (evaporation, sputtering, etc.) as solid-state joining processes because the deposit forms as a solid, and chemical bonds are usually formed when a metal is deposited on another material. Deposition requires that the interface is atomically clean for the deposit to be joined effectively to the substrate.

Solid-state joining constitutes a subject in its own right, quite separate from brazing and soldering, which rely on liquid state metal joining. However, the development of friction brazing and diffusion brazing processes, which are both hybrids between solid-state joining and brazing, require some consideration of the solid-state joining (see section 1.1.7). Pressure welding is sometimes used to prepare filler metals in various geometries and for tacking preforms in position.

Characteristic features of solid-state joining are:

- This method generally involves heating of the joint to a temperature below the melting point of the components.

- Pressure welding (especially in the form of explosive welding) and friction welding are often much faster processes than soldering or brazing (<1 s), while diffusion bonding is much slower (>10 min).
- The joints have no fillets.
- The service temperature of joined assemblies can be higher than the joining temperature and tend toward the melting point of the components.
- Solid-state joining is limited in application to specific combinations of materials that provide specific combinations of mechanical or diffusion characteristics.
- Of all the joining methods, solid-state joining is the least tolerant to poor mating of the joint surfaces.
- Joint surfaces need to be scrupulously clean because solid-state joining is a fluxless process.
- The properties of solid-state joints can approach those of the parent materials.

Further details on pressure welding are given in section 1.1.7.1, friction welding in section 1.1.7.2, and diffusion bonding in section 1.1.7.3 of this chapter.

### 1.1.6 Comparison between Brazes and Solders

In many respects, it is fruitful to consider brazes together with solders. This integrated treatment can be justified on metallurgical grounds. These two classes of filler cannot simply be demarcated by the 450 °C (840 °F) temperature boundary as is habitually done. This distinction has a historical origin: the earliest brazes were based on alloys of copper, while solders were based on alloys of tin (see the introductory section “History: Origins of Brazes and Brazing” in this volume and the similar historical summary on solders and soldering in the companion volume *Principles of Soldering*).

The type of metallurgical reaction that occurs between a molten filler metal and parent metal is sometimes used to differentiate brazing from soldering. Brazes mostly alloy with the parent materials to form solid solutions, which are mixtures of the constituents on an atomic scale. By contrast, solders usually react to form intermetallic phases, that is, compounds of the constituent elements that have different atomic arrangements from the elements in solid form.

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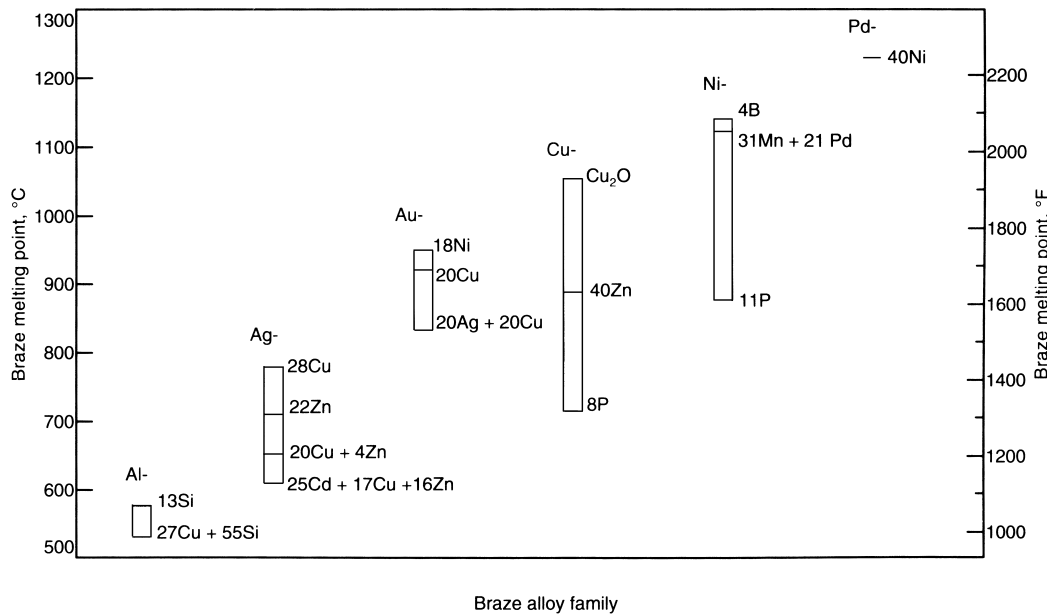
However, this distinction does not have universal validity. For example, silver-copper-phosphorous brazes react with steels to form the interfacial phase of  $Fe_3P$  in a similar manner to the reaction of tin-base solders with iron and steels to form  $FeSn_2$ . As for the temperature convention used to differentiate brazes from solders, there exist brazes for aluminum that melt below  $450\text{ }^\circ\text{C}$  ( $840\text{ }^\circ\text{F}$ ) and gold-indium solders above this temperature.

Brazing and soldering involve essentially the same bonding mechanism: that is, reaction with the parent material, usually alloying, so as to form metallic bonds at the interface. In both situations, good wetting promotes the formation of fillets that serve to enhance the strength of the joints. Similar processing conditions are required and the physical properties of both classes of filler metal are fairly comparable, provided the same homologous temperature (the temperature at which the properties are measured as a fraction of the melting temperature, expressed in degrees Kelvin) is used for the comparison.

The perpetuation of the distinction of brazes from solders based on the temperature convention of a  $450\text{ }^\circ\text{C}$  ( $840\text{ }^\circ\text{F}$ ) demarcation has arisen from the significant gap that exists between the melting points of available brazes and solder alloys. The highest melting point commercially

produced solder is Au-3Si that melts at  $363\text{ }^\circ\text{C}$  ( $685\text{ }^\circ\text{F}$ ), and the lowest temperature standard braze is the Al-10Si-4Cu alloy, which melts at  $524\text{ }^\circ\text{C}$  ( $975\text{ }^\circ\text{F}$ ) but, being a noneutectic alloy, is fully liquid only above  $585\text{ }^\circ\text{C}$  ( $1085\text{ }^\circ\text{F}$ ). Eutectic alloys are defined in Chapter 2, section 2.3. For now, it shall suffice to state that eutectic alloys are akin to pure metals in melting and freezing at a unique temperature. The temperature ranges of the principal braze and solder alloy families are shown in Fig. 1.3 and 1.4, respectively.

For most purposes, the temperature gap between brazes and solders is substantially wider than  $160\text{ }^\circ\text{C}$  ( $290\text{ }^\circ\text{F}$ ). This is because the gold-base solders are very expensive and are largely limited in use to high added-value manufacturing applications in the electronics and photonics industries. Removing the high-gold-content alloys from consideration, the highest melting point solders are the lead-rich alloys, which melt at about  $300\text{ }^\circ\text{C}$  ( $570\text{ }^\circ\text{F}$ ). On the other hand, the lowest melting point brazes that are used commercially in significant quantities are the reasonably ductile aluminum-silicon-base alloys, which melt at  $577\text{ }^\circ\text{C}$  ( $1071\text{ }^\circ\text{F}$ ). However, these have limited compatibility with many components and “low” melting point brazes are generally considered to be silver-base alloys that melt at about  $600\text{ }^\circ\text{C}$  ( $1112\text{ }^\circ\text{F}$ ). The practical



**Fig. 1.3** Principal braze alloy families and their melting ranges

gap in temperature between brazes and solders is therefore closer to 300 °C (540 °F).

The dearth of filler metals with melting points in the range 300 to 600 °C (570 to 1112 °F) is not necessarily a handicap. Techniques are available for making joints using molten filler metals with effective melting points in this temperature range. Transient-liquid-phase diffusion bonding (otherwise known as *diffusion soldering* when carried out below 450 °C, or 840 °F), or *diffusion brazing* when this temperature threshold is exceeded) is one such example and is discussed in Chapter 6 of this volume and in Chapter 5, section 5.9 of the companion volume *Principles of Soldering*.

From the “maps” of brazes and solders in Fig. 1.3 and 1.4, it might appear that there are far fewer brazes than solders. In fact, the contrary is true. The alloys that are specifically indicated in these figures are mostly eutectic compositions or those characterized by minimum melting ranges. Most commercially used solders are included because these solders are almost all of (different) eutectic composition, but whole families of brazes have been omitted because there is no eutectic in the alloy system. Instead, these particular alloys exhibit complete intersolubility so that a continuum of alloy compositions exists that are suitable as brazes. Examples are the copper-nickel, silver-gold, silver-palladium, and silver-gold-palladium alloys. Alloys in such sys-

tems melt over a temperature range that varies with the composition.

Solders are usually referred to directly by composition in weight percentage, e.g., Pb-63Sn. Brazes are often denoted by commercial (or common) names. Some of these are coded such that they indicate the principal constituents. Some examples are listed in Table 1.1.

Because more thermal activation energy is present, the higher process temperatures needed to make a brazed joint have important consequences:

- More extensive metallurgical reaction between the filler metal and the substrate. Solders typically do not dissolve more than a few microns of the component surfaces, whereas brazes often dissolve tens of microns. Larger changes in the composition of the filler metal therefore occur during brazing, which in turn significantly affects the fluidity of and wetting by the molten filler as well as the properties of the joint.
- Greater reactivity with the atmosphere surrounding the workpiece. All other factors being equal, brazes are less tolerant to oxidizing atmospheres than solders but, for the same reasons, are also better suited to cleaning by reducing atmospheres. When joints are made in air with the aid of a flux, the greater reactivity of brazes means that a

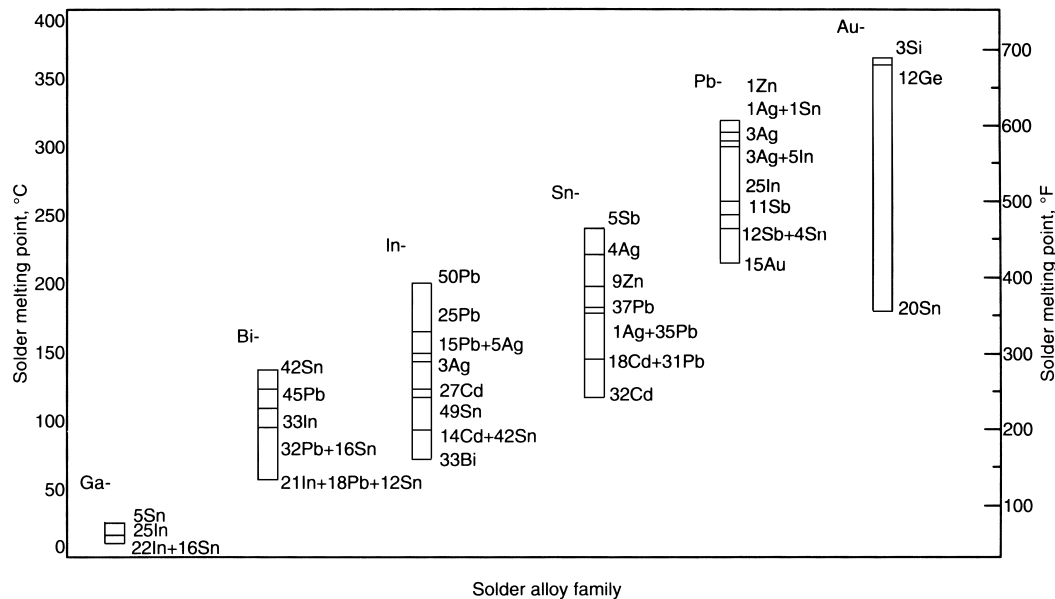


Fig. 1.4 Principal solder alloy families and their melting ranges

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higher ratio of flux to filler metal is generally required. In consequence, flux-cored solders are adequate for use in air, while brazing rods intended for use in ambient atmosphere must be provided with a higher volume of flux, achieved by an external coating on the braze preform. Fluxes are discussed in Chapter 3, section 3.2.

Several general features distinguish the majority of common brazes from solders:

- Most brazes possess mutual solid solubility between their constituents and are therefore offered with a wide range of compositions and melting ranges.
- Most commercial solders, by comparison, are of eutectic composition because there is usually a need to minimize the processing temperature while maintaining reasonable fluidity of the molten filler. Also, solders are generally soft, even at room temperature, and must be conferred with optimum mechanical properties; generally, these are achieved by having a fine-grained microstructure, which is a characteristic feature of a true eutectic alloy. The low degree of intersolubility and the propensity to form intermetallic compounds possessed by solder alloys is related to their low melting-point constituent elements, principally tin and indium, having a noncubic crystal symmetry.
- Brazes tend to be used at temperatures that are usually below half their melting point in degrees Kelvin. The principal failure modes of brazed joints are traditional metallurgical processes such as fatigue, stress overload, and corrosion. Solders find application at temperatures at a fraction of between 50 and 90% of their melting point in degrees Kelvin, under strain levels that often exceed 10%. Under these conditions, the alloys are not metallurgically stable and the joint microstructure tends to change with time.
- Brazes are predominantly used for structural applications, while the major use of solders is for making electrical connections in electronic circuits.

These points are discussed in further detail in Chapters 2 and 3 and reference should also be made to the companion volume *Principles of Soldering*. Notwithstanding the differences, brazes and solders operate on similar principles, and hence the frequent use of the collective term *filler metal* throughout this book and the com-

panion volume *Principles of Soldering* has some justification.

### 1.1.7 Pressure Welding, Friction Welding, and Diffusion Bonding

Solid-state joining methods are not new and examples of gold-base artifacts fabricated using pressure welds have been dated to between 1400 and 1000 BC [Tylecote 1968]. A gold ribbon used as a torch or neck ornament, found in a Celtic grave, was joined by the same method. Other ancient examples of welding from Egypt and the Black Sea region are cited by Tylecote [1967]. Although more recent interest in welding has been almost totally dominated by fusion welding processes, pressure welding, friction welding, and diffusion bonding continue to satisfy niche applications because of the unique combination of process and joint parameters they offer. Among the principal advantages of these nonfusion welding processes are:

- Melting of the components either does not occur or is very slight and highly localized so that changes to their microstructure are minor.
- Because there is very little alloying between components joined in these processes, formation of brittle intermetallic compounds is minimized so that a wider range of materials are amenable to joining by nonfusion welding than by fusion welding.

Some solid state joining procedures are a combination of pressure welding, friction welding, and diffusion bonding, as evidenced by the fundamental characteristics of each.

**Table 1.1 Examples of brazing alloys with commercial (now common) names that indicate the principal constituents**

The name may be augmented by a number if there are several brazes in the family in which the proportion of one element varies while the ratio of the other constituents is largely constant.

Commercial/common name	Typical composition
Cusil	Ag-28Cu
Cusiltin 5	Ag-27Cu-5Sn
Gapsil	Ag-9Ga-9Pd
Incuro 60	Au-37Cu-3In
Nicuman 23	Cu-23.5Mn-9Ni
Palco	Pd-35Co
Palcusil 10	Ag-32Cu-10Pd
Palnicusil	Ag-22.5Pd-18.9Cu-10Ni
Silcoro 60	Au-20Ag-20Cu
Ticusil	Ag-26.7Cu-4.5Ti

### 1.1.7.1 Pressure Welding

Pressure welding utilizes pressure to rupture surface films at the joint interface and also to extrude virgin parent metal between islands of surface contamination so that metallic bonding can take place. Thus, the process is characterized by high pressures, applied for short periods of time, on metals that may be either cold or hot. By necessity, bulk plastic deformation of the metals will occur. The pressure can be exerted through the application of a uniaxial force, alternatively isostatically, or by rolling, or explosively. Of these, explosion welding is the most “exotic” form of pressure welding; controlled detonation is used to force metal workpieces together under a rapid impulse. During this event, air between the parts is expelled in the form of a supersonic jet, which strips away surface oxides and causes localized heating, to promote bonding. The deformation at high strain rate that results from the impact of the components supplies additional heating in explosion welding. The different types of pressure welding are succinctly described by Messler [1999]. Possibly the most common examples of pressure welding that are pertinent to brazing are butt-welding to join lengths of wires, roll-bonding, and indentation welding.

In pressure welding, it is generally accepted that bond formation is controlled by the extent of deformation of the faying surfaces. The term *threshold deformation* is used extensively in the literature on this subject and is defined as the minimum deformation needed to achieve any bonding, although the strength of a bond at this level of deformation is generally much less than that of the parent metal (Fig. 1.5). The pressure that must be exerted to achieve flow by a ductile member between two effectively rigid components increases with the width-to-thickness ratio of the interface. In accordance with the von Mises criterion, the pressure is  $(2/\sqrt{3})\sigma_s$  for a width-to-thickness ratio of 1:1, and nearly six times this value for a ratio of 20:1, where  $\sigma_s$  is the yield stress of the ductile member. Consequently it is preferable that pressure welded joints are small and radially symmetric.

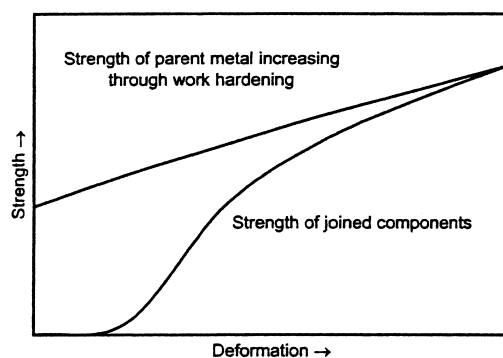
The bonding process can be described as involving four consecutive stages:

- Removal of surface contamination and breakup of brittle surface layers, in particular, oxides. This is frequently assisted by mechanically abrading the surface immediately prior to bonding. Adsorbed water is believed

to be the main surface contaminant and responsible for preventing bonding if the plastic deformation is less than 8%. Typically, 40% deformation is required to affect a sound joint when bonding base metals in atmospheres other than vacuum.

- Establishing physical contact between regions of uncontaminated metal as virgin metal extrudes between gaps in the ruptured surface films
- Activation of contacting atoms to form a metallic bond. The contact area determines the extent of bonding.
- Subsequent atom rearrangement as a consequence of post-weld heat treatment and/or stress relaxation

Pressure welding is particularly effective when joining dissimilar metals. For good weldability, the softer metal of the two abutting components should have the more brittle and stronger oxide film and vice versa. The hard oxide layer on the softer metal component can then promote and assist in the breakup of the surface layers on the harder metal but is itself easily ruptured by yielding of the metal supporting it. For example, the oxide on aluminum fulfills the requirements of hardness in relation to the oxides of most other metals, while the metal itself is relatively soft. Therefore, pressure welding of aluminum to harder metals occurs at lower deformations than when autogenously welded to itself. Also, the different deformation characteristics of dissimilar metals may result in interfacial movement that will enhance bonding com-



**Fig. 1.5** The strength of pressure-welded joints as a function of the deformation induced during the bonding process. No joining occurs below the threshold deformation level. With increasing deformation the joint strength also increases eventually up to that of the parent materials. Note that the joining process modifies the properties of the parent material as it will work-harden when mechanically deformed.

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pared with autogenous welding. The use of pressure welding to fabricate ductile preforms of brittle alloys, by partitioning of their constituents, is discussed further in Chapter 4, section 4.1.5.

### 1.1.7.2 Friction Welding

Friction welding is a thermally activated process in which mechanical energy is converted into heat at the interface between two impacting parts through their rapid, relative movement. Metal contact is achieved under the combination of pressure and rubbing together of the parts, which generates the heat of the process [Elmer and Kautz 1993; Messler 1999]. Material transport occurs through plastic deformation of the parts and thermally activated diffusion.

Frictional welding processes have proved difficult to model quantitatively, although they are fairly well understood at a qualitative level. The quality of a friction weld depends on five conditions:

- The pressure applied to the area forming the joint
- The relative velocity of the impacting surfaces
- The temperature at the interface
- Specific bulk material characteristics
- Condition of the surfaces to be joined together

The first three parameters are self-evident, being also common to other nonfusion welding processes, relating to pressure and temperature. The relative velocity of the impacting surfaces relates to the kinetic energy available for conversion to heat at the interface. The relevant bulk material characteristics involve greater complexity. However, from a pragmatic point of view, intrinsic property criteria that favor good friction welds between materials are:

- The materials have good forging characteristics
- The materials generate sufficient frictional resistance when rubbed together

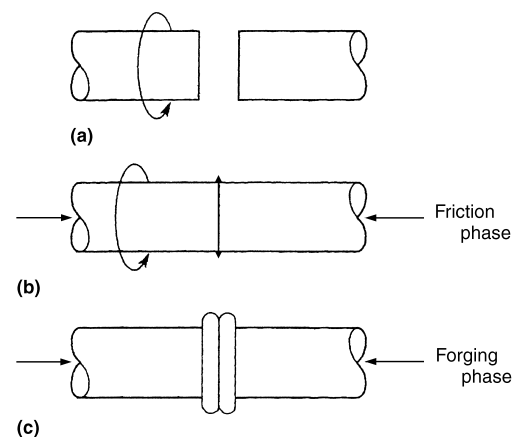
The first criterion excludes pairs of brittle materials, such as ceramics; cemented carbides; and hard, brittle materials in general, although it is occasionally possible to friction weld a ductile material to a hard material. The second criterion excludes materials that contain constituents that provide dry lubrication, such as cast iron and other graphite-containing alloys. Lead-bearing

bronzes are also unsuitable candidates for friction welding.

The relative movement most commonly involves:

- Rotation
- Angular or linear reciprocation
- Ultrasonic agitation
- Frictional stirring

Rotational friction welding equipment operates by direct drive or inertia drive. The first of these arrangements makes use of a motor running at constant speed to rotate one of the parts as it is driven into contact with the second, stationary part. The resulting friction and abrasion heats up the two surfaces (the friction phase), and a point is reached when the rotation is stopped and pressure is applied to join the parts together (the forging phase) (Fig. 1.6). The conditions used for the process cycle need to be optimized for the material combinations and dimensions of the parts. In inertia-drive friction welding, energy stored in a flywheel is imparted to the joint. Axial pressure is applied to force the part connected to the freely rotating flywheel against the stationary part, and this pressure is maintained until the welding operation is completed. Here, the moment of inertia of the flywheel and its initial speed are two important parameters of the process because they govern the energy available to the joining process. Typical spindle speeds in rotational friction welding are



**Fig. 1.6** Schematic showing fundamental steps in the frictional welding process (involving rotational movement). (a) One part or workpiece is rotated and the other part is held stationary. (b) Both parts are brought together, and axial stress is applied to begin frictional welding. (c) Rotation is stopped and the welding operation is completed. Source: Elmer and Kautz [1993]

in the range 1000 to 10,000 rpm, and the total process time is under 3 s, making this process relatively fast. Other procedures for frictional welding by rotation and other means such as friction stir welding are described in the literature [Messler 1999].

Similar materials that have been joined by friction welding, and reported in the literature, include low-alloy steels, austenitic stainless steels, and various aluminum and titanium alloys. This nonfusion welding technique has also proved successful for joining copper, tool steels, nickel alloys, and austenitic stainless steels to low-alloy steels, aluminum to austenitic stainless steel, and copper to aluminum alloys. It has also been possible to join high-carbon steel to low-alloy steel by friction welding [Elmer and Kautz 1993]. However, when joining dissimilar materials together, the quality of the joint is more sensitive to surface preparation of the joint surfaces than for friction welds made to similar materials. This is particularly the case where aluminum and its alloys constitute one of the dissimilar materials. Then, the alumina on the surface of the former tends to attract contaminants such as water and hydrocarbons, which results in mechanical weakness at the interface.

### 1.1.7.3 Diffusion Bonding

Diffusion bonding relies on a combination of temperature, pressure, and time to remove voids from the free interfaces between two abutting metal parts [Messler 1999]. Fundamentally, the process is defined as one in which no plastic deformation of the components being joined takes place, although it is normal to apply some pressure to ensure that the nominally flat faying surfaces are indeed in intimate contact. Typically, diffusion bonding requires process times of up to several hours at temperatures that may be as high as two-thirds of the melting point of the least thermally stable metal in the bonded couple. The use of long times at relatively high temperatures necessitates some form of atmosphere control to preserve surface cleanliness. Soft (roughing) vacuum and controlled atmospheres are equally suitable.

Since diffusion processes are the main mechanisms for bonding by this process, with no means for the physical displacement of any intervening nonmetallic surface films, two related requirements need to be satisfied. The first of these is that these films must be prevented from constituting a barrier to atom migration. Sec-

ondly, in bimetallic or higher order systems, the formation of intermetallic compounds and porosity resulting from an imbalance of the diffusion rate of different atomic species (Kirkendall porosity) must be controlled. Table 1.2 presents some of the better-known direct diffusion bonding combinations of metals and metalloids.

In a simplified model of diffusion bonding, it is assumed that the process occurs in three sequential stages [Messler 1999]:

- Contact between asperities in the abutting or overlapping parts, i.e. intermittent contact. The application of pressure causes the asperities to deform plastically, resulting in the formation of metallic interfaces between the parts in these contact regions.
- Under the combined effect of pressure and temperature, migration of grain boundaries and of material occurs through creep, and gaps between the abutting parts are progressively reduced to leave isolated pores.
- Surface and volume diffusion of metallic constituents occurs and the pores are eliminated.

In reality, one or more of these mechanisms is dominant and they may operate in parallel rather than sequentially. Each mechanism results in material (or void) transport so that the surface energy associated with the interface is progressively reduced as joining proceeds.

A detailed theoretical treatment of solid-state diffusion bonding is provided by Hill and Wallach [1989]. In practice, the extent of bonding and the rate at which it is achieved is governed both by materials properties (such as surface, grain boundary and volume diffusion coefficients, creep and yield strength, etc.) and process parameters of which the four main variables are:

- *Pressure:* Adequate pressure is required to achieve contact on an atomic scale by localized deformation of asperities on the nominally flat surfaces being joined and also to allow creep mechanisms to contribute to bonding.
- *Temperature:* Thermal energy promotes faster bonding because plastic deformation, creep, and all diffusion mechanisms are temperature dependent. Typically, temperatures around  $0.7 T_m$  are used, where  $T_m$  is the absolute melting temperature of the lowest melting point component, in order to decrease the yield stress of the metals and en-

**Table 1.2 Matrix of metals and metalloids that can be diffusion bonded**

X indicates potentially workable combinations

	Ag	Al	Au	Be	Cr	Co	Cu	Fe	Nb	Mg	Mo	Ni	Pd	Pt	Ta	Ti	U	V	W	Stainless steel	Cast iron	Carbides	Graphite
Ag	X			X			X									X				X			
Al	X	X		X			X									X				X			
Au			X	X			X													X			
Be			X	X			X												X				
Cr												X											
Co						X						X											
Cu	X	X		X			X		X		X	X				X				X			
Fe							X				X	X				X				X			
Nb							X		X		X	X			X					X		X	
Mg										X		X								X			
Mo							X		X		X	X								X		X	
Ni						X	X		X		X	X				X				X			
Pd							X				X	X								X			
Pt											X	X								X			
Ta											X	X			X					X			
Ti							X		X		X	X			X					X			X
U												X								X			
V												X								X			
W											X	X								X			
Stainless steel				X							X	X								X			
Cast iron								X				X								X			
Carbides									X			X										X	
Graphite																X							

Adapted from [Feature 1976]



sure that diffusion occurs at a useful rate. Heating rates are not critical.

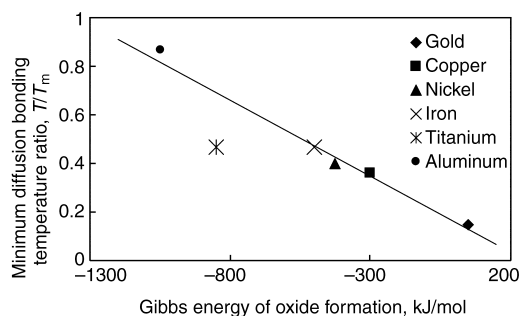
- **Time:** Creep and diffusion mechanisms are also strongly time dependent and there must be a sufficient interval afforded to allow for void closure by material transfer. As the temperature increases, so the time required for bonding decreases.
- **Surface condition:** The height and frequency of surface asperities defining the joint control the extent of initial surface contact and thus influence the bonding rate. Generally, flatter and more highly polished surfaces are easiest to bond. The removal of surface contamination and thick oxides prior to bonding is essential because these will either persist at the joint line or must be removed by solution in the parent material as bonding proceeds. It, therefore, takes higher relative temperatures and pressures to bond aluminum-base alloys than copper-base alloys or gold, as can be seen from Fig. 1.7.

Of these four process variables, temperature is the most important, followed in order by pressure, time, and surface condition. The trade-off between temperature and pressure can be seen in Fig. 1.8. Changing the process time by almost an order of magnitude affects the bonded area by less than 10%, which is within the limits of experimental error. The reason for the order of the variables is that temperature plus pressure cause creep, which operates at both the macro-level and microlevel to remove interfacial gaps. The combination of temperature and time promotes diffusion, which is usually a much slower mechanism for material transport. Without raising the temperature, the combination of pressure

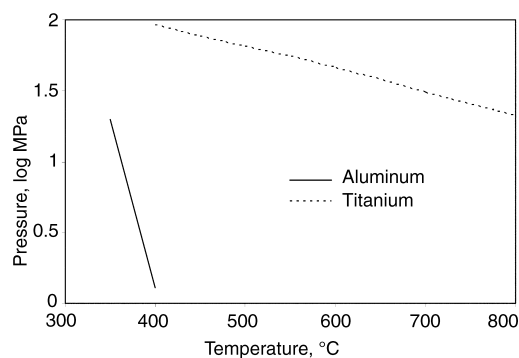
and time generally results in inelastic deformation, i.e., pressure welding. Reducing the surface roughness from several microns to one micron has little effect on the extent of bonding because this process in itself does not ensure significant metal-to-metal contact between the abutting parts—pressure is also needed. However, when the surface roughness is reduced further to an optically polished surface, the bond quality tends to improve measurably, with the other variables being unchanged.

Diffusion-bonded joints normally exhibit 80 to 100% of the strength of the parent materials. One perceived problem with diffusion bonding is the relatively long process cycle time, particularly in comparison with fusion welding. However, a complex welding operation may require several hours to prepare and jig the components, in which case diffusion bonding might offer overall advantages. Unlike most welding processes, the process time curve for diffusion bonding is almost flat in relation to the size of the joint because the process time is essentially independent of joint area, provided adequate compressive stress is applied.

Titanium and some of its alloys (Ti-6Al-4V, Ti-6Al-2Sn-2V, etc.) are of particular industrial interest because they can be diffusion bonded and super-plastically shaped in one processing operation (Fig. 1.9). This is made possible by the fact that, above temperatures of about 925 °C (1700 °F), titanium and certain of its alloys exhibit creep and superplasticity (both congenial for shaping and forming), and titanium can dissolve oxygen into its bulk as fast as a surface scale can form, thereby facilitating diffusion bonding. Indeed, at these temperatures, material



**Fig. 1.7** Relationship between the stability of metal oxides (in terms of the Gibbs free energy of formation) and the ratio of the process temperature ( $T$ ) to the melting point of the metal ( $T_m$ )



**Fig. 1.8** Effect of temperature on the pressure necessary to produce good quality diffusion bonds in titanium and aluminum by diffusion bonding

## 14 / Principles of Brazing

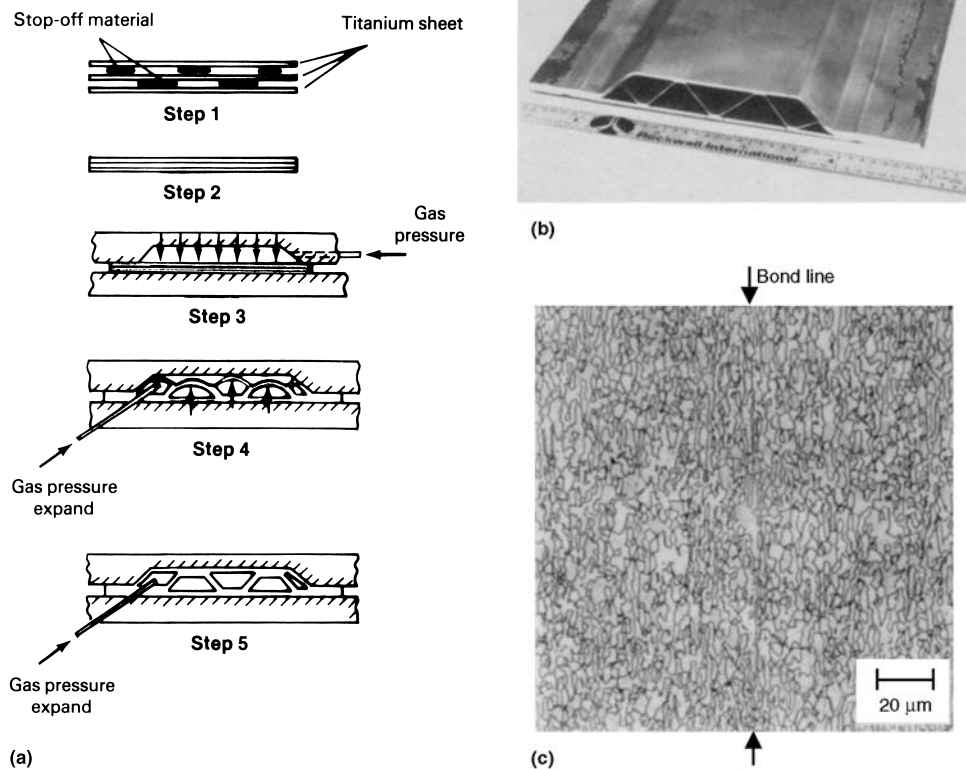
flow by creep or superplasticity occurs at such low applied stress that gas pressure at just a few MPa ( $\sim 1$  ksi) can be used to form and weld these materials in any chosen order. Diffusion bonding occurs so readily that inert oxides need to be applied to areas to prevent bonding where it is not required. This conjunction explains the anomalously low position of titanium in the representation of metals shown in Fig. 1.7.

Interlayers are often used to facilitate diffusion bonding dissimilar metals. For example, silver foil is used for bonding steel to titanium and nickel foil is often used to bond high-carbon steel to itself and other materials. A gold flash applied to a precleaned surface permits diffusion bonding of nickel and copper components. An obvious extension to this approach is making use of interlayers that melt, thereby increasing diffusion rates, helping to fill the joint gap and

to disrupt surface films. These benefits are characteristic of diffusion brazing and diffusion soldering processes. Diffusion brazing is discussed in Chapter 6 of this volume and diffusion soldering in Chapter 5, section 5.9 of the companion volume *Principles of Soldering*.

### 1.2 Key Parameters of Brazing

The quality of brazed joints depends strongly on the combination of filler and component materials and also on the processing conditions that are used. It is precisely for this reason that a sound understanding of the metallurgical changes accompanying the sequence of events that occur in making brazed joints is so vital for developing reliable joining processes.



**Fig. 1.9** Superplastic forming and diffusion bonding of titanium. (a) Schematic of the steps involved. (b) Typical three-sheet titanium alloy component formed superplastically and diffusion bonded. (c) Cross section through a diffusion-bonded joint in titanium alloy, made at 980 °C (1795 °F) for 2 h, under an applied pressure of 10 MPa (1.5 ksi), and in a vacuum of 0.1 mPa

Brazing technology has generally evolved in an empirical manner, largely by trial and error. Theoretical principles have helped to furnish insights, guidelines, and qualitative explanations for this technology but have rarely provided reliable data for use in the design of joining processes. The basic difficulty is that the real situation is highly complex because it brings into play a large number of variables, some of which may not be easy to recognize. Among the relevant factors are the condition of the solid surfaces (i.e., the nature of any oxides or other coatings, surface roughness, etc.); the temperature gradients that develop during the joining operation, not to mention the metallurgical reactions involving the filler and parent materials and also the chemical reactions with fluxes, where these are used; and the process atmosphere.

Key aspects of joining with brazes are the manner and extent of flow of the molten filler into the joint. These aspects are influenced by:

- Dimensions of the joint
- Surface condition of the components
- Spreading characteristics of the filler metal
- Alloying between the filler metal and components

The limitation of theory in accounting for observed behavior is well illustrated by the classical model of wetting and spreading. In this model, the surface of the solid is taken to be invariant as a liquid droplet spreads over it. That is, the reaction between the liquid and the solid components across their common interface is considered negligible. It is also assumed that the composition and other characteristics of the solid and liquid components, likewise, do not change with time. These assumptions are not generally valid, as will be shown. The model nevertheless does provide useful guidance so the principles on which it is founded, namely surface energy and surface tension, are worth reviewing.

### 1.2.1 Surface Energy and Surface Tension

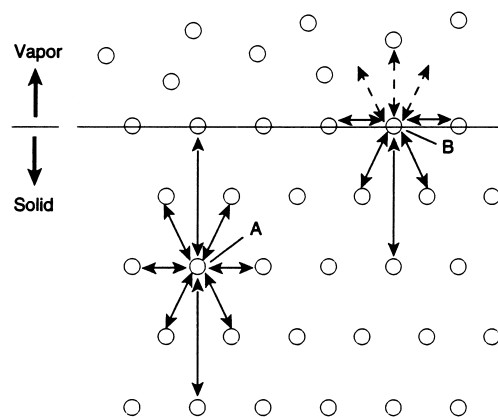
A simplified representation of the atomic structure of a solid close to one of its free surfaces is provided in Fig. 1.10. The atom at position A, in the bulk of the solid, has a balanced array of neighboring atoms, whereas atom B at the surface of the solid is lacking in neighbors above it, apart

from the occasional vapor molecule and, therefore, it has some unsaturated bonds.

The potential energy of atoms at the free surface, such as B, is higher than the energy of atoms within the bulk of the solid, such as A, by the energy of the unsaturated bonds. The aggregate of this excess energy that is possessed by atoms in the vicinity of the free surface constitutes the surface energy of the solid. In a similar manner, a liquid also possesses a surface energy, which is directly manifested in the tendency to draw up into drops. If small, the droplets are perfect spheres. Because a sphere has the smallest surface-to-volume ratio, it is clear that the surface energy of a liquid is greater than its volume energy. In the classical model, when a liquid spreads over a surface, the volume remains constant because evaporation and reaction with the substrate are excluded. Therefore, only surface energy changes must be considered.

The surface of a liquid acts like an elastic skin covering the volume; in other words, the surface is in a state of tension. The tensile force ( $F$ ), known as surface tension ( $\gamma$ ), is defined as the force acting at right angles to a line of unit length drawn in the surface. The relationship between surface tension and surface energy under specific conditions can be seen as follows.

Consider a liquid film of length  $L$  and width  $W$ . Apply a force  $F$  at a barrier AB, as shown in Fig. 1.11, parallel to one surface of the film, so as to extend the liquid film a distance  $x$ . The increase in area of the film is  $x \cdot L$ . The work done in obtaining this increase is the mathematical product of the force applied times the distance moved, or  $F \cdot x$ .



**Fig. 1.10** Simplified diagram of surface energies. Atom B, at the surface, has unsaturated bonds and thus a higher energy than atom A. This difference in energy is the origin of surface energy  $\gamma_{sv}$ .

The work done by the liquid film in opposing the increase in area, under isothermal conditions (constant temperature), is  $2 \cdot \gamma \cdot x \cdot L$ , where  $\gamma$  is the surface tension force acting on each surface at the prescribed temperature.

At a fixed temperature (under isothermal conditions):

$$Fx = 2\gamma xL$$

Rearranging,  $F/L = 2\gamma$  or  $F/L = \gamma$  for each surface.

Thus, surface energy is equivalent to surface tension under isothermal conditions. In the modern metric or International System of Units (SI), the unit of surface energy is joule per square meter ( $J/m^2$ ) and that of surface tension is newton per meter (N/m). Because these parameters are properties of an interface (e.g., between liquid and air), surface energy and tension must be defined with reference to the appropriate pair of materials that meet at the interface, and the test conditions, such as temperature and atmosphere, also must be specified.

Modeling of liquid droplets in contact with surfaces can be done with a program called "Surface Evolver" [Brakke 2003]. A search of the World Wide Web using this as the keyword should identify a site from which the latest version of the software can be obtained.

### 1.2.2 Wetting and Contact Angle

The classical model of wetting is based on the behavior of a liquid drop on a solid with a flat surface, which is rigid and is inert with respect to the liquid material. Accordingly, the liquid will spread over a solid surface until the three surface tensions—between the liquid droplet

and the solid substrate, the liquid droplet and the atmosphere, and the substrate and the atmosphere—are in balance as shown in Fig. 1.12.

According to the balance of forces:

$$\gamma_{SL} = \gamma_{SV} - \gamma_{LV}\cos\theta \quad (\text{Eq 1.1})$$

where,  $\gamma_{SL}$  is the surface tension between the solid and liquid,  $\gamma_{LV}$  is the surface tension between the liquid and vapor,  $\gamma_{SV}$  is the surface tension between solid and vapor, and  $\theta$  is the contact angle of the liquid droplet on the solid surface.

Equation 1.1, known as the wetting or Young's equation, shows that  $\theta < 90^\circ$  corresponds to the condition  $\gamma_{SV} > \gamma_{SL}$ . This imbalance in surface tension (i.e., surface energy) provides the driving force for the spreading of liquid over the solid surface and diminution of the unwetted surface area.

The contact angle  $\theta$  provides a measure of the quality of wetting. Thus, if  $90^\circ < \theta < 180^\circ$ , some wetting is said to occur, but a liquid droplet will not spread on the surface with which it is in contact. On the other hand, if  $\theta < 90^\circ$ , a liquid droplet will wet the substrate and also spread over an area defined by the contact angle  $\theta$ . Clearly, the area of spreading will increase with decreasing contact angle. For further details of the interrelationship between these two parameters, refer to Appendix A1.1. The relationship between contact angle spreading can be demonstrated by a numerical model. Figures 1.13(a), (b) and (c) show a droplet of constant volume wetted onto a planar surface at three different contact angles. The boundary between spreading and diminution of the wetted area occurs for  $\theta = 90^\circ$ .

Rewriting Eq 1.1 in terms of  $\cos\theta$ :

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

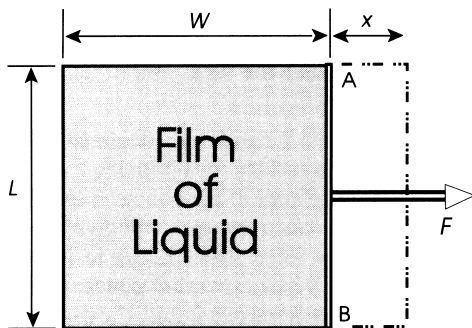


Fig. 1.11 Relationship between surface energy and surface tension

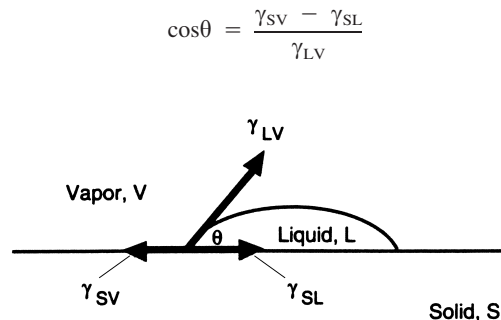
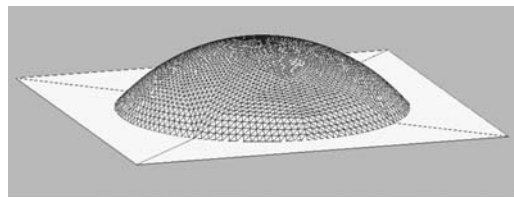


Fig. 1.12 Surface tension forces acting when a liquid droplet wets a solid surface, according to the classical model

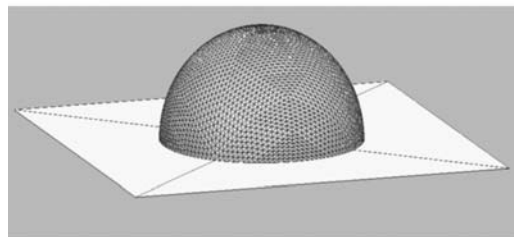
Thus, wetting is improved by decreasing  $\theta$ , i.e., as  $\cos\theta$  increases, i.e., as  $\theta$  approaches zero, and  $\cos\theta$  may be maximized by:

- Increasing  $\gamma_{SV}$
- Decreasing  $\gamma_{SL}$
- Decreasing  $\gamma_{LV}$

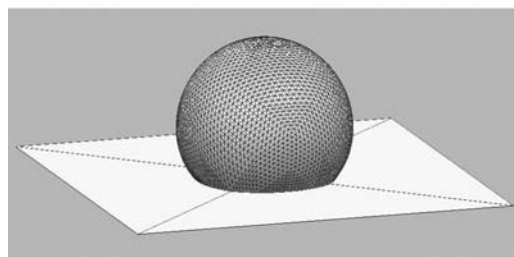
The term  $\gamma_{SV}$  can be maximized for a given solid by cleaning the surfaces. The presence of adsorbed material such as water vapor, dust, and other nonmetallic surface films on a metal surface markedly reduces  $\gamma_{SV}$  and correspondingly raises the contact angle  $\theta$ . Therefore, it is important in brazing operations that joint surfaces are clean and metallic, hence the need for fluxes or protective atmospheres to achieve and then sustain this condition. This is exemplified by molten silver spreading on a solid nickel surface at 970 °C (1780 °F). The intersolubility of nickel in molten silver is extremely low and so the



(a)



(b)



(c)

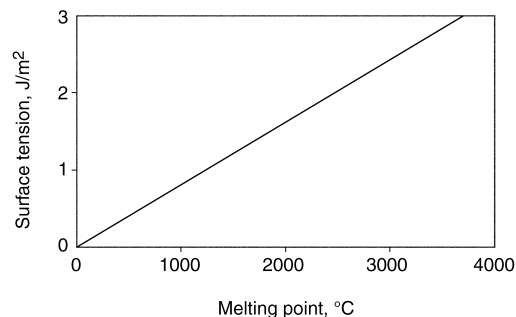
**Fig. 1.13** Numerical model of a liquid droplet of constant volume wetted on a plane at contact angles of (a) 45°, (b) 90°, and (c) 135°. Spreading occurs if the contact angle is less than 90°.

nickel may be considered as essentially unreactive toward silver. After 30 min of exposure to air, the contact angle of the molten droplet is 90°, whereas in a helium atmosphere it is close to 10°. The difference between these two cases is the degree of oxidation of the nickel substrate because silver oxide is unstable at typical brazing temperatures.

The term  $\gamma_{SL}$  is a constant at a fixed temperature for a particular solid-liquid combination, according to the classical model of wetting. This parameter can be reduced by changing the composition of the materials system, but this is not usually easy to achieve in practice because component materials are specified to fulfill certain functional requirements. Fortunately,  $\gamma_{SL}$  is temperature dependent, declining in the range 0.1 to 1%/K, and thereby providing a ready means of controlling spreading.

According to the classical model, the term  $\gamma_{LV}$  is constant at a fixed temperature and pressure for a particular liquid-vapor combination but can be varied by altering the composition of the atmosphere. Although the composition of the atmosphere used for the joining operation is known to affect the contact angle, in practice it is often easier to promote spreading (at constant temperature) by reducing the pressure of the atmosphere. This is one of the reasons for the popularity of vacuum-based joining processes, especially when chemical fluxes need to be excluded for various reasons.

In general, the relative magnitudes of the surface energies are  $\gamma_{SV} > \gamma_{SL} > \gamma_{LV}$ . The surface energies of pure metals correlate quite well with their melting points [Howe 1993]. This relationship, which is illustrated in Fig. 1.14, is to be expected because the temperature stability of metals reflects the strength of the bonds between adjacent atoms in the lattice, and the difference



**Fig. 1.14** Surface tension,  $\gamma_{LV}$ , of liquid elemental metals at their melting points [Howe 1993]

between the potential energy of atoms within the bulk of a solid metal and that of atoms of the same metal in the vapor is responsible for surface energy and tension. It is possible to calculate the surface tension of brazes from thermodynamic principles using data for the pure metals. To a first approximation it varies as an essentially linear relationship between the values for the constituent pure metals, with appropriate corrections for temperature. Thus, the surface tension of molten silver at its melting point is 0.903 N/m and molten copper at its melting point is 1.285 N/m, giving a calculated surface tension for silver-copper braze at the eutectic temperature of 0.967 N/m, which is reasonably close to the measured value of 0.952 N/m at 781 °C (1438 °F).

As noted previously, the contact angle,  $\theta$ , is an important measure of wetting, but from a thermodynamic perspective, the work of adhesion,  $W_a$ , is the appropriate parameter used to characterize the extent of wetting of a liquid (i.e., molten) braze on a solid substrate material and also provides an index of the mechanical adhesion.

The work of adhesion,  $W_a$ , may be expressed in terms of  $\gamma_{SV}$ ,  $\gamma_{SL}$ , and  $\gamma_{LV}$ , according to the Dupré equation:

$$W_a = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \quad (\text{Eq 1.2})$$

That is, the work of adhesion equals the work required to incrementally increase liquid-vapor and solid-vapor interfaces from a liquid-solid interface.

Combining Eq 1.1 and 1.2 yields the Young-Dupré equation:

$$W_a = \gamma_{LV} (1 + \cos\theta)$$

The Young-Dupré equation permits  $W_a$  to be calculated from values of  $\gamma_{LV}$  and  $\theta$ .

As just mentioned, the wetting equation (Eq 1.1) applies when the liquid is practically insoluble in the solid over which it spreads (i.e., the solubility is less than 0.1%). For binary metal systems where this condition is satisfied (e.g., molten silver on iron or on nickel), it has been shown that the wetting equation can be reduced to:

$$\cos\theta = 1 + k \left[ \frac{T_m^s}{T_m^l} - 1 \right]$$

where  $k$  is a constant equal to approximately 0.3,  $T_m^s$  is the melting point of the solid metal, and  $T_m^l$  is the melting point of the liquid metal. This expression has been verified experimentally [Eustathopoulos and Coudurier 1979]. Higher-order metal systems (ternary, quaternary, etc.) are considerably more complex, and the wetting equation cannot be truncated to such a simple form. A more sophisticated analysis of wetting that takes into account the influence of certain microscopic features, including the influence of local defects and van der Waal forces, is provided by de Gennes [1985]. However, this is still a continuum analysis and does not consider the local atomic environment. Indeed, it has been suggested that Young's equation is valid only under certain special cases and there are some difficulties with the theoretical definition of solid-surface tension [Xian 2000].

Another assumption of the classical model of wetting that has recently been challenged is the static equilibrium of surface tensions and surface energies. Recent studies examining the wetting of molten aluminum on sapphire ( $\alpha\text{-Al}_2\text{O}_3$ ) in ultrahigh vacuum have shown that the measured contact angle of the molten drop for these combinations declines from values above 90° to below 90° over time, regardless of temperature above the melting point of the metal involved [Levi and Kaplan 2003a; 2003b]. Experimental investigations, using a variety of surface analysis techniques, have revealed that wetting in these cases occurs through a nonequilibrium mechanism, characterized by dissolution of the sapphire at the boundary of the molten drop, or triple junction where the liquid, solid, and vapor are in contact with one another, and epitaxial deposition of sapphire at the liquid-solid interface beneath the drop.

Further academic endeavor is clearly needed to advance our understanding of wetting of molten metals. A review of recent theories of wetting is provided by Asthana and Sobczak [2000].

So far this chapter has considered filler spread over a single surface. In a joint there are always two facing surfaces. If both contact angles are less than 90°, the surface energies will give rise to a positive capillary force that will act to fill the joint. For a pair of vertical parallel plates  $D$  mm apart and partly immersed in a liquid, the capillary force per mm length of joint is equal to  $2\gamma_{LV} \cos\theta$ . Under this force, the liquid will rise to an equilibrium height  $h$  at which the capillary force balances the hydrostatic force (as shown schematically in Fig. 1.15, such that:

$$h = \frac{2\gamma_{LV} \cos\theta}{\rho \cdot g \cdot D} \quad (\text{Eq 1.3})$$

where  $\rho$  is the density of the liquid and  $g$  is the acceleration due to gravity.

As might be expected, experimental assessment of capillary rise of brazes reveals that capillary rise is less than predicted by theory, although the general principles of Eq 1.3 are substantiated. Meniscus rise is usually greatest for brazes that exhibit the lowest contact angle and surface tension and in the narrowest gaps. However, the correlation with gap width is generally weak, with other practical issues becoming manifest when the joint gap is narrow. (see Chapter 4, section 4.3.3.1 in this book).

The actual situation in brazing is much more complex than that represented by Eq 1.3 and the classical wetting model, as has already been shown. The irreversible nature of spreading and the time dependence of contact angle that is commonly observed are at variance with this equilibrium model. These and other departures from the classical model occur because the joining process almost invariably involves a degree of chemical reaction between the filler metal and the solid surface.

Reactions between a filler metal and the substrate often result in dissolution of the surface of the substrate; this process usually leads to a change in composition and sometimes the growth of new phases. These changes occur only because it is energetically favorable to do so. The energy of formation considered is the thermodynamic function known as the Gibbs free energy. This function and its properties are briefly explained in the Appendix A3.1.

Calculations made by Yost and Romig [1988] and Wang and Conrad [1995] have shown that the free energy of formation of new phases between a molten filler and a substrate is approximately two orders of magnitude larger than the energy release created by the surface energy imbalance during the advance of a spreading droplet, that is exclusively considered in the classical model. Therefore, in these cases, and probably more generally in brazing processes, the Gibbs free energy change that occurs on reaction by a filler with a substrate is demonstrably the dominant driving force for wetting. Empirical evidence for this is provided, for example, by the fact that the measured contact angle of molten germanium on silicon carbide at 1430 °C (2600 °F) is approximately 120°, whereas that of molten silicon on this ceramic at the same tempera-

ture is 38° [Li and Hausner 1991]. The substantial difference in these two contact angles cannot be accounted for by the difference in  $\gamma_{LV}$  in the wetting equation (Eq 1.1). It can be due only to the greater intersolubility of silicon with silicon carbide. This example, as that of molten aluminum and nickel on sapphire described previously, clearly demonstrates that the simple classical wetting equation cannot be relied on for a quantitative description of wetting, contact angle, or spreading. Another example is provided in Fig. 1.16. In this simple system of copper-silicon braze wetted on to vitreous carbon substrates, the final contact angle is insensitive to alloy composition, but the rate of attainment of steady-state wetting is directly related to the concentration of silicon, which is the active ingredient in the braze.

Modifications have been proposed to incorporate the Gibbs free energy change accompanying metallurgical reaction into the classical wetting equation by adding additional terms. In particular, the following equation has been developed for the contact angle in reactive wetting [Kritsalis, Coudurier, and Eustathopoulos 1991; Laurent, Chatain, and Eustathopoulos 1991]:

$$\cos\theta = \cos\theta^0 + \frac{\gamma_{SL} + \gamma_{SL}^0}{\gamma_{LV}} - \frac{\Delta G_r}{\gamma_{LV}} \quad (\text{Eq 1.4})$$

where  $\gamma_{SL}$  is the solid-liquid interfacial energy after reaction,  $\gamma_{SL}^0$  is the interfacial energy before reaction,  $\theta^0$  is the contact angle before reaction, and  $\Delta G_r$  is the Gibbs free energy of the reaction. Equation 1.4 is probably more of theo-

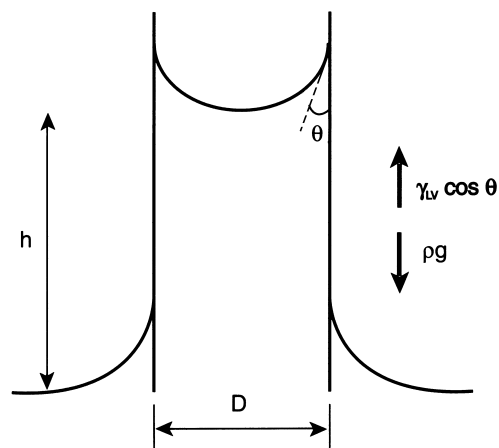


Fig. 1.15 Rise of a liquid between two parallel plates by capillary force

retical interest than practical value because its use presupposes knowledge not only of the Gibbs free energy of reaction but also values of the before-and-after contact angle, or the interfacial energy.

The effect of metallurgical interaction between a braze and the component (or parent) materials in promoting wetting is exploited in active brazes: the addition of a small fraction of a reactive metal such as titanium, hafnium, or zirconium to conventional brazes enables them to wet and spread over ceramic materials. In this instance, wetting of and reaction with the ceramic are inextricably linked. Activated filler alloys are discussed briefly in Chapter 4, section 4.1.2.2 and in detail in Chapter 7.

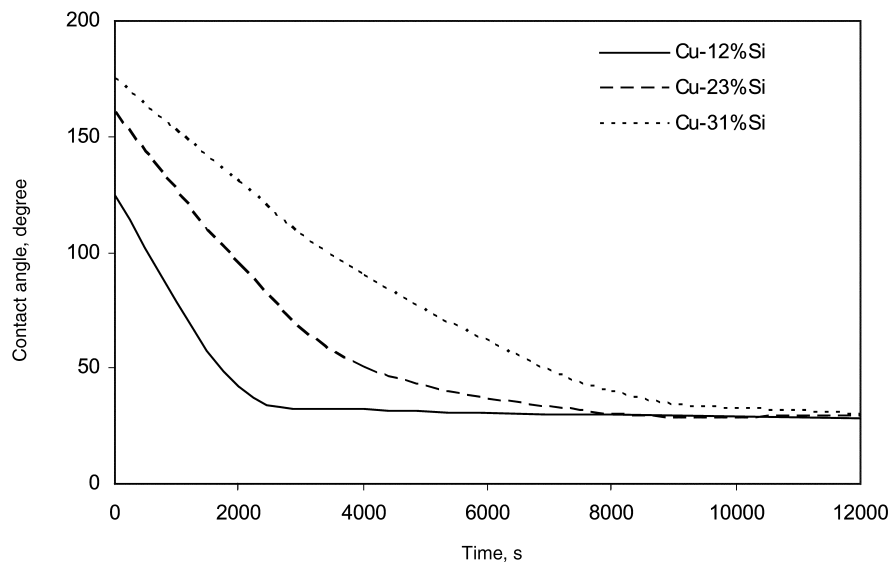
Although a low-contact angle is used as an index for judging the quality of wetting, there are situations where higher contact angles are preferred. This can be illustrated with reference to Fig. 1.17, which shows two joints, one between two component surfaces of unequal area and the other between component surfaces that correspond entirely. In the first case, a low-contact angle serves to form a gentle concave fillet, which enhances the mechanical properties of the joint. In the other configuration, a low-contact angle encourages the formation of a neck in the joint, which can be a source of weakness. A contact angle close to  $90^\circ$  and an interference fit joint gap will eliminate this problem.

A further point to be aware of in connection with wetting is that a situation can arise where the molten filler is physically prevented from achieving its equilibrium contact angle, as, for example, when a “stop-off” compound is used to confine the braze to a defined area. The enforced wetting angle is then not representative of the true wettability.

From a purely theoretical perspective, spreading driven by alloying should occur only when there is solution of an element of the liquid phase in the solid. Dissolution of an element from the solid phase into the liquid, or melt, requires the input of energy and hence this process cannot drive spreading. Rather, it has been observed that brazes spread preferentially along the exposed grain boundaries of substrates. Grain boundaries are disordered regions that have surface energy,  $\gamma_{SV}$ , up to 30% larger than the free surface, depending on the angular mismatch of adjacent grains.

### 1.2.3 Fluid Flow

The wetting equation does not provide information on the rate of wetting. Knowledge of the contact angle(s) enables the surface energy to be determined, assuming that the classical wetting model applies, and hence the force that acts to fill the joint gap with liquid may be estimated. The liquid will flow into the joint under this



**Fig. 1.16** Contact angle of copper-silicon brazes of different composition on vitreous carbon substrates demonstrating the effect of driving force of alloying on wetting rate and the dependence of the equilibrium wetting angle on the reaction product, which is the same in the three cases represented [Landry, Rado, and Eustathopoulos 1996]



force at a rate governed by its viscosity. Simple fluid flow theory assumes that:

- There is no interaction between the liquid and the solid surfaces with which it is in contact.
- All surfaces are smooth and perfectly clean.
- Flow is laminar, not turbulent.

For a detailed treatment of this subject, the reader is referred to the classic paper by Milner [1958]. Here, we shall merely quote the expression (given as Eq 8 in Milner's paper) for the volume rate of liquid flow,  $dV/dt$ , between a pair of horizontal parallel plates, length  $l$ , separated a distance  $D$ , under a pressure  $P$  per unit area transverse to the plates. The viscosity of the liquid is  $\eta$ .

$$\frac{dV}{dt} = \frac{PD^3}{12\eta l}$$

It is assumed that the liquid front will advance at a rate ( $dl/dt$ ) equal to the mean velocity of flow, that is:

$$\frac{dl}{dt} = \left(\frac{1}{D}\right)\left(\frac{dV}{dt}\right) = \frac{PD^2}{12\eta l}$$

From the wetting equation (Eq 1.1), under isothermal conditions the change in surface energy as a unit area of a surface becomes wetted by the liquid is:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta$$

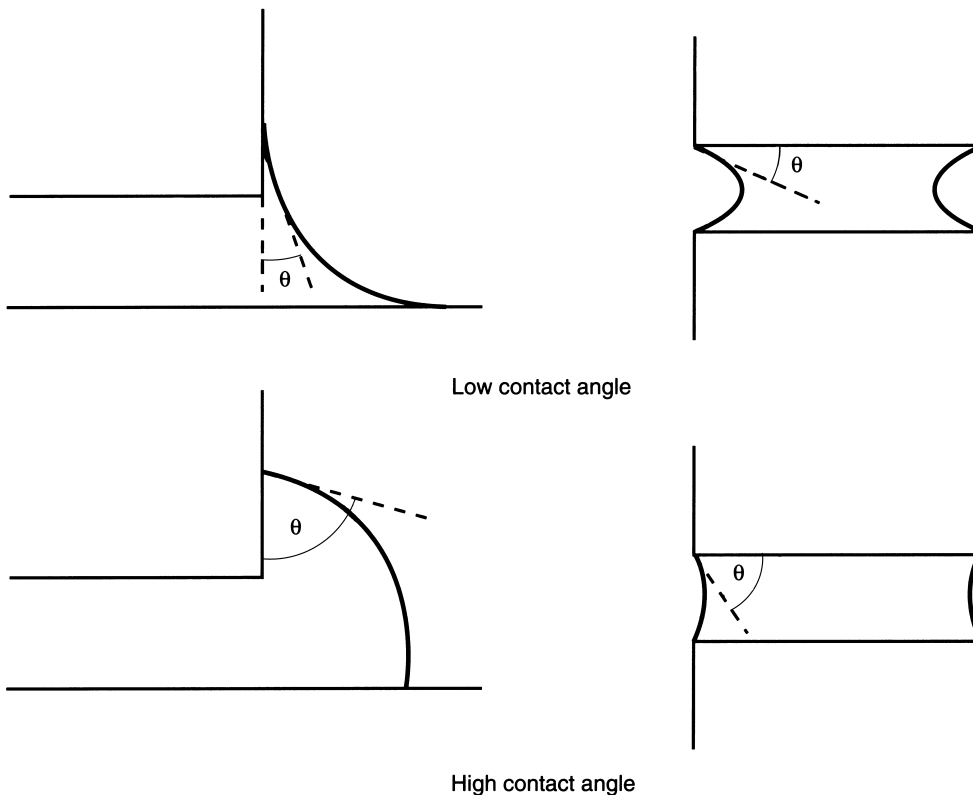
Therefore, the change in surface energy when the pair of parallel plates becomes wetted is:

$$2l (\gamma_{SV} - \gamma_{SL}) = 2l \gamma_{LV} \cos\theta$$

It follows that the force acting on the liquid to cause it to wet the plates is:

$$F = \frac{2l \gamma_{LV} \cos\theta}{l}$$

so that the pressure is:



**Fig. 1.17** Effect of contact angle on fillet formation and joint filling. Low contact angles tend to be preferred when external fillets can form. In other geometries, higher contact angles result in lower stress concentrations.

$$P = \frac{2\gamma_{LV} \cos\theta}{D}$$

and the velocity of flow of the liquid into the space between two parallel surfaces, of separation  $D$ , according to this simple model is given by:

$$\frac{dl}{dt} = \frac{\gamma_{LV} D \cos\theta}{6 \cdot \eta \cdot l} \quad (\text{Eq 1.5})$$

Equation 1.5 shows that the rate of liquid flow increases when:

- The liquid-vapor surface tension,  $\gamma_{LV}$ , increases.
- The joint gap,  $D$ , increases.
- The contact angle  $\theta$  decreases.
- Filler metal viscosity is low

Andrade [1952] derived an empirical formula relating viscosity, when molten, to the molecular weight of metals (in SI units):

$$\eta_m = \frac{1.65 \times 10^{-7} T_m^{0.5} A^{0.5}}{V^{2/3}}$$

where  $\eta_m$  is the viscosity at the melting point of the metal,  $T_m$  is the absolute melting point,  $V$  is the molar volume, and  $A$  is the atomic weight of the metal. By assuming limited solubility between the constituents in an alloy and applying the rule of mixtures, it is thereby possible to provide an estimate of the theoretical viscosity of a braze.

Rates of flow calculated from Eq 1.5 for molten brazes in joints 50  $\mu\text{m}$  (2000  $\mu\text{in.}$ ) wide are typically 0.3 to 0.7 m/s (1 to 2.3 ft/s). In other words, a joint 5 mm (0.2 in.) long will be filled in a time of the order of 0.01 s. This implies that joint filling by the molten braze occurs virtually instantaneously and that transient effects associated with fluid flow can generally be neglected in joining processes. It should be noted that, although the rate of filling is proportional to the joint gap  $D$ , the driving force for filling, according to the classical model, is inversely proportional to  $D$ ; that is, these two aspects of filling act in opposition.

This simple model needs to be modified in situations where interfacial reaction occurs while liquid spreading is proceeding. Models that have been tentatively proposed for this situation have been reviewed by Meier, Javernick, and Edwards [1999]. Currently, the lack of relevant data on reaction-rate kinetics, interfacial

energy before and after reaction, and diffusion hampers a more complete understanding of spreading of molten brazes, especially where interfacial reaction with solid components is significant. However, much can be learned from empirical observations, as shown in the following section.

### 1.2.4 Filler Spreading Characteristics

All molten filler metals do not have the same spreading characteristics, although, with few exceptions, the degree of spread over an “ideal” substrate increases as the temperature is raised and the environment is made more reducing. In this context, an “ideal” substrate, suitable for reference purposes, needs to be defined. This is understood to possess a perfectly clean metal surface, which is highly wettable by the braze under consideration, but with which it does not significantly alloy. Any alloying reactions will be highly specific to the combination of materials in question so that the substrate will lose its ideal characteristics. This is particularly true for brazes where extensive reaction with the substrate is the norm rather than the exception. Thus, while it is often possible to draw comparisons within an alloy family (e.g., McDonald 1989), it is difficult to obtain true comparative data between different families of brazing alloys.

Alloys with narrow melting ranges, ideally of eutectic composition, are often regarded as having the best spreading characteristics, and this is frequently one of the reasons cited for their selection in preference to filler metals with wide melting ranges. The superior spreading of brazes with small melting ranges, in comparison with those in the same alloy system, but having wide melting ranges, as frequently observed, can be explained by the different melting characteristics in the two cases. In the ideal case, a pure metal or alloy of eutectic composition melts instantly. Spreading of the molten alloy is then driven by interaction with the substrate [Ambrose, Nicholas, and Stoneham 1992]. In the case of a non-eutectic filler metal, wetting commences before the alloy is entirely molten and when its flow is relatively sluggish. By the time the alloy is completely molten, the filler will have partly alloyed with the substrate, and the driving force for spreading will have been diminished.

Whether the filler alloy has a narrow melting range is of much less importance to the phenomenon of spreading than the composition per se.

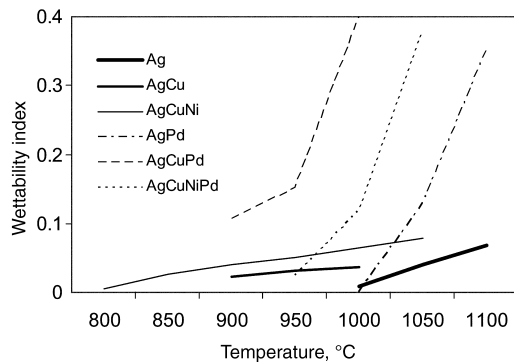
The spreading of a filler metal depends greatly on the elemental constituents present and the composition of the substrate. For example, Fig. 1.18 shows the spreading characteristics of a selection of alloys on stainless steel substrates, as a function of temperature. The data clearly show that the incorporation of palladium has a major beneficial effect, despite the associated widening of the melting range.

Although high fluidity of a filler metal is a desirable property when it is required to flow into the joint gap of a heated assembly by capillary action, it is not quite so important when the preferred method of applying the filler is to sandwich a thin foil preform between the components, which are then joined together in an appropriate heating cycle. For this type of configuration, a high degree of spreading is detrimental to joint filling, because then the filler tends to flow out of the joint. Placement of the filler metal and its influence on joint filling is discussed in Chapter 4, section 4.3.1.1.

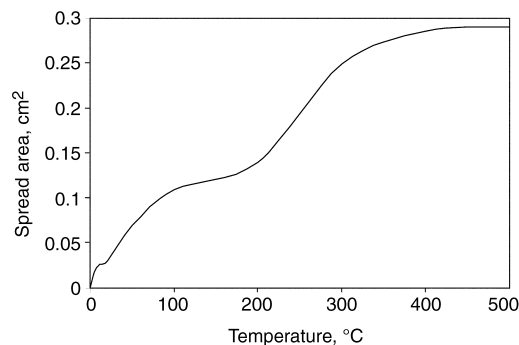
Detailed investigation reveals that even an ostensibly simple characteristic such as spreading exhibits somewhat complex behavior. Figure 1.19 shows the spread area of silver-copper braze on nickel at 820 °C (1510 °F) as a function of the wetting time [Weirauch, Jr., and Krafick 1996]. The results indicate that there are at least four distinct stages of wetting and spreading. During the first tens of seconds of melting, the braze forms a spherical cap and spreads rapidly with a corresponding decline in the contact angle. The contact angle then temporarily sta-

bilizes with the formation of a halo at the periphery of the braze pool. This region of the braze has a very different composition to the bulk and is formed by a selection of elements in the braze reacting preferentially with the substrate [Yunchen, Xiaoming, and Hongying 1992]. During this stage, the braze pool spreads by wetting up to an interface, demarcated by the halo. This situation persists for about 100 seconds. Thereafter, a further reduction in contact angle, accompanied by additional spreading, occurs. This stage is thought to be associated with a progressive alteration in the composition of the braze, which produces a sudden change in the phases formed in the halo at the edge of the pool of the molten braze. This, in turn, gives rise to a further reduction in the wetting angle. Finally, after many minutes, the contact angle reaches a settled value as the braze pool becomes saturated with the substrate metal, which is nickel in the reported case study [Weinrauch, Jr., and Krafick 1996]. The molten liquid then commences to freeze isothermally as the solidus temperature progressively increases, owing to the change of composition, caused by alloying with the substrate metal.

Depending on the braze/substrate combination, one or other of these four stages of interaction may be more dominant and visually obvious than the rest. Thus, while molten silver spreads readily on copper and forms an extensive halo, molten copper barely spreads at all on a titanium substrate but reacts strongly with it in the direction perpendicular to the interfacial surface. Molten aluminum wetted on copper represents a situation somewhere intermediate be-



**Fig. 1.18** Wettability index (defined as the product of the contact angle and spread area [Feduska 1959]) of silver-base brazes on 316L stainless steel, heated in vacuum for 5 min. Palladium additions clearly have a beneficial effect on wetting and spreading by the braze, despite widening of the melting range of the filler metal. Note: 316L stainless steel is sensitive to liquid metal embrittlement by copper-base brazing alloys. Adapted from Keller et al. [1990]



**Fig. 1.19** Spread area of 0.5 mg spheres silver-copper eutectic braze on a nickel substrate in a nitrogen-10% hydrogen atmosphere as a function of holding time at 820 °C (1500 °F). Four distinct stages are observed, demonstrating the complexity of the wetting process. [Weirauch, Jr., and Krafick 1996]

tween these extremes, spreading quite well, with penetration into the substrate being most pronounced where the braze and substrate are in contact for longest; i.e., the reaction zone extends outward from the center of the pool of molten braze.

Some attempt has been made to undertake a theoretical analysis of the kinetics of spreading of a molten metal over a wettable solid surface. The current theoretical approach considers the spreading of an inert sessile drop on a smooth and perfectly wetted substrate as a balance between surface energy driving it forward and viscosity, which acts to impede spreading [de Gennes 1985]. However, comparison of this somewhat reductive theoretical model with practical experience discloses that it contains a number of flaws, not least that measured flow rates are about four orders of magnitude slower than predicted by theory. These discrepancies may be ascribed largely to the added metallurgical and physical complexity of the wetting and spreading of a filler metal, as discussed previously, which are not adequately taken into account in this analytical model.

Nevertheless, the de Gennes model does predict some interesting dependencies of spreading. First, the initial spreading of molten filler metal is described by the imbalance between surface tension forces and viscous damping. This model also predicts a relative insensitivity of spreading to excess temperature in filler/substrate combinations where wetting is good, as can be seen in Fig. 1.18. Continued research in this area may eventually achieve a more complete mathematical description of wetting and spreading by filler metals that takes into account the physical and chemical states of the surface and also the situation where isothermal solidification occurs in the course of spreading and interalloying.

### 1.2.5 Surface Roughness of Components

The roughness of joint surfaces can have a significant effect on both the wetting and spreading behavior of a braze. It is well known that for each parent material there is an optimum surface roughness for maximizing the spreading of a filler metal. For example, when brazing aluminum alloys with the Al-12Si filler alloy in high vacuum and in the absence of fluxes, the best results in terms of spreading of the molten filler metal and fillet formation have been obtained when the surface of the components were pre-

pared by dry grinding with silicon carbide papers of between 400 and 600 grit size [Okamoto, Takemoto and Den 1976]. Table 1.3 indicates values of surface roughness that can be obtained by abrasion of copper by various means.

Surface roughness reduces the effective contact angle  $\theta^*$ , where  $\theta^*$  is related to  $\theta$ , the contact angle for a perfectly flat surface through the relation:

$$\cos\theta^* = r \cos\theta$$

where

$$r = \frac{\text{Actual area of rough surface}}{\text{Plan area}}$$

$R_a$  is the average roughness measured as the average deviation from the center line of the surface profile. In the equation, it is expressed as a ratio of surface areas.

At the same time, by producing a network of fine channels, the texturing may increase the capillary force acting between the filler and the component surfaces. Both phenomena will tend to aid spreading. A directionally orientated surface texture promotes preferential flow parallel to the channeling [Nicholas and Crispin 1986].

It is possible to show from surface energy calculations that if the instantaneous contact angle of the molten filler is less than the surface angle (i.e., the root angle of v-shaped valleys), then profuse wetting tends to occur along the valleys. This is a frequent observation and, indeed, represents a problem when brazing to rough machined surfaces in that the filler does not spread uniformly in all directions. Another factor that should be considered in connection with texturing is the extent of alloying between the filler and the parent material because the roughness will increase the interaction for a given area of spread. As wetting of the parent metals usually

**Table 1.3 Surface roughness ( $R_a$ ) of cold-rolled copper after sanding with wet silicon carbide paper or polishing with a colloidal suspension of alumina in water**

Abrasive	Nominal particle size, $\mu\text{m}$	$R_a$ obtained on cold-rolled copper, $\mu\text{m}$
80 grit	200	2.2
240 grit	63	0.95
400 grit	23	0.51
1200 grit	5	0.23
Polishing alumina	0.05	0.012

For comparison, copper surfaces on electronic component leads usually have an orientated  $R_a$  of approximately 0.1  $\mu\text{m}$  (4  $\mu\text{in.}$ ).

serves to increase the melting point and stifle spreading, a rough surface can prove to be detrimental.

### 1.2.6 Dissolution of Parent Materials and New Phase Formation

It is frequently observed that a filler metal will continue to spread beyond an initially wetted surface area over an extended period of time ( $>10$  s), which would not be expected from classical fluid flow theory. Clearly, classical expressions for fluid flow, exemplified by Eq 1.5, which assume that the solid substrate is inert toward the liquid braze, do not strictly apply in such cases. Indeed, this type of flow can usually be associated with solid-liquid interfacial reactions, which have been seen in section 1.2.4 to play a major role in the spreading behavior, but are neglected in the model described in Milner's paper [1958]. Where joint filling is sluggish because of reactions occurring between the filler and the solid surface, increasing the temperature to reduce the viscosity of the molten filler is unlikely to enhance filling because the reactions that are occurring transverse to the flow directions will accelerate [Tunca, Delamore, and Smith, 1990]. The alternative of widening the joint gap is not usually an option because this is likely to lead to a reduction in joint filling and/or joint strength, as discussed in Chapter 4, section 4.3.4. The solution then is to change the materials system; several means by which this can be achieved without changing the parent materials are described in Chapter 4, section 4.1.

Dissolution of a substrate in a braze and growth of intermetallic compounds, where these occur, both follow Arrhenius type rate relationships, represented by the expression:

$$\text{Rate} = \exp\left[\frac{-Q}{kT}\right]$$

where  $Q$  is an activation energy that characterizes the reaction taking place at temperature  $T$  (in degrees Kelvin) and  $k$  is the Boltzmann constant.

Interfacial reactions are important, not only in determining the flow characteristics of the filler and its wetting behavior, but also the properties of the resulting joints. Evidence of intersolubility between a molten filler and the parent materials is provided by erosion of the surfaces of the parent materials in the joint region and the formation of new phases at either interface be-

tween the parent materials and the molten filler or within the filler itself when it solidifies. The effects of dissolution of the parent materials and compound formation on joints are discussed in detail in Chapter 2, section 2.3.

The following expression describes the rate of dissolution of a solid metal in a molten metal [Weeks and Gurinsky 1958; Tunca, Delamore, and Smith 1990]:

$$\frac{dC}{dt} = \frac{K A (C_s - C)}{V} \quad (\text{Eq 1.6})$$

where  $C$  is the instantaneous concentration of the dissolved metal in the melt,  $C_s$  is the concentration limit of the dissolved metal in the melt at the temperature of interest,  $t$  is the time,  $K$  is the dissolution rate constant,  $A$  is the wetted surface area, and  $V$  is the volume of the melt. This equation is known as both the Nernst-Shchukarev and the Berthoud equation. In the integral form, Eq 1.6 becomes:

$$C = C_s \left[ 1 - \exp\left(\frac{-KA t}{V}\right) \right] \quad (\text{Eq 1.7})$$

assuming initial conditions of  $C = 0$  and  $t = 0$ .

Equation 1.7 reflects the fact that, in general, the concentration of dissolved metal in the molten filler increases in an inverse exponential manner with respect to time. That is, the dissolution rate is initially very fast but then slows as the concentration of the dissolved parent material tends toward its saturation limit (i.e., equilibrium), as shown in Fig. 1.20. Substituting measured values into Eq 1.7 shows that, for a brazed joint of typical geometry, the equilibrium condition is reached within seconds at the process temperature. Thus, it is possible to use an equilibrium phase diagram to predict the change in the composition of the filler metal that will occur in typical joining operations and the associated depth of erosion of the joint surfaces. Equilibrium phase diagrams and their use in brazing are considered more fully in Chapter 2, section 2.3.

In some materials systems, the product of reaction between a molten filler metal and the parent materials takes the form of a continuous layer of an intermetallic compound over the joint interface. Once this intermetallic layer is established, the rate of erosion greatly decreases because it is then governed by the rate at which atoms of the parent material can diffuse through the solid intermetallic compound. As a rough guide, solid-state diffusion processes are two

orders of magnitude slower than solid-liquid reactions, and thus continued dissolution of the parent materials effectively ceases within the timescales of typical joining processes. Inter-metallic growth will, however, continue throughout the life of the product, even if it is barely detectible. The practical implications of this phenomenon are discussed in Chapter 4, section 4.1.4.

### 1.2.7 Significance of the Joint Gap

The joint gap at the process temperature influences both the joint filling and the mechanical properties of the resulting joint. The relationship between joint dimensions and mechanical properties is discussed in Chapter 4, section 4.3. In summary, the thinner a joint is, the greater its load-bearing capability tends to be, until a limiting condition is reached when joint filling becomes unreliable.

Contact angle, surface tension, and viscosity all reduce with increasing temperature, making good joint filling in narrow joints more readily achievable as the joining temperature is raised above the melting point of the filler metal. On the other hand, spreading by the braze will generally decline as the temperature is raised on account of increasing interdiffusion between the braze and parent material, leading to premature solidification before joint filling is complete. Therefore, it is generally good practice not to exceed the liquidus temperature of the braze by more than about 50 °C (90 °F), particularly where joints of normal or narrow width (<100 μm, or 4 mils) are required.

A lower practical limit to the joint gap is imposed by three factors:

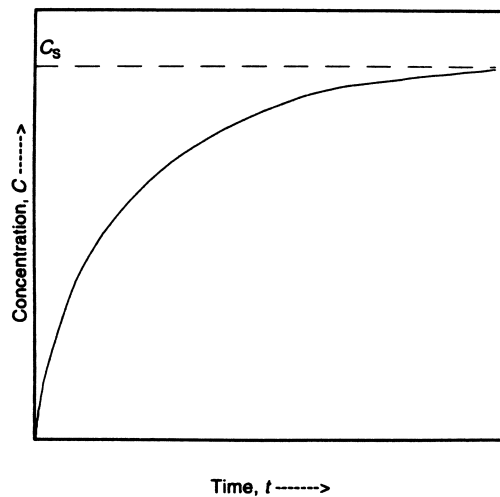
- *The need to provide a path for vapors to escape:* Vapors evolved within the joint and pockets of air must be allowed to escape if the formation of voids through gas entrapment is to be prevented (see Chapter 4, section 4.3.1.1). At the same time, any reducing agent needs to gain access to all joint surfaces and be present in sufficient concentration to work effectively. This requirement is not nearly as critical for brazing as it is for soldering. Especially for brazing carried out at temperatures above about 750 °C (1380 °F), the pressure exerted by pockets of vapor is usually high enough to result in their expulsion from a joint while the braze is molten (a consequence of the Gas Law), especially

if the geometry is planar and there are no reentrant features.

- *Reaction with the components:* The metallurgical reaction that occurs between a molten filler metal and the surfaces of the components can take one of two forms.
  - a. *The surface region of the workpiece has limited solubility in the molten braze:* This is the preferred situation. The dissolution of metal from the surface of the components can result in either compound formation at the interface, which may prevent further dissolution, or alloying with the filler, which will change its composition and hence its melting point.

On the whole, brazes usually exhibit extensive interalloying with the parent materials. This can be explained partly by the fact that most brazes are based on elements with crystal structures that are similar to most engineering metals and alloy metals. Consequently, solid solutions tend to form in preference to intermetallic compounds.

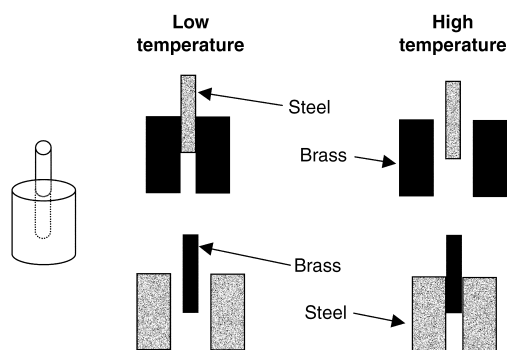
A reaction that depresses the melting point of the filler metal is desirable for narrow joints because the fluidity of the braze will be enhanced by such a reaction at a constant temperature. A reaction that raises the melting point of the filler metal will tend to increase its viscosity and



**Fig. 1.20** The concentration of a solid metal in a liquid metal wetted by it changes in an inverse exponential manner with respect to time and is limited by the saturation concentration of the solid constituent in the liquid at that temperature.

holds out the danger that the filler will solidify isothermally at the process temperature before it has filled the entire joint. Wider joints mitigate this effect because the alloying will tend to be diluted.

- b. *Dissolution of the filler in the parent metal:* In this situation, the volume of braze may shrink as the reaction progresses; therefore, a larger volume of filler metal accommodated in a wider joint gap is preferred. However, absorption of the filler is generally undesirable because its constituents will tend to penetrate into the parent materials, preferentially along grain boundaries, generally to the detriment of the mechanical properties of the assembly and sometimes resulting in embrittlement and/or hot shortness (sometimes also referred to as *liquid metal embrittlement*).
- *Control of the joint gap:* The width of the joint, i.e., the joint gap, should be predictable during the bonding cycle. The size of the gap will be influenced by the respective coefficients of thermal expansion of the components, and allowances need to be made for any differences. This is illustrated for tubular brazed joints between brass and steel members in Fig. 1.21. The coefficients of thermal expansion (CTEs) of a representative range of engineering materials at room temperature (25 °C, or 77 °F) are listed in Table 1.4. A joint gap that widens as the temperature is raised will cause the capillary forces to diminish, as noted in section 1.2.2. At the same time, the capillary forces are relied on to fill the joint with brazing alloy. This consideration is of added importance in relation to the



**Fig. 1.21** Effect of temperature on the joint clearance between tubular brass and steel components arising from the difference in their thermal expansion coefficients

widely used practice in brazing of drawing the filler into the joint from a preform placed adjacent to it.

An upper practical limit to the joint gap is determined by two factors:

- *Mechanical properties of the joint:* As the gap is increased, the mechanical properties of the braze declines progressively to those of the bulk filler metal, which are usually inferior to most structural materials. This aspect is discussed further in Chapter 4, section 4.3.3.1.
- *Joint filling requirements:* Because the capillary force decreases as the joint gap increases, this will place a practical upper limit on the joint gap. At the same time, a sufficient quantity of filler must be supplied to the joint to fill it entirely. Hydrostatic forces will promote the flow of low-viscosity filler metals out of wide gap joints.

The optimal balance of these factors is achieved when the joint gap is about 10 to 100 μm (400 to 4000 μin.) wide, depending on the type of reaction that occurs between the braze

**Table 1.4** Typical thermal expansivities of common engineering materials at normal ambient temperature

Material	Linear expansivity, 10 <sup>-6</sup> /K
<b>Polymers</b>	
Polymers, rubbers	150–300
Polymers, semicrystalline	100–200
Polymers, amorphous	50–100
<b>Metals</b>	
Zinc alloys	25–30
Aluminum alloys	20–23
Copper alloys	16–19
Stainless steels	15–17
Iron alloys	13–15
Nickel alloys	12–15
Cast irons	10–13
Titanium alloys	8–10
Tungsten/molybdenum alloys	4–7
Low expansion alloys (Fe-Ni-base)	1–5
Graphite	7–9
<b>Ceramics</b>	
Ceramics, glass	6–10
Ceramics, oxide	4–8
Ceramics, porcelain/clay	3–7
Ceramics, nitride/carbide	2–6
Diamond/silica/carbon fiber	– 1 to 1

The values given are representative of the most widely used materials, rather than provide absolute limits for the different classes listed. The thermal expansivity will depend not only on elemental composition but also on microstructure and temper. Composite materials can have expansivities that effectively range between those of the constituents and depend on the relative proportions of the matrix and reinforcement phases. To convert to customary units of 10<sup>-6</sup>/°F, multiply given values by 0.55556.

and the parent part, or component. This estimate is supported by theoretical calculations of capillary force and viscous drag of liquid flow (Fig. 1.22). A gap of this magnitude is usually readily achieved without resorting to expensive pre-machining operations. Generally, when components rest freely on one another and the assembly is heated until the filler is molten, the joint will tend to self-regulate to widths around 50 μm (2 mils), depending on the viscosity of the filler at the brazing temperature. Indeed, it has been demonstrated that, for a fixed combination of filler metal, component materials, and process conditions, the joint gap will tend to a fixed value specific for that combination. This value must be established by experiment. If there is insufficient brazing alloy to fill this gap, the joint will contain voids, or, if too much braze is made available, the excess will spill out and generate droplets on the free surfaces of the components [Bakulin, Shorshorov, and Shapiro 1992]. Where thinner or wider joints are required, it is necessary to insert spacers (such as wires) of the desired width between the components and, for thin joints, combine this measure with the application of a compressive loading on the joint during the bonding cycle to overcome the hydrostatic forces that will act to levitate the upper component.

Copper and silver are notable exceptions to this criteria governing the width of brazed joints. These metals possess the characteristic of exceptional fluidity, enabling the pure metals to be used as brazes to form exceedingly narrow (<1 μm, or 40 μin.) joints with steel components. Although copper and silver are soft and weak, the narrowness of the joints together with the high degree of joint filling that can be achieved and the negligible intersolubility with the parent material (i.e., steel), can result in joints that are stronger than the steel parts [Sloboda 1961]. The enhanced strength of extremely narrow, well-

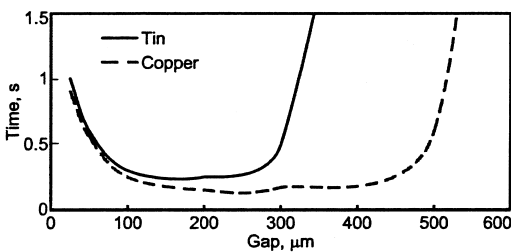


Fig. 1.22 Calculated time for molten tin and copper to flow up a perfectly wetted capillary [Nicholas 1989]

filled joints is explained in Chapter 4, section 4.3.3.1.

### 1.2.8 The Strength of Metals

The purpose of making brazed joints is usually to form a metallic bond between components. A fundamental question, therefore, is how strong is the interface between the parent material and the braze?

The cohesive strength of metals results from attractive forces between the constituent atoms. Normally, each atom will occupy a physical location where the net force upon it is zero. When the solid metal is strained by the application of an external load and the atoms move from their equilibrium positions, an opposing stress is set up in the crystal lattice of the metal. The attractive force between atoms that share the same electron cloud increases with the distance between them up to a maximum and thereafter decreases abruptly, when failure occurs. A perfect metal lattice (i.e., a defect-free crystal) will fail at this point by cleavage across the crystallographic plane because this is the region where the interatomic forces are weakest.

To a first approximation, the interatomic force per unit area varies with interatomic separation,  $x$ , according to a sine wave with wavelength  $\lambda$ , as shown in Fig. 1.23. The interatomic force per unit area may then be represented by a sine wave, as:

$$\sigma = \sigma_0 \sin 2\pi \frac{x}{\lambda} \quad (\text{Eq 1.8a})$$

where  $\sigma_0$  is the maximum theoretical strength. The work done per unit area in completely separating neighboring planes of atoms, which are

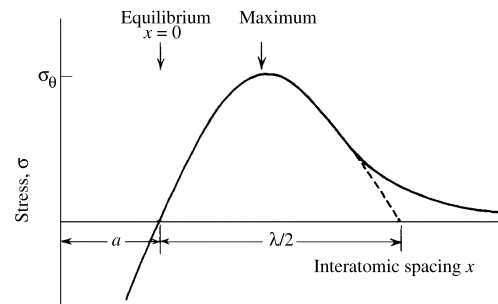


Fig. 1.23 Variation of interatomic force, per unit area, with distance



an equilibrium distance ( $x = 0$ ; i.e.,  $a \sim \lambda/4$ ) apart, is then:

$$\int_0^{\lambda/2} \sigma dx = \int_0^{\lambda/2} \sigma_0 \sin 2\pi \frac{x}{\lambda} dx = \frac{\lambda \sigma_0}{\pi}$$

This work corresponds to the total surface energy of the two new surfaces created in the fracture, i.e.,  $2\gamma_{SV}$ , where  $\gamma_{SV}$  is the surface energy per unit area of the solid.

Accordingly:

$$\sigma_0 = \frac{2\pi\gamma_{SV}}{\lambda} \quad (\text{Eq 1.8b})$$

Within the elastic range of strain, Hooke's law applies; that is:

$$\delta\sigma = E \frac{\delta x}{a}$$

Differentiating Eq 1.8(a) gives:

$$\frac{d\sigma}{dx} = \sigma_0 \frac{2\pi}{\lambda} \left( \cos 2\pi \frac{x}{\lambda} \right)$$

At zero strain; that is,  $x = 0$ :

$$\left( \frac{d\sigma}{dx} \right)_{x=0} = \sigma_0 \frac{2\pi}{a}$$

Hence:

$$\sigma_0 = \frac{E\lambda}{2\pi a} \quad (\text{Eq 1.9})$$

From Eq 1.8(b) and 1.9:

$$\lambda = \frac{2\pi\gamma_{SV}}{\sigma_0} = \sigma_0 \frac{2\pi a}{E}$$

so that:

$$\sigma_0 = \left( \frac{E\gamma_{SV}}{a} \right)^{1/2} \quad (\text{Eq 1.10})$$

The theoretical fracture stress is about  $\sigma_0/10$  for metals, although, in practice, strengths of metals tend to be only one-tenth of this value (i.e.,  $\sigma_0/100$ ), owing to the presence of lattice defects and other discontinuities.

Possibly somewhat surprisingly, brazed joints subject to simple mechanical stress will often

fail in a brittle manner. The reasons for this are elaborated in Chapter 4, section 4.3.3. In brittle materials, failure takes place by the propagation of cracks that either preexist in the structure or nucleate at lattice imperfections. The stress to cause fracture can be deduced from Eq 1.10 by replacing the denominator with  $c$ , where  $c$  is the crack length; thus:

$$\sigma_b = (E\gamma_{SV}/c)^{1/2}$$

Because  $c$  is much larger than  $a$ , the mechanical strength of a brittle material is low relative to its theoretical strength. Only in special materials, which are regularly ordered on an atomic scale, such as carbon fiber, are the two values remotely comparable.

In ductile metals, application of stress results in the movement of dislocations and other defects through the lattice of individual grains. The interfaces between grains represent another region where physical material transport and plastic flow takes place. Failure occurs when the rate of increase in strength of the material due to work hardening falls below the rate of decrease in the load-bearing cross section resulting from the plastic flow.

The preceding discussion pertained to bulk materials, i.e., the components and the filler metal, when considered in isolation. In reality, the joint interfaces will often be a source of voids, microcracks, local interfacial mismatch stresses, and brittle intermetallic phases. These features tend to be a common source of joint weakness and should be minimized through judicious choice of the filler/parent material and joining conditions.

### 1.3 The Design and Application of Brazing Processes

A brazed joint is usually required to satisfy a specific set of requirements. Most frequently, it must achieve a certain mechanical strength, which it must retain to the highest service temperature in the intended application. The joint must also endure a particular service environment, which may be corrosive, and it may have to provide good electrical and thermal conductance. In addition, the joint must be capable of being formed in a cost-effective manner without detriment to other parts of the assembly.

## 30 / Principles of Brazing

The principal aspects that need to be addressed can be divided as:

- The functional requirements of the application and the means of satisfying these through appropriate structural design.
- The achievement of the specified assembly through successful processing.

In the following sections, where these aspects are considered further, it is presumed, unless otherwise stated, that the faying surfaces of the components are metallic and, therefore, fundamentally wettable by a molten braze. Brazing of nonmetals is discussed in Chapter 7.

### 1.3.1 Functional Requirements and Design Criteria

All brazed joints used in manufactured products must remain solid in service and retain the associated components in fixed positions when subjected to stress. These requirements are usually satisfied by suitable design of the geometry and metallurgy of the joint, but there are also other aspects to consider. Several factors that affect the functional integrity of brazed joints are discussed next.

#### 1.3.1.1 Metallurgical Stability

For a joint to remain solid, the melting point (solidus temperature) of the filler metal needs to exceed the peak temperature that the component is ever likely to experience in service. There are exceptions to this rule, which are discussed in Chapter 6. Because the strength of all metals decreases rapidly as the melting point is approached, in general, the peak operating temperature should not exceed about 70% of the melting point of the filler, in degrees Kelvin, if the joint is required to sustain a load.

The solidified filler metal and parent materials have different compositions and so the microstructural equilibrium is rarely achieved in practice. The composition of these materials and the phases that form on solidification in a brazed joint are frequently unstable or the relative proportions of these phases can change at elevated service temperatures. Instability of phases present in the joint at the service temperature may be undesirable. Such changes can result in a decrease in fracture toughness, if the new phases are brittle, or in a general loss of joint integrity should Kirkendall voids develop as some phases evolve at the expense of others. Therefore, the

effects of continued reactions between the filler and the components also must be considered in relation to the application, as explained in Chapters 2 and 3.

#### 1.3.1.2 Mechanical Integrity

The durability of engineering and consumer products often depends on joints maintaining their mechanical integrity for the duration of their expected service life. The mechanical integrity of a brazed joint depends on a number of factors:

- The mechanical properties of the bulk filler metal (Chapter 4, sections 4.3.3 and 4.3.4)
- The joint geometry, namely, area, width, and shape (Chapter 4, sections 4.3.1 and 4.3.3)
- The mechanical properties of any new phases formed in the joint by reaction between the filler and the components, either during the joining operation or subsequently in service (i.e., there is an interdependence with the microstructure) (Chapter 4, section 4.1.4)
- The number, size, shape, and distribution of voids within the joint (Chapter 4, section 4.3.1)
- The quality of fillets formed between the filler and the surface of the components at the edge of the joint (i.e., their radius of curvature and extent of continuity) (Chapter 4, section 4.2.5)

The mechanical properties of joints, taking into account the influence of joint geometry, are reviewed extensively elsewhere. The reader is particularly referred to Schwartz [2003] and Nichol [1998]

#### 1.3.1.3 Environmental Durability

Joints are normally expected to be robust in relation to the service environment. This may involve exposure to corrosive gases, including sulphur dioxide and other constituents of a polluted atmosphere; to moisture, perhaps laden with salt; and to variable temperature. The corrosion and stress-corrosion characteristics of the joint are then of relevance. Corrosion mechanisms are often somewhat complex and specific to a given combination of materials, chemical environment, and joint geometry. Therefore, each situation should be determined empirically. A typical example is provided by the case study of corrosion of brazed stainless steel pipes con-

veying drinking water, an environment in which extensive corrosion would not normally be expected [Jarman, Linekar, and Booker 1975].

The temperature of a joint can be shifted well beyond a normal ambient range, especially in aerospace applications and in situations where heat is generated within the assembly itself. Then, thermal fatigue and other changes to the metallurgical condition of the joint, such as the growth of phases, can occur, and these invariably affect the properties of the joint. In other words, there is interdependence between environmental stability and microstructural stability. An appropriate choice of the materials combination used should enable these changes to be constrained within predictable and acceptable limits. In other words, brazes should be used at service temperatures that are sufficiently below their melting points, with respect to the thermodynamic reference point of absolute zero temperature ( $-273\text{ }^{\circ}\text{C}$ , or  $-459\text{ }^{\circ}\text{F}$ ) so that they are metallurgically stable and microstructural changes take place only very slowly.

#### 1.3.1.4 Electrical and Thermal Conductivity

In certain applications, brazed joints are required to perform the function of providing electrical and/or thermal conductance between components. Generally, thin, well-filled brazed joints amply satisfy this requirement. Only in a few extreme situations are the thermal and electrical properties of such joints close to the allowed limits. A case in point is silicon high-power device assemblies, where the joint between the silicon device and the metal backing plate is required to conduct  $1\text{ W/mm}^2$ , or more, of thermal power. Here, it is crucial to ensure that the brazed joints, which are conventionally made using an aluminum-silicon alloy, are kept thin ( $<30\text{ }\mu\text{m}$ , or  $1200\text{ }\mu\text{in.}$ ) and essentially void-free ( $<5\%$  by volume), in order to meet the device performance specifications [Humpston et al. 1992].

### 1.3.2 Processing Aspects

An important aspect that must be considered when designing a joint is the practicality of the process involved. Among the relevant issues are:

- Jigging of the components
- Form of the filler metal
- Heating method

- Temperature measurement
- Joining atmosphere
- Coatings applied to surfaces of components (as necessary)
- Cleaning treatments
- Heat treatments prior to joining
- Heating cycle of the joining operation
- Post-joining treatments

Each of these aspects is considered in turn.

#### 1.3.2.1 Jigging of the Components

Normally, the components being joined, and sometimes also the filler metal itself, must be held in the required configuration until the filler metal has solidified. Even if the components can be preplaced without a fixture, the use of some form of jig is still frequently beneficial to ensure that the components are not disturbed by capillary forces originating from the molten filler metal. On the other hand, it is also possible to exploit the capillary forces to make an assembly self-align during the brazing process. Self-alignment is widely practiced in the fabrication of electronic circuits using lightweight surface-mounted components and flip-chip assembly involving soldering (see the companion volume *Principles of Soldering* for details of these processes).

The jig can be used to fulfill more than a holding function. For example, it can serve as a heat spreader, as a heat sink, or as a heat source. A jig should be constructed from a nonporous material to prevent contamination of the atmosphere surrounding the workpiece. Moreover, the jig material should not be wettable by the molten filler metal, in case they come into contact through accidental spillage. Materials such as brass should be avoided as zinc readily volatilizes at elevated temperatures used for brazing. Care should be taken in designing jigs so as not to stress the constrained components through thermal expansion mismatch.

Graphite is often favored as a jig material. It is inexpensive, easy to machine to precise tolerances, is a good thermal conductor (making it an effective heat spreader), is an absorber of radiant heat, and is not wetted by the majority of molten filler metals. It can also be used as a heater by the passage of electric current. Graphite has the merit of “mopping-up” oxygen in an oxidizing atmosphere to form carbon monoxide and carbon dioxide, although the presence of these gases can result in carburization of some steel components. Care should be taken to en-

sure that the graphite used for jigs is of a dense grade so that it will be mechanically robust and have a low porosity to minimize outgasing. The desorption of water vapor, in particular, frequently determines the quality of a gas atmosphere in the vicinity of a workpiece.

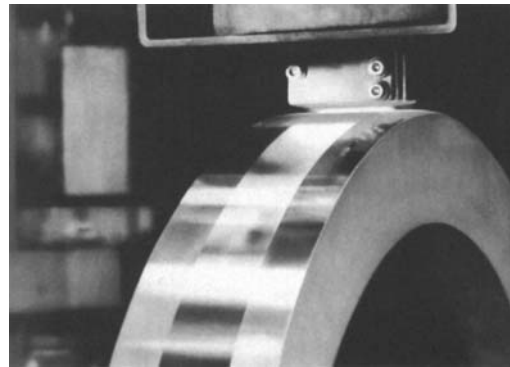
Jigs are sometimes used to apply a controlled pressure to a joint in an assembly. One component can then be deliberately and elastically distorted to bring it into close and uniform contact with its mating part. This is an advantage when very narrow joints are required and when solid state diffusion constitutes an important part of the joining process. Compressive loading on the joint also aids expulsion of air and vapors from the joints, which are otherwise trapped in pockets and produce voids. An applied force also helps to puncture the oxide films on the surfaces of the filler and, when the filler metal melts, it acts against any dewetting capillary force of the liquid and ensures adequate spreading over the joint. The combination of these factors leads to improved joint filling. Typical pressures are in the range 1 to 5 kPa (0.14–0.72 psi).

Fixturing (i.e., jiggling) represents an expensive add-on cost in a brazing operation, and many ingenious methods of self-supporting and integral jigs have been devised. They generally involve some means of mechanical fastening such as crimping, swaging, interlocking, peening, riveting, dimpling, knurling, and so forth, including spot welding. The jiggling must be designed to provide the correct joint clearance at the brazing temperature, as discussed in section 1.2.7.

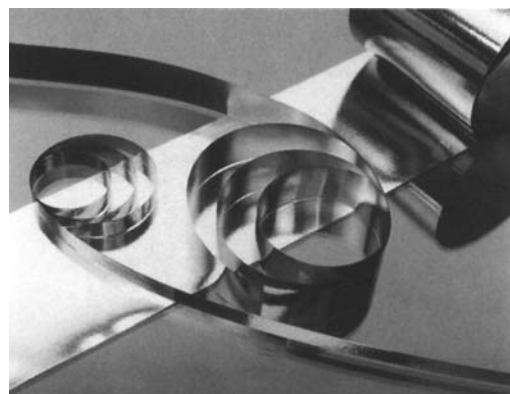
### 1.3.2.2 Form of the Filler Metal

Filler metals are available in many different forms. These forms include configurations that normally can be produced from an ingot by mechanical working, for example, wire, rings, and foil. Such geometries are not restricted to ductile alloys. If the constituents are individually ductile, the preform can be partitioned. This approach is discussed further in Chapter 4, section 4.1.5. The development of rapid-solidification processes has led to the availability of foils and wire of joining alloys that are inherently brittle. These foils are produced directly from the melt: the process involves forcing molten metal through a hole or slot onto a rapidly spinning, water-cooled, metal wheel. Fig. 1.24 shows such a strip casting process in operation, and Fig. 1.25 illustrates some typical foils produced by this

route. The high rate of heat extraction that occurs in this process causes the molten metal to solidify almost immediately on striking the wheel, resulting in the formation of a strip of the alloy with a fine crystalline, or occasionally amorphous, microstructure. The dimensions of the cast material can be controlled by varying the nozzle dimensions, the ejection pressure, the speed of rotation of the wheel, and other parameters of the casting process [Otooni 1995; Srivatsan and Sudarshan 1993; Jones 1982]. The refined microstructure of the rapidly solidified alloys, together with their homogenous composition, generally improves strength and ductility compared with the same alloys produced by conventional casting and mechanical working (Fig. 1.26). A good example is the family of silver-copper-titanium brazes. These alloys are generally brittle in ingot form, but, when pre-



**Fig. 1.24** Production of foil directly from a molten charge by strip casting. Source: Vacuumschmelze GmbH, Germany

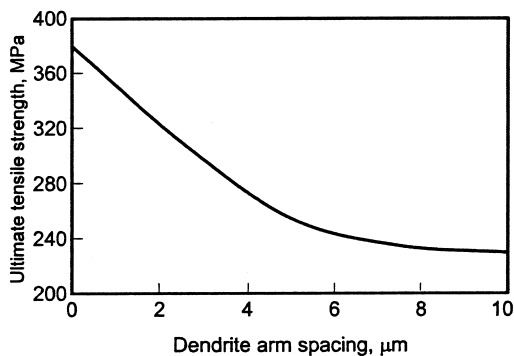


**Fig. 1.25** Examples of foil strip produced by rapid-solidification casting technology. Source: Fleetwood et al. [1988]

pared as a foil by rapid solidification, their ductility is comparable to that of other brazes.

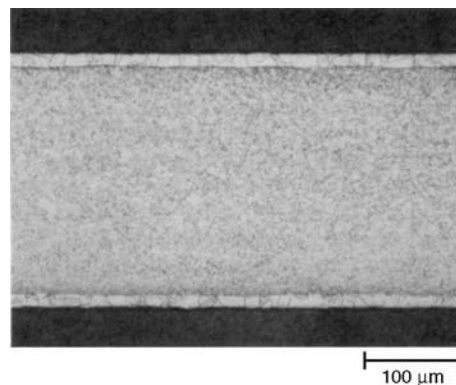
Brazes are also available as finely divided powders that can be mixed with a binder to form a paste capable of being screen printed onto a substrate or applied to the workpiece, via a dispenser, to suit an automated production line. Much industrial brazing is carried out in this manner. However, powders, and pastes containing powders, have an extremely high ratio of surface area to volume of braze, which generally results in high oxide fractions and, in the absence of suitable precautions, would be detrimental to the quality of the resulting joints. Braze paste manufacturers go to great lengths to produce spherical granules with smooth, clean surfaces specifically for this very reason. Powdered brazes can also be admitted to the joint gap in the form of tapes. These are powder compacts that are often supplied on an adhesive support. Preforms can thus be shaped with a sharp blade and are easily placed in the joint gap. The adhesive is selected to burn cleanly along with the other organic constituents.

In specialized joining processes, the braze can be deposited as a coating on the components by electroplating and by vapor deposition techniques such as evaporation. Where it is not possible to deposit the actual alloy, sequential layers of the constituent elements can be applied. The former is generally preferred because the melting point of an alloy is well defined, whereas there is no guarantee that melting will take place at the desired temperature in the case of the composite layers, unless significant solid-state diffusion has occurred first to form the appropriate low-melting-point phases.



**Fig. 1.26** Dendrite arm spacing decreases with increasing cooling rate and hence fine-grained microstructures have improved mechanical properties. The data pertain to hypereutectic cast iron. Adapted from Seah, Hemanth, and Sharma [1998]

The use of some form of preplaced filler metal has a number of advantages. Most particularly, because the thickness and area of filler metal are predetermined, the volume of molten braze may be carefully controlled. Also, the number of free surfaces is reduced from four (corresponding to a foil preform sandwiched in the joint) to just two, thereby considerably reducing the proportion of oxides and other impurities deriving from exposed surfaces. Piece-part inventory is reduced and jigging is simplified. Having the filler metal ready placed within the joint gap means there is no need for it to spread to effect joining and this arrangement eliminates operator error in placement or omission of brazing paste or preforms. Fine details and intricate parts are readily brazed and, generally, more consistent joints are obtained by this means. "Self-brazing metals," which offer these benefits, consist of a base metal that is clad on one or both sides with braze and are produced in many variants. A metallographic section through a commercial product of this type is shown in Fig. 1.27. The cladding is usually achieved by roll bonding, and typical cladding thicknesses range from 5 to 30%. Standard clad products include aluminum, copper, and ferrous alloys. Figure 1.28 shows two aluminum parts, one brazed with a preform and the other with a roll-clad substrate. Braze claddings can be made much thinner than brazing foils, a feature that generally benefits the mechanical properties of the joints. Once the brazing alloy is clad to the base metal, subsequent forming operations will not significantly alter the cladding ratio. The presence of a soft copper braze on medium-to-hard carbon steels is actually ben-



**Fig. 1.27** Metallographic cross section of a stainless steel strip clad on both sides with copper braze. In this case, the ratio of braze cladding to core material is in the ratio 5/90/5.

eficial in reducing tool wear when parts are worked [Karavolis 1993].

### 1.3.2.3 Heating Methods

Heat must be supplied to the joint to raise the temperature of the filler metal and joint surfaces above the melting point of the filler. If the joint surfaces are maintained below the melting temperature of the braze, it will freeze on contact with the parent materials and “ball up.” To prevent this situation, it is good practice always to heat the filler metal via the components to be joined and never vice versa.

The available methods of heating are:

- Local heating, in which only that part of the components in the immediate vicinity of the joint is heated to the desired temperature
- Diffuse heating, where the temperature of the entire assembly is raised

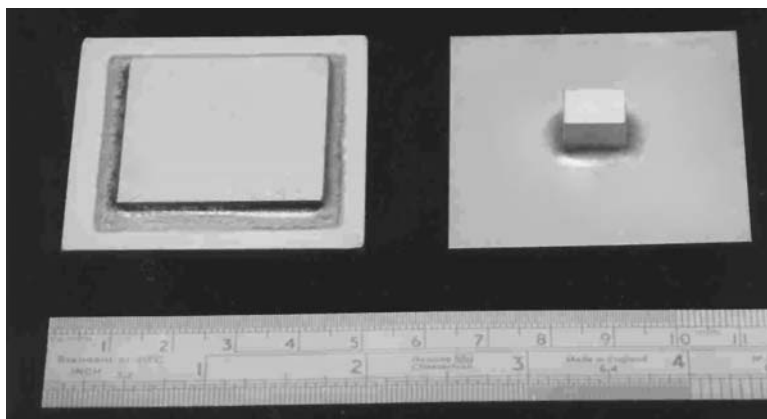
Common local heat sources include gas torches and resistance heating using the assembly as the resistive element and also heating elements external to the assembly. Other heating techniques that are now commonly used include induction heating and laser heating. Although some methods of local heating are applicable to joining in a controlled atmosphere, this is not usually the case with a gas torch and a flux must then be used.

In local heating, the rate of heat energy input must be high to swamp the heat conducted away by the components and jigging. A high rate of heat input can achieve the characteristic of fast

heating and cooling of the joint. Fast heating coupled with short brazing cycles minimizes erosion of substrate surfaces and therefore restricts the formation of undesirable phases, while rapid cooling ensures a fine grain size in the solidified filler and thereby superior mechanical properties. However, these potential benefits can be offset by the generation of thermally induced stresses and distortion, and even cracking, in the components being joined (see also section 1.3.2.9). Local heating can be used to create specified temperature gradients that will restrict the flow of the molten filler metal to the immediate vicinity of the joint.

Diffuse heating sources include systems such as furnaces (both resistance and optical) and induction coils. The features of diffuse heating methods are the opposite of those of the local heating methods. For example, the total energy requirement is higher because the temperature of the entire assembly has to be raised, which also significantly increases the process cycle time. On the other hand, there is less risk of high-temperature gradients and thermal distortion, and accurate control of temperature at the joint is easier to achieve. Diffuse heating methods tend to impose fewer constraints on the atmosphere surrounding the workpiece because the source of heat is relatively remote from the components.

If diffuse heating is to be used in the fabrication of complex assemblies, the designer must ensure that all of the component parts are able to withstand the peak process temperature. With local heating, heat sinks can be used to protect



**Fig. 1.28** Aluminum components brazed using a preform of (left) braze and (right) one component roll-clad with brazing alloy. In both cases, the brazing process was fluxless. Because roll-clad braze is generally thinner than a preform, the upper component needs to be smaller in area to achieve a comparably sized fillet. Courtesy of BAE Systems

sensitive areas from excessive thermal excursions. A related consideration when using diffuse heating in a situation where several joints must be made is that the melting point of the filler metal used for the preceding joining operations must be higher than the peak process temperature used in the current cycle. Several different filler metals will therefore be required to fabricate a multijointed product in a step joining process.

The oldest method of heating joints is by naked flame. The gases predominantly used now are acetylene and propane, burnt in oxygen. These gases are cheap, widely available, easy to use, and can be made oxidizing, reducing, or neutral by adjustment of the oxygen-to-gas ratio. These three combustion conditions are also readily discernible by eye allowing a skilled operator to adjust the torch to satisfy the requirements of the job in hand. The thermal characteristics of some common fuel gases burnt in oxygen are given in Table 1.5.

One of the more exotic methods of heating for making brazed joints is self-propagating high-temperature synthesis (SHS). The principle of the method is to place within the joint gap, or its vicinity, a mixture of two or more metals in the form of a powder compact or multilayer foil. The heating reaction is initiated by applying a spark, thermal energy (e.g., a lighted match), or passage of electric current (Fig. 1.29). The two metals are carefully chosen, for example a stoichiometric mix of palladium and aluminum, so that they react exothermically, in this case to form palladium aluminide with a large excess of heat ( $\Delta G^0 = -94$  kJ/mol). An SHS heat source can be entirely internal to the joint. In brazing applications, either one or more of the reactants or products of the SHS acts as the filler metal itself, or the heat is used to melt a conventional filler metal [Hawk et al. 1993]. The intermetallic compounds formed as a result of SHS have relatively poor thermal conductivity (approximately 70 W/mK, or  $1.2 \times 10^{-2}$  Btu/h · ft · °F), com-

pared with brazes that may need to be taken into account where this characteristic is important and the reactants constitute an appreciable volume fraction of the joint. Self-propagating high-temperature synthesis foils and powder mixtures are available commercially.

Ideally, during heating, the faying surfaces and brazing alloy should reach the brazing temperature at exactly the same time. In designing the brazing process it is therefore necessary to take into account the different thermal mass, conductivity, and heat capacity of the components together with their proximity to the heat source. Molten brazes flow preferentially toward the hottest region of the substrate. In recognition of this fact, it is best practice to place the filler metal in the joint gap, or, next best, to apply the filler metal to the edge of the joint and apply most heat to the central portion of the joint area.

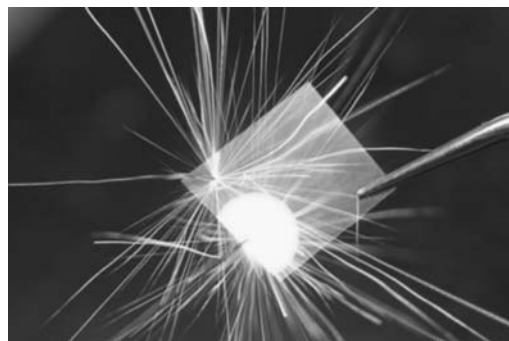
#### 1.3.2.4 Temperature Measurement

The liquid-solid metallurgical reactions that occur during brazing operations are highly temperature dependent. Therefore, reliable measurement of temperature is essential. Thermocouples and pyroelectric elements are the most common types of temperature sensors used in brazing operations.

A number of precautions should be taken when employing thermocouples. Regular in situ calibration checks should be made to determine whether the thermoelectric characteristics of the thermocouple materials have altered and to test for electrical interference affecting the display system. Correct temperature measurement requires good thermal contact between the ther-

**Table 1.5 Thermal characteristics of common fuel gases burnt in oxygen. In each case, the flame temperature is in the region of 3000 °C (5430 °F)**

Fuel gas	Thermal output, kW/cm <sup>3</sup>
Acetylene	15
Methane	7
Propane	6
Hydrogen	9



**Fig. 1.29** A quite remarkable photograph of a self-propagating high-temperature synthesis (SHS) reaction moments after ignition of a foil of a proprietary metal combination. The excess energy is sufficient to heat the foil to white heat. Courtesy of Maximilian Franz

thermocouple and the object being monitored. This tends to present a problem in vacuum joining processes where thermal contact by mechanical means, namely, resting the thermocouple against a surface, tends to be inadequate. The thermal mass of the thermocouple and its protective sheath impedes the thermocouple junction from sensing the true temperature of the component surface. These effects can be minimized by embedding the thermocouple within the workpiece to improve thermal transfer.

Even when thermocouples are used for temperature measurement in gas atmospheres, where the thermal contact with the heated surface is better than it is in a vacuum, a change in the measured temperature will lag behind that actually occurring. This delay, which can be of the order of seconds, is difficult to measure accurately, but it must be taken into account if a thermocouple is being used to monitor the temperature of assemblies exposed to high heating and cooling rates.

Pyrometers have one important advantage over thermocouples: they are noncontacting sensors of temperature. Traditional pyrometers are designed primarily for operation above about 750 °C (1380 °F) and are widely used for monitoring brazing processes. Measurements may be made remotely from the workpiece, and the response time of the instrument can be determined accurately. However, it is necessary for the edge of the joint to be visible to the pyrometer and not obscured by jiggling and other objects. Pyrometers and thermocouples provide only a localized measurement of temperature. As this might not be representative of the entire joint region, it is common to measure temperature at several places on an assembly, at least until a process is well established.

A new form of spot temperature measurement involves the use of lasers. A helium-neon laser is used to illuminate a surface and highly sensitive silicon photodiodes used to monitor the reflected light. Because reflectivity has a temperature dependence, known as *thermoreflectance*, this enables the temperature of the illuminated spot to be ascertained [Lee and Norris 1997]. The accuracy that can be achieved is about 1 °C (1.8 °F) with a low-cost, handheld instrument.

In manual brazing, the flux can function as an indicator of temperature. For example, many of the fluxes formulated for use with low melting point silver-base brazes transform from a white powder to a clear molten glass just as the tem-

perature of the components approaches the solidus temperature of the braze.

### 1.3.2.5 Joining Atmosphere

For a molten filler metal to wet and bond to a metal surface, the latter must be free from non-metallic surface films. Although it is possible to ensure that this condition is met at the beginning of the heating cycle, by prescribed cleaning treatments, significant oxidation will generally occur if the components are heated in air. Steps must therefore be taken to either prevent oxidation or remove the oxide film as fast as it forms.

The approach adopted will depend largely on the atmosphere surrounding the workpiece. Brazing processes are conducted in one of three types of atmosphere, defined according to the reaction that occurs between the atmosphere and the constituent materials, as:

- Oxidizing (e.g., air)
- Essentially inert (e.g., nitrogen, vacuum)
- Reducing (e.g., hydrogen, carbon monoxide, halogen containing)

The implications associated with using each of these atmospheres are considered next.

*Oxidizing atmospheres.* Air is the most common oxidizing atmosphere. The principal advantages of joining in air are that no special gas-handling measures are required and that there are no difficulties associated with access to the workpiece during the brazing operation. However, because most component surfaces and those of the filler metal are likely to form oxide scale when heated in air, normally fluxes must be applied to the joint region. A flux is capable of chemically and/or physically removing an oxide film. The flux may be applied either as a separate agent or may be an integral constituent of the joining alloy. The subject of fluxes is discussed in detail in Chapter 3, section 3.2.

Gold and some of the platinum-group metals do not oxidize when heated in air. These precious metals are therefore sometimes applied as metallizations to the surfaces of the components being joined in fluxless processes. The use of wettable metallizations is discussed in Chapter 4, section 4.1.2.1. Brazes that contain significant proportions of precious metals, including silver, are generally less susceptible to oxidation than other alloys, enabling mild fluxes to be used.

An oxidizing atmosphere is occasionally desirable during brazing. Not only do some fluxes



require the presence of oxygen in order to function, but in some instances, it is a prerequisite for successful joining that oxygen be present. An example is provided by the copper-copper oxide eutectic brazing process in which copper is brazed to oxide ceramic materials, such as alumina, by a eutectic that is formed in situ between copper and  $\text{Cu}_2\text{O}$  just below the melting point of copper [Schwartz 1990]. This process is used to manufacture so-called direct-copper-bonded substrates of controlled coefficient of thermal expansion; see Chapter 4, section 4.2.1.3.

*Inert atmospheres.* From a practical point of view, an atmosphere is either oxidizing or reducing. This is because it is not possible to remove and then totally exclude oxygen from the workpiece, except perhaps under rigorous laboratory conditions. Thus, when defining an atmosphere as inert, it must be taken as meaning that the residual level of oxygen present is not sufficient to adversely affect the joining process under consideration. An atmosphere that might be suitable for brazing silver jewelry may be inadequate for joining nickel-base superalloys.

Because the “inertness” of an atmosphere is judged relative to the specific application, it is necessary to define a quantitative measure of the oxygen present. This parameter is the oxygen partial pressure. Partial pressure provides a measure of the concentration of one gas in an atmosphere containing several gases. The partial pressure of a gas in a mixture of gases is defined as the pressure it would exert if it alone occupied the available volume. Thus, dry air at atmospheric pressure (0.1 MPa, or 14.5 psi) contains approximately 20% oxygen by volume so that the oxygen partial pressure in air is 0.02 MPa (2.9 psi).

Typical inert atmospheres among the common gases include nitrogen and argon. The oxygen partial pressure in standard commercial-grade bottled gases is of the order of 10 mPa ( $1.5 \times 10^{-6}$  psi). Higher quality grades are available, but their cost is usually too prohibitive to permit their use in most industrial applications.

Vacuum is frequently used as an inert, protective environment for filler metal joining processes. Vacuum offers several advantages compared with a gas atmosphere, particularly the ability to readily measure and control the oxygen partial pressure. In a substantially leak-free system, the oxygen partial pressure is one-fifth of the vacuum pressure, which is relatively easy to determine. Although a roughing vacuum of 100 mPa ( $1.5 \times 10^{-5}$  psi) will provide an atmo-

sphere with the same oxygen partial pressure as a standard inert gas, it is possible to improve on this value, by several orders of magnitude, using a high-vacuum pumping system. Alternatively, a low-oxygen partial pressure may be achieved by obtaining a roughing vacuum, back filling with an inert gas and then roughing out again. The effect of the second pumping cycle will be to reduce the oxygen partial pressure to less than typically one-thousandth of that in the inert gas, that is, approximately 100  $\mu\text{Pa}$  ( $1.5 \times 10^{-8}$  psi). This estimate assumes that the furnace chamber is completely leak-tight and does not outgas from interior surfaces, nor does any oxygen or water vapor backstream through the pump.

The disadvantages of using a vacuum system for carrying out a joining process are, principally, restricted access to the workpiece and the inadvisability of using either fluxes or filler metals with volatile constituents, such as cadmium, because the vapors can corrode the vacuum chamber, degrade its seals, and contaminate the pumping oils. This problem is not limited to the well-known volatile elements. Many metals that have negligible vapor pressure at normal ambient temperatures will volatilize during high-temperature brazing processes ( $>1000^\circ\text{C}$ , or  $1830^\circ\text{F}$ ), particularly when these entail using reduced pressure atmospheres. Manganese-containing brazes and base materials fall into this category because the vapor pressure of this element is 1 Pa ( $1.5 \times 10^{-4}$  psi) at  $1000^\circ\text{C}$  ( $1830^\circ\text{F}$ ).

A frequently overlooked consideration in reduced-pressure atmospheres is adsorbed water that exists naturally on surfaces that are exposed to ambient atmospheres. The continuous streaming of water vapor that desorbs from surfaces and flows past the workpiece as the pressure in a vacuum chamber is reduced is a source of oxidation. In a vacuum system operating at 10 mPa ( $1.5 \times 10^{-6}$  psi), the desorbing water vapor constitutes the major proportion of the residual atmosphere. An adsorbed monolayer of water vapor of just  $100\text{ mm}^2$  ( $0.16\text{ in.}^2$ ) in area desorbs to a gas pressure of 4 mPa ( $6 \times 10^{-7}$  psi) per liter of chamber volume. The surfaces of the chamber should therefore be smooth to minimize the surface area, and also dry. In order to reduce this problem further, the walls of the vacuum chamber should be heated and the system should always be vented to a dry atmosphere. To effectively desorb water vapor, the bakeout temperature should be at least  $250^\circ\text{C}$  ( $480^\circ\text{F}$ ), which may be difficult to achieve in

practice owing to design constraints and the employment of seals of rubber and other organic materials.

Another source of oxidizing contamination in a vacuum system is oil vapor mixed with air and water vapor, backstreaming from a rotary pump. This can occur whenever the pressure inside the vacuum chamber drops below 1 Pa ( $1.5 \times 10^{-4}$  psi) but can be largely eliminated by employing a foreline trap, or by isolating the pump from the chamber once the required pressure reduction has been obtained. The widespread adoption of turbomolecular pumps on modern vacuum equipment has rendered this problem obsolete.

The practice of relying on an open gas shroud, as in various welding processes, to provide an inert atmosphere for brazing is often unsatisfactory because it is extremely difficult to control such an atmosphere reliably. For example, turbulence in the inert gas shroud can result in a supply of air actually being directed at the workpiece. Recent advances in furnace technology now permit open furnaces, which often take the form of belt furnaces intended for continuous brazing processes, such as jewelry chain making. These are capable of achieving very high specification atmospheres in the working zone, through careful design of the gas flow at the open portals.

*Reducing atmospheres.* A reducing atmosphere is one that is capable of chemically removing surface contamination from metals. Gases that provide reducing conditions are, principally, hydrogen and carbon monoxide, and generally, proprietary mixtures that liberate halogen radicals. Specific gas-handling systems are usually needed for these in order to satisfy health and safety legislation.

For a few metals, notably copper and silver, hydrogen is satisfactory as a reducing atmosphere in a brazing furnace. No less important for meeting its functional requirement than the oxygen partial pressure of the gas is its water content. Hydrogen is a relatively difficult gas to dry, and the water vapor present can present a serious problem. A frost point of  $-70^\circ\text{C}$  ( $-95^\circ\text{F}$ ) is equivalent to a water content of 0.0002% by volume—that is, an oxygen partial pressure of about 10 mPa ( $1.5 \times 10^{-6}$  psi). There is also the risk of explosion when dealing with hydrogen at high temperatures, and hydrogen can embrittle some materials. A more detailed treatment of reducing atmospheres and their use is given in Chapter 3, section 3.1.

### 1.3.2.6 Coatings Applied to Surfaces of Components

Occasionally, the desired joining alloy (chosen on the basis of melting temperature and physical properties) is metallurgically incompatible with the substrate in the sense that the filler either does not wet the substrate, will wet nonuniformly, or forms embrittling phases by reaction. A solution is to apply a surface coating that will promote wetting by the braze and reacts with it in a benign manner. For example, the native oxide on titanium prevents this metal's being wet by low-melting-point silver-base brazes in an inert atmosphere. However, a gold coating, applied by electroplating and diffused in by heat treatment, akin to that used in sherardizing (sherardizing), substitutes for the oxide and renders the titanium wettable. Stainless steels are often plated with nickel for similar reasons. As a general guide, plating of stainless steels and other heat-resistant alloys to facilitate brazing is generally recommended when the titanium content of the components exceeds 0.7%, the aluminum content exceeds 0.4%, or the combined aluminum and titanium contents exceed 0.7%. The nickel plating will need to be at least  $10\ \mu\text{m}$  ( $400\ \mu\text{in.}$ ) thick to prevent these species' diffusing through to the surface during the heating stage of a typical brazing cycle and also to accommodate the depth of alloying that usually takes place between a braze and a substrate. Coatings can be applied by a variety of techniques and to thicknesses that suit the particular application.

On substrates destined for brazing, it is normal to apply coatings that are required by wet-plating methods, which are quick, economical, and flexible with regard to the coating thickness. If the substrate is refractory in character, adhesion of metal coatings tends to be poor or impossible unless the braze contains a suitable activating ingredient; see Chapter 4, section 4.1.2.2. An alternative is to use a thick-film coating. A conventional thick film comprises metal particles embedded in a glass or ceramic matrix. On firing, segregation of the constituents occurs so as to leave a metal-rich surface that is wettable by molten brazes, while the nonmetallic part accumulates at the interface with the substrate and bonds to it in the manner of a glaze. These and other metallizations, and the principles on which they are designed, are described in Chapter 4, section 4.1.2.1.

### 1.3.2.7 Cleaning Treatments

The surfaces of the components to be joined and the filler metal preforms must be free from any nonmetallic films, such as organic residues and metal oxides, to enable the molten filler metal to wet and alloy with the underlying metal. Fluxes are often capable of removing surface oxides, provided they are reasonably thin.

Organic films can be removed with petroleum and chlorinated solvents, which obviously should not react with the underlying materials. Although organic films will burn to leave carbon at the brazing temperature, their presence can cause difficulties with flux application as these are usually water-base materials. Thick oxides and other nonmetallic surface layers can be removed mechanically and chemically. Chemical cleaners can be either alkaline or acidic and may employ electrolytic activation. Iron and stainless steel are best cleaned chemically and mechanically to ensure complete removal of organic matter and thin native oxides as far as is practicable. A wide variety of chemical agents, including sulphuric, nitric and hydrochloric acids, phosphate-based solutions, and salt baths, can be used. Removal of copper oxides can also be achieved mechanically and by pickling. The formulation of the pickle will vary with the alloy type, but most are based on sulfuric acid at a concentration of 5 to 15%. Nickel alloys are chemically cleaned prior to brazing using nitric acid, often containing sodium chloride and sulfuric acid in addition. Any residual etchant left after rinsing is neutralized by a dilute sodium hydroxide solution. Molybdenum and its alloys can be cleaned by inorganic etches as well as in molten salt baths such as 70% sodium hydroxide and 30% sodium nitrate at about 300 °C (570 °F). Light oxide films can be removed from tungsten by a hydrogen atmosphere at 1065 °C (1950 °F). For most metals, mechanical cleaning, followed by a light acid etch generally gives the best results. Carbides and ceramics do not require cleaning because they do not form “native” oxides, but they benefit from chemical treatments to remove residues from earlier processes, particularly embedded fine particles picked up from grinding, cutting, and polishing media that otherwise interfere with spreading of the braze.

### 1.3.2.8 Heat Treatments Prior to Joining

Prejoining heat treatments are occasionally useful in providing stress relief and thereby pre-

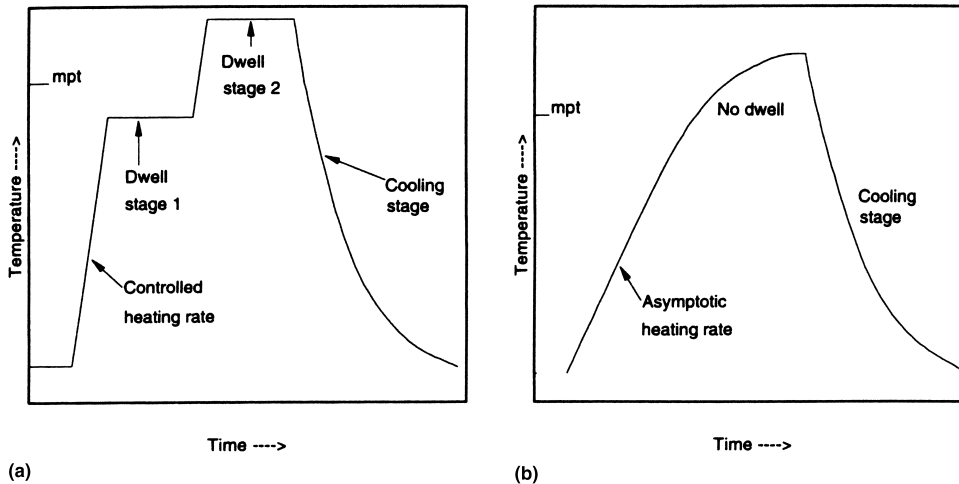
venting unpredictable distortion during heating of the components to the bonding temperature. Brasses and bronzes have a tendency to form stress cracks when cold worked and then heated rapidly. Although any cracks in the vicinity of the joint will be filled by molten braze, the integrity of the assembly in such a case is likely to be unreliable. It is therefore normal to perform a stress relief by heat treatment at about 300 °C (570 °F) prior to brazing. In a controlled atmosphere process, this step can be integrated into the heating cycle of the brazing operation. Other situations where prejoining heat treatments can be beneficial include those involving components with metallic or nonmetallic surface films that are thermally unstable. In the case of silver, for example, the oxide will dissociate readily when heated above 190 °C (375 °F) in an ambient atmosphere. Likewise, silver sulfide dissociates on heating above 842 °C (1548 °F).

An additional note of caution needs to be sounded with regard to the brazing of stressed components. The joining operation can lead to brittle failure of stressed components through a mechanism known as *liquid metal embrittlement*. For example, stainless steels are exceptionally prone to embrittlement by copper and high-copper brazing alloys [Heiple, Bennette, and Rising 1982].

### 1.3.2.9 Heating Cycle of the Joining Operation

The prepared components and filler metal, possibly mounted in jigs, are joined by applying heat. The heating cycle involves four important processing parameters: the heating rate, the peak bonding temperature, the holding time above the melting point of the filler, and the cooling rate.

In general, it is desirable to use a fast heating rate to limit reactions that can occur below the prescribed bonding temperature. However, the maximum heating rate is normally constrained by adverse temperature gradients developing in the assembly. These gradients can produce distortions in the components and give rise to non-uniform reactions between the filler and the pair of joint surfaces. Also, temperatures are difficult to measure reliably during fast heating schedules. A better practice, especially when joining in a vacuum or controlled-atmosphere furnace, is to heat the assembly rapidly to a preset temperature that is just below the melting point of the filler metal and then hold it at this temperature for sufficient time (which can range from a



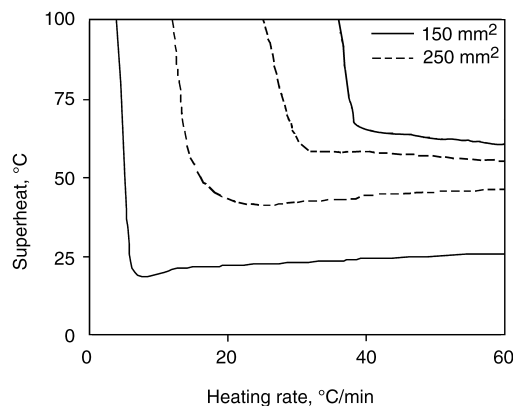
**Fig. 1.30** Profiles of typical temperature cycles. (a) Heating cycle with a controlled profile incorporating dwell stages to reduce thermal gradients. (b) Heating cycle defined solely by attainment of a peak temperature

few seconds to over one hour, depending on the size of the assembly and the heating method) to allow the assembly to thermally equilibrate and for water vapor to flush out of the joint. Following this dwell, the assembly may then be rapidly heated to the bonding temperature. Profiles of typical temperature cycles are shown schematically in Fig. 1.30.

The joining temperature should be such that the filler is guaranteed to melt but at the same time should not be so high that the filler degrades through the loss of constituents or by reaction with the furnace atmosphere. The optimum temperature is normally determined by metallurgical criteria, most importantly, the nature and extent of the filler-substrate interaction. The peak process temperature is frequently set at about 50 to 100 °C (90–180 °F) above the melting point of the braze because accurate temperature measurement and control is not always possible, especially in reduced-pressure atmospheres, where bulky jiggling is used or where conduction between the heat source and the workpiece is poor. Moreover, the reported melting temperatures of some filler metals are not always based on accurate measurements, and it is prudent to make some allowance for this uncertainty. The minimum time that the assembly is held above the melting point must be sufficient to ensure that the filler has melted over the entire area of the joint, and the maximum time is usually a compromise based on practical and metallurgical considerations. Extended dwell times tend to result in ex-

cessive spreading by the molten filler and reaction with the substrate, oxidation gradually taking place (depending on the nobility of metallic workpieces), and deterioration of the properties of the parent materials.

The variables of heating rate and peak process temperature combine to give a window for maximum spread by the filler metal that depends on the filler/substrate combination, volume of the filler metal, and process atmosphere or flux. Iso-spread contours for silver-copper braze on nickel are shown in Fig. 1.31. From this it can be seen that the conditions for maximum spreading are



**Fig. 1.31** Combined effects of superheat and heating rate on the spreading of 0.5 mg spheres of Ag-29Cu braze on nickel substrates in a nitrogen-10% hydrogen atmosphere. Area of isospread contours in mm<sup>2</sup> are shown. Adapted from Weirauch and Krafick [1996]

a peak temperature of 830 °C (1526 °F), reached at a rate of 25 °C/min (45 °F/min).

The cooling stage of the cycle is seldom controlled by the operator but tends to be governed by the thermal mass of the assembly and jig. Forced cooling can lead to problems such as exacerbating mismatch stresses. Occasionally, one or more dwell stages are required, either to provide stress relief to the bonded assembly or to induce some requisite microstructural change. An example of the latter is joining of tool steels with copper. The brazing operation is performed at 1120 °C (2050 °F) for a few minutes, but the assembly is cooled to only approximately 850 °C (1560 °F). This temperature is maintained for about an hour in order to convert the base material to the austenitic phase. The component is then quench-cooled in oil and finally tempered at about 500 °C (930 °F) to achieve the desired hardness. Another example is the solution treatment, quench and temper, steps necessary to endow copper-beryllium alloys with their “spring-like” properties. In this process the components are solution treated at 760 to 790 °C (1400 to 1455 °F), water quenched, and then aged at 315 to 345 °C (600 to 655 °F).

A heat treatment temperature of about 75% of the melting point (solidus temperature) of the filler metal in Kelvin usually provides the optimal relief of residual stresses. For many steel components, controlled cooling is vital in order to achieve the desired microstructure and hence the correct temper. Stainless steels are susceptible to surface cracking if a martensitic transition is allowed to occur, owing to the associated volumetric strain. This phase change can be prevented by performing an isothermal anneal above the transition temperature; thereafter, the component should be cooled sufficiently slowly to prevent cracks from developing.

There are also situations in which a particular bonding cycle is required to dovetail with other thermal processes that are required in the fabrication of the assembly, for example spheroidization of the graphite particles in cast iron, to give it a steellike strength and ductility. In such instances, the economics of production of the complete assembly often need to be taken into account when specifying the parameters of the process cycle.

### 1.3.2.10 Post-Joining Treatments

Various types of post-joining treatments can be applied, by far the most common of which is

some form of cleaning operation. A cleaning schedule is used to remove flux residues and tarnishing from the components. Flux residues tend to be corrosive, particularly those containing halide species as active ingredients. These become reactive in moist air and they can affect the long-term reliability of components in service. Both chemical and mechanical means of flux residue removal are employed. Most brazing flux residues are soluble in hot water to a greater or lesser extent, particularly if the solution is mildly acidic. If the assembly can withstand quench cooling, the thermal shock helps crack and craze the solidified glassy flux residue, facilitating its removal. Ultrasonic agitation can also be used. If the brazing operation is conducted in air, components are often disfigured with oxide bloom. This is usually removed by an acid pickle and/or mechanical polishing. Stop-off compounds mostly have to be removed by mechanical means.

There are two alternatives to cleaning: use a fluxless process, or simply not clean at all.

At face value, fluxless processes are highly attractive because no flux is present and therefore no cleaning of residues is required. However, fluxless processes are more difficult to implement and tend to be incompatible with low cost, volume manufacturing. In order to obtain satisfactory wetting and spreading, the process atmosphere needs to be depleted of oxygen and water vapor to levels that can be obtained only in closed vessels. Details on fluxless brazing are given in Chapter 3, section 3.4.

The ultimate alternative to cleaning is simply not to do it. Cleaning adds to the capital and consumable process cost and results in an assembly yield loss. Provided the flux residues do not adversely impact the reliability of the product, then the merits of cleaning are questionable. Aluminum heat exchangers are manufactured by the tens of thousand per annum using a process that uses a flux with residues that are stable under normal environmental conditions for the typical life of such products. However, the presence of halides in many brazing fluxes presents a significant corrosion risk because these compounds are aggressive toward most base metals, especially in the presence of moisture. It is possible to manage this risk, to a degree, by sealing the joint area with an impervious lacquer or paint. Obviously for life- or mission-critical products, cleaning will probably always be undertaken, but in many instances, accepting a compromise

of a finite life may be considered a technically and economically sound approach.

### 1.3.2.11 Statistical Process Control

All processes are subject to variation, and achieving stability of processes is an important step in any quality improvement program. The application of statistics to monitor and control the variability is termed *statistical process control* (SPC) [Ledolter and Burrill 1999]. Many industrial brazing processes are subject to SPC. A modern jewelry chain assembly line can achieve joint defect rates of a few parts per million (ppm). This means that, quite literally, only one or two brazed joints in every million made would fail a quality inspection. This degree of manufacturing consistency is achieved only through SPC.

A fundamental tool in SPC is a graphical display, known as a control chart. This chart provides the basis for deciding whether the variation in the output of a process is due to common, randomly occurring variations or to unusual causes, which requires investigation and action. The control chart is a chronological plot of particular characteristics, such as joint strength or peak reflow temperature, sampled at periodic intervals. This information furnishes data on the process stability and provides an understanding of improvements, where made. Whenever a significant deviation from the norm is detected, a decision can be made to adjust a process variable in order to restore the output to the required quality level. Obviously, to accomplish this, there must be a proper understanding of the relationship between the process variables and the output.

There are different types of control charts, designed for different situations, which are classified by the type of data they contain. Control charts designed to monitor the proportion of defective items are referred to as p-charts, while charts that track the number of defects in the product are known as c-charts. Both are used to describe attribute data, that is, a record of the presence and absence of certain characteristics. Quantitative data are monitored using a mean or x-bar chart, while process variability is measured using range charts (r-chart) and standard deviation charts (s-chart).

The basis of SPC is, for each parameter tracked, to select upper- and lower-control limits (see Fig. 1.32). These limits are set at a multiple number of standard deviations from the

mean such that there will be a high probability that the data will fall between these limits when the process is working as desired. Intervention is required only when the process metrics drift further from the acceptable average.

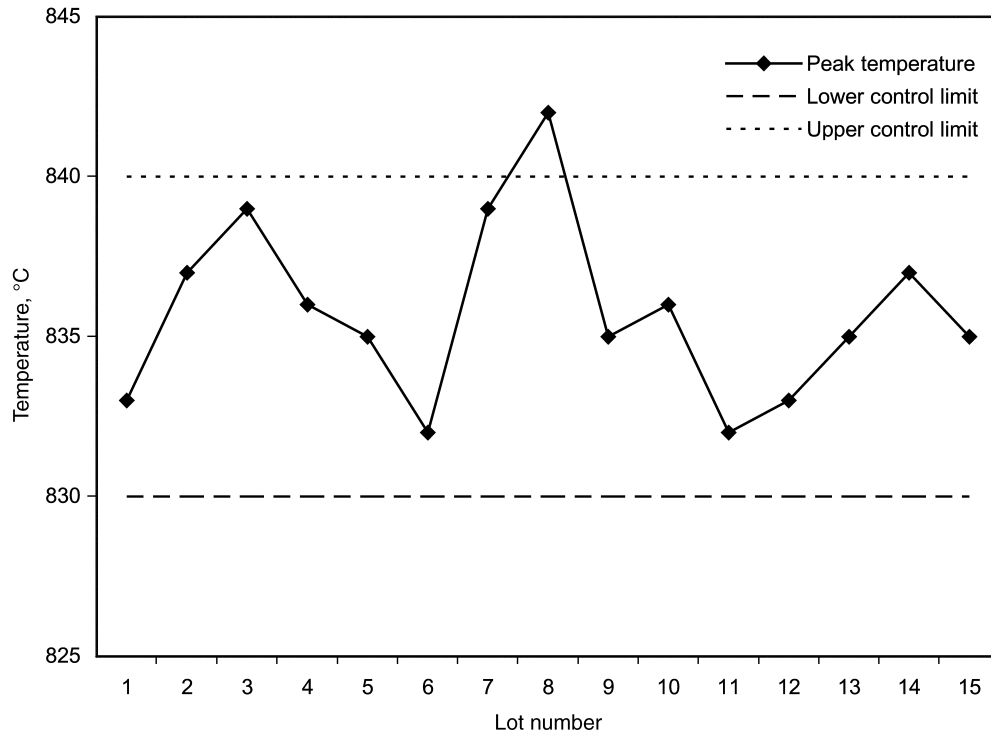
It is possible to apply SPC to virtually any process or machine output. In many instances this methodology provides a highly effective basis for controlling manufacturing processes. As with any tool, it is necessary to use some discretion and critical thought to ensure that SPC is appropriate and the cost of implementing and sustaining it is justified.

### 1.3.3 Health, Safety, and Environmental Aspects of Brazing

Brazing encompasses the use of a large number of different materials, covering metallic and nonmetallic elements for the fillers and the parent materials, and organic and inorganic chemicals used in fluxes, controlled atmospheres, and for removing flux residues. Several of these materials are hazardous in varying degrees to the operators, or to the environment [Sax and Lewis 1989]. Accordingly, they must be handled, used, and disposed of as appropriate, according to national codes of practices or regulations governing hazardous substances. Official listings produced by national health and safety authorities classify materials according to their toxicity level, e.g., the exposure limits for hazardous vapors and dusts.

The main problem with brazes and brazing fluxes arises when they are heated to make a joint in air. The fume contains a cocktail of gases that can cause eye and nose irritation, dermatitis, asthma, and respiratory problems. The fume contains fine particles, in the range 0.1 to 1  $\mu\text{m}$  (4–40  $\mu\text{in.}$ ), which is the most dangerous size distribution for causing long-term lung damage. The recommended solution is to ensure that the workplace or work chamber is ventilated using an appropriately designed extraction system that is able to exhaust the gases and trap the particulates [Jakeway 1994]. Preventing exposure to the hazard by appropriate measures should always be given higher priority than protective measures.

All materials that are likely to be encountered in a joining context will have an assigned value of maximum exposure limit, usually in weight per unit volume (normally in  $\text{mg}/\text{m}^3$ ). Examples



**Fig. 1.32** Statistical process control (SPC) chart for peak process temperature measured at a test point on a component, showing the upper- and lower-control (i.e., intervention) points for this process

of occupational exposure limits for metals commonly used in brazing alloys, constituents of brazing fluxes, and fumes from brazing torches are given in Table 1.6. The difference between the long- and short-term exposure limits reflects the capability of the average constitution to excrete ingested material. The form of the material is also relevant. Powders and dusts are more hazardous than nonvolatile liquids and monolithic solids. Both are ranked according to the maximum inhalable quantity in  $\text{mg}/\text{m}^3$ , time weighted over a period of time, either short term, meaning minutes, or over a longer period of many hours. For correct interpretation of the rules, regulations and audits, reference should always be made to a qualified safety practitioner because there are often legal aspects to consider also.

Care must be taken also in the storage of materials both prior to use and in the procedures for the subsequent disposal of residues, exhaust emissions, and other associated effluent, such as solutions containing rinsed fluxes. These are usually subject to statutory controls. For many organic chemicals and gases, in this context

binders used in flux pastes and halogenated gases, there may also be fire risks to consider. The flammability is rated according to flash-point, which is the lowest temperature at which the substance can spontaneously ignite when it is in a saturated condition.

**Table 1.6** Guidance occupational exposure limits for metals commonly used in brazing alloys, constituents of brazing fluxes, and fumes from brazing torches

Element or compound	8 h exposure limit, $\text{mg}/\text{m}^3$	10 min exposure limit, $\text{mg}/\text{m}^3$
Cadmium oxide fume	0.05	0.05
Copper fume	0.2	...
Manganese fume	1.0	3.0
Nickel	0.5	...
Silver	0.1	...
Zinc oxide fume	5.0	10.0
Hydrogen fluoride fume	...	2.5
Fluorine	2.5	...
Boron trifluoride	...	3.0
Nitric oxide	30	45
Nitrogen dioxide	5	9

The user should consult suppliers' materials safety data sheets (MSDS) and national health and safety standards. Ellipses indicate that there is no established limit. Values are time-weighted averages.

## Appendix A1.1 Relationships Among Spread Ratio, Spread Factor, and Contact Angle of Droplets

Expressions describing the spread of a molten metal droplet are derived under the following set of idealized conditions:

- The original metal pellet is in the form of a spherical bead of radius  $a$  (and diam  $D = 2a$ ).
- The droplet resolidifies after spreading on the substrate as a spherical cap of radius  $R$  and height  $h$ , its interface with the substrate having a diameter  $2A$ , as shown in Fig. 1.33.
- The volume of the original pellet is equal to the volume of the resolidified droplet. This means that any volatilization of the molten droplet and reaction with the substrate do not affect its volume measurably.

The volume of the spherical cap is

$$V = \frac{1}{6} \pi h(h^2 + 3A^2)$$

### Spread Ratio and Contact Angle

The spread ratio,  $S_r$  is defined as:

$$S_r = \frac{\text{Plan area of spread on the substrate surface}}{\text{Plan area of the original spherical pellet}}$$

$A$  and  $a$  are related by the conservation of the volume of the droplet, that is:

$$V = \frac{4}{3} \pi a^3 = \frac{1}{6} \pi h(h^2 + 3A^2)$$

Therefore:

$$a = \frac{1}{2} [h(h^2 + 3A^2)]^{1/3}$$

and

$$S_r = \frac{4A^2}{[h(h^2 + 3A^2)]^{2/3}}$$

From the geometry (Fig. 1.33),  $A = R \cdot \sin\theta$  and  $h = R \cdot (1 - \cos\theta)$ :

$$S_r = \frac{4A^2/h^2}{(1 + 3A^2/h^2)^{2/3}} = \frac{4\cot^2\theta/2}{(1 + 3\cot^2\theta/2)^{2/3}}$$

for  $0^\circ < \theta < 180^\circ$

### Spread Factor and Contact Angle

The spread factor is defined by the formula:

$$S_f = \frac{D - h}{D} = \frac{(h^3 + 3A^2h)^{1/3} - h}{(h^3 + 3A^2h)^{1/3}} = 1 - \frac{1}{(1 + 3A^2/h^2)^{1/3}} = 1 - \frac{1}{(1 + 3\cot^2\theta/2)^{1/3}}$$

for  $0^\circ < \theta < 180^\circ$

### Contact Angle and the Dimensions of the Solidified Pool of Filler

From Fig. 1.33 it can be seen that:

$$A^2 + (R - h)^2 = R^2$$

according to the Pythagorean Theorem.

Rearranging this equation:

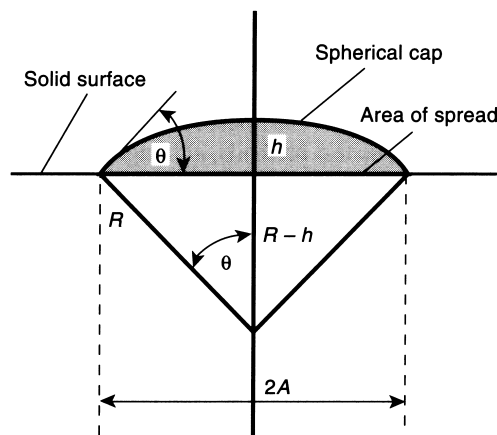


Fig. 1.33 Spherical cap geometry



$$R = \frac{A^2 + h^2}{2h}$$

Therefore:

$$\sin\theta = \frac{2}{(A/h) + (h/A)}$$

# Background: History of Brazing

## References

- F. Bradbury, 1912. *History of Old Sheffield Plate*, MacMillan doi: [10.5479/sil.136812.39088002812014](https://doi.org/10.5479/sil.136812.39088002812014)
- H.R. Brooker, E.V. Beatson, and P.M. Roberts, 1975. *Industrial Brazing*, 2nd ed., Newnes-Butterworth
- E.R. Caley, 1926. The Leiden Papyrus X, *J. Chemical Education*, Vol 3, p 1149–1168 doi: [10.1021/ed003p1149](https://doi.org/10.1021/ed003p1149)
- G. Hawthorne and C.S. Smith, (Ed. and Transl.), 1963. *On Divers Arts; The Treatise of Theophilus*, Chicago University Press
- J. Lang and M.J. Hughes, 1991. *Joining Techniques*, in *Aspects of Early Metallurgy, British Museum Occasional Papers No. 17*, British Museum, p 169–177
- H. Maryon, 1936. Soldering and Welding in the Bronze and Early Iron Ages, *Technical Studies*, (No. 5), p 75–108
- H. Rackham (Transl.), 1952. *Pliny: Natural History*, Vol 10, Harvard University Press
- J. Wolters, 1883. *Die Granulation: Geschichte und Technik einer alten Goldschmiedekunst*, Callwey [in German]

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## References

- J.C. Ambrose, M.G. Nicholas, and A.M. Stoneham, 1992. Kinetics of Braze Spreading, *Proc. Conf. British Association for Brazing and Soldering*, 1992 Autumn Conference, Coventry, U.K. doi: [10.1016/0956-7151\(92\)90317-8](https://doi.org/10.1016/0956-7151(92)90317-8)
- E.N.C. Andrade, 1952. The Viscosity of Liquids, *Proceedings of the Royal Society, A*, Vol 215, p 36–356 doi: [10.1098/rspa.1952.0193](https://doi.org/10.1098/rspa.1952.0193)
- R Asthana. and N. Sobczak, 2000. Wettability, Spreading and Interfacial Phenomena in High Temperature Coatings, *J. Mater. Sci.*, Vol 52 (No. 1), <http://www.tms.org/pubs/journals/JOM/0001/Asthana/Asthana-0001-text.html>
- S.S. Bakulin, M.Kh. Shorshorov, and A.E. Shapiro, 1992. A Thermodynamic Approach to Optimising the Width of the Brazing Gap and the Amount of Brazing Alloy, *Weld. Int.*, Vol 6 (No. 6), p 473–475 doi: [10.1080/09507119209548226](https://doi.org/10.1080/09507119209548226)
- M.B. Bever, Ed., 1986. *Encyclopedia of Materials Science and Engineering*, Pergamon Press
- K.A. Brakke, 2003. “Surface Evolver,” Version 2.20, Susquehanna University, PA, <http://www.susqu.edu/brakke>
- P.G. de Gennes, 1985. Wetting: Statistics and Dynamics, *Reviews of Modern Physics*, Vol 57 (No. 3), p 827–863 doi: [10.1103/RevModPhys.57.827](https://doi.org/10.1103/RevModPhys.57.827)
- J.W. Elmer and J.D. Kautz, 1993. Fundamentals of Friction Welding, *ASM Handbook*, Vol 6, *Welding, Brazing, and Soldering*, ASM International doi: [10.31399/asm.hb.v06.a0001349](https://doi.org/10.31399/asm.hb.v06.a0001349)
- N. Eustathopoulos and L. Coudurier, 1979. Wettability and Thermodynamic Properties of Interfaces in Metallic Systems, *Proc. Conf. British Association for Brazing and Soldering*, Third International Conference (London, U.K.), Paper 5
- Feature, 1976. Diffusion Bonding—Tomorrow’s Low-Cost Fabrication Tool, *Met. Mater.*, Feb, p 37–39
- W. Feduska, 1959. High-Temperature Brazing Alloy—Base Metal Wetting Reactions, *Weld. J. Res. Suppl.*, Vol 38 (No. 3), p 122s–130s
- M.J. Fleetwood *et al.*, 1988. Control of Thin Strip Casting, Proceedings of the Second International Conference on Rapidly Solidified Materials, March 7–9 (San Diego, CA)

- J.A. Hawk *et al.*, 1993. Self-Propagating, High Temperature Synthesis as a Technique to Join Metals, *Materials Research Society Symposium Proceedings*, Vol 314, p 183–196 doi: [10.1557/PROC-314-183](https://doi.org/10.1557/PROC-314-183)
- C. Heiple, W. Bennette, and I. Rising, 1982. Embrittlement of Several Stainless Steels by Liquid Copper and Liquid Braze Alloys, *Mater. Sci. Eng.*, Vol 52, p 277–289 doi: [10.1016/0025-5416\(82\)90157-4](https://doi.org/10.1016/0025-5416(82)90157-4)
- A. Hill and E.R. Wallach, 1989. Modeling Solid State Diffusion Bonding, *Acta Mater. Metall.*, Vol 37 (No. 9), p 2425–2437 doi: [10.1016/0001-6160\(89\)90040-0](https://doi.org/10.1016/0001-6160(89)90040-0)
- J.M. Howe, 1993. Bonding, Structure and Properties of Metal/Ceramic Interfaces: Part 1 Chemical Bonding, Chemical Reaction and Interfacial Structure, *Int. Mater. Rev.*, Vol 38 (No. 5), p 233–256 doi: [10.1179/imr.1993.38.5.233](https://doi.org/10.1179/imr.1993.38.5.233)
- G. Humpston *et al.*, 1992. Recent Developments in Silicon/Heat-Sink Assemblies for High Power Device Applications, *GEC Review*, Vol 7 (No. 2), p 62–78
- P. Jakeway, 1994. The Healthy Solderer, *The Health and Safety Practitioner*, April, p 20–23
- R.A. Jarman, G.A.B. Linekar, and C.J.L. Booker, 1975. Interfacial Corrosion of Brazed Stainless Steel Joints in Domestic Tap Water, *Brit. Corros. J.*, Vol 8, p 33–37; Vol 10, p 150–154 doi: [10.1179/000705975798320684](https://doi.org/10.1179/000705975798320684)
- H. Jones, 1982. “Rapid Solidification of Metals and Alloys,” Monograph No. 8, The Institution of Metallurgists
- M. Karavolis, 1993. Self-Brazing Metals Open up Design Options, *Weld. Des. Fabr.*, Vol 66 (No. 12), p 36–37
- D.L. Keller *et al.*, 1990. Wettability of Brazing Filler Metals, *Weld. J. Res. Suppl.*, Vol 69 (No. 10), p 31s–34s
- P. Kritsalis, L. Coudurier, and N. Eustathopoulos, 1991. Contribution to the Study of Reactive Wetting in the CuTi/Al<sub>2</sub>O<sub>3</sub> System, *J. Mater. Sci.*, Vol 26, p 3400–3408 doi: [10.1007/BF01124693](https://doi.org/10.1007/BF01124693)
- K. Landry, C. Rado, and N. Eustathopoulos, 1996. Influence of Interfacial Reaction Rates on the Wetting and Driving Force in Metal/Ceramic Systems, *Metall. Mater. Trans. A*, Vol 27A, p 3181–3186 doi: [10.1007/BF02663868](https://doi.org/10.1007/BF02663868)
- V. Laurent, D. Chatain, and N. Eustathopoulos, 1991. Wettability of SiO<sub>2</sub> and Oxidized SiC by Aluminum, *Mater. Sci. Eng. A*, A135, p 89–94 doi: [10.1016/0921-5093\(91\)90542-U](https://doi.org/10.1016/0921-5093(91)90542-U)
- J. Ledolter and C.W. Burrill, 1999. *Statistical Quality Control—Strategies and Tools for Continual Improvement*, John Wiley and Sons

- A.S. Lee and P.M. Norris, 1997. A New Optical Method for Measuring Surface Temperature at Large Incident Probe Angles, *Rev. Sci. Instr.*, Vol 68, p 1307–1311 doi: [10.1063/1.1147889](https://doi.org/10.1063/1.1147889)
- G. Levi and W.D. Kaplan, 2003a. Aluminium-Alumina Interface Morphology and Thermodynamics from Dewetting Experiments, *Acta Mater.*, Vol 51 p 2793–2802 doi: [10.1016/S1359-6454\(03\)00084-3](https://doi.org/10.1016/S1359-6454(03)00084-3)
- G. Levi and W.D. Kaplan, 2003b. Adhesion and Microstructure at Metal-Ceramic Interfaces, *Proc. Conf. International Symposium on Microelectronics and Packaging*, June 18, Herzliya, Israel
- J.G. Li and H. Hausner, 1991. Wettability of Silicon Carbide by Gold, Germanium and Silicon, *J. Mater. Sci. Let.*, Vol 10, p 1275–1276 doi: [10.1007/BF00720944](https://doi.org/10.1007/BF00720944)
- M.M. McDonald *et al.*, 1989. Wettability of Brazing Filler Metals on Molybdenum and TZM, *Weld. J. Res. Suppl.*, Vol 70 (No. 10), p 398s–395s
- A. Meier, D.A. Javernick, and G.R. Edwards, 1999. Ceramic-Metal Interfaces and the Spreading of Reactive Liquids, *JOM* (No. 1), p 44–47 doi: [10.1007/s11837-999-0209-1](https://doi.org/10.1007/s11837-999-0209-1)
- R.W. Messler, 1999. *Principles of Welding: Processes, Physics, Chemistry and Metallurgy*, John Wiley and Sons doi: [10.1002/9783527617487](https://doi.org/10.1002/9783527617487)
- R.D. Milner, 1958. A Survey of the Scientific Principles Related to Wetting and Spreading, *Brit. Weld. J.*, Vol 5, p 90–105
- M.G. Nicholas, 1989. Metal Surface Energies and Capillarity, Pub. 466, *Physical and Electrical Characterisation of Metals*, M. McLean, Ed., The Institute of Metals, London, U.K., p 177–227
- M.G. Nicholas, 1998. *Joining Processes: Introduction to Brazing and Diffusion Bonding*, Kluwer Academic
- M.G. Nicholas and R.M. Crispin, 1986. Some Effects of Anisotropic Roughening on the Wetting of Metal Surfaces, *J. Mater. Sci.*, Vol 21, p 522–528 doi: [10.1007/BF01145518](https://doi.org/10.1007/BF01145518)
- R.L. O'Brien, Ed., 1991. *Welding Handbook*, Vol 2, *Welding Processes* (8th ed.), American Welding Society
- I. Okamoto, T. Takemoto, and K. Den, 1976. Vacuum Brazing of Aluminium Using Al-12%Si System Filler Alloy, *Trans. Jap. Weld. Res. Inst.*, Vol 5 (No. 1), p 97–98
- M.A. Otooni, Ed., 1995. *Science and Technology of Rapid Solidification and Processing*, Dordrecht: Kluwer Academic doi: [10.1007/978-94-011-0223-0](https://doi.org/10.1007/978-94-011-0223-0)

- N.I. Sax and R.J. Lewis Sr., 1989. *Dangerous Properties of Industrial Materials*, 7th ed., Van Nostrand Reinhold
- M.M. Schwartz, 1990. *Ceramic Joining*, ASM International
- M.M. Schwartz, 2003. *Brazing*, 2nd ed., ASM International
- K.H.W. Seah, J. Hemanth, and S.C. Sharma, 1998. Effect of the Cooling Rate on the Dendrite Arm Spacing and the Ultimate Tensile Strength of Cast Iron, *J. Mater. Sci.*, Vol 33, p 23–28
- M.H. Sloboda, 1961. Design and Strength of Brazed Joints, *Weld. Met. Fabr.*, Vol 7, p 291–296
- T.S. Srivatsan and S. Sudarshan, 1993. *Rapid Solidification Technology: An Engineering Guide*, Technomic
- N. Tunca, G.W. Delamore, and R.W. Smith, 1990. Corrosion of Mo, Nb, Cr, and Y in Molten Aluminium, *Metall. Trans. A*, Vol 21A (No. 11), p 2919–2928 doi: [10.1007/BF02647212](https://doi.org/10.1007/BF02647212)
- R.F. Tylecote, 1967. Diffusion Bonding: Part 1, *Weld. Met. Fabr.*, Vol 35 (No. 12), p 483–489
- R.F. Tylecote, 1968. *The Solid Phase Welding of Metals*, Edward Arnold
- X.H. Wang and H. Conrad, 1995. Kinetics of Wetting Ag and Cu Substrates by Molten 60Sn40Pb, *Metall. Mater. Trans.*, Vol 26A, p 459–469 doi: [10.1007/BF02664682](https://doi.org/10.1007/BF02664682)
- J.R. Weeks and D.H. Gurinsky, 1958. *Liquid Metals and Solidification*, American Society for Metals
- D.A. Weirauch Jr., and W.J. Krafick, 1996. The Spreading Kinetics of Ag-28Cu on Nickel: Part 1, Area of Spread Tests on Nickel Foil, *J. Mater. Res.*, Vol 11 (No. 8), p 1897–1916 doi: [10.1557/JMR.1996.0241](https://doi.org/10.1557/JMR.1996.0241)
- A. Xian, 2000. Thermodynamic Discussion on Young's Equation in Wetting, *Zeitschrift für Metall.*, Vol 91 (No. 4), p 316–322
- F.G. Yost and A.D. Romig, 1988. Thermodynamics of Wetting by Liquid Metals, *Materials Research Society Symposium Proceedings*, Vol 108, p 385–390 doi: [10.1557/PROC-108-385](https://doi.org/10.1557/PROC-108-385)
- Y. Yunchen, Q. Xiaoming, and W. Hongying, 1992. Research on the Welding Behaviour of the Liquid Phase of Eutectic Reaction, *China Weld.*, Vol 1 (No. 1), p 75–82
- I.V. Zvolinskii *et al.*, 1995. Special Features of Brazewelding Metal Matrix Composites, *Weld. Int.*, Vol 9 (No. 1), p 41–43 doi: [10.1080/09507119509548750](https://doi.org/10.1080/09507119509548750)

# Chapter 2: Brazes and Their Metallurgy

## References

- *Alloy Phase Diagrams*, 1992. *ASM Handbook*, Vol 3, ASM International
- B. Altschuller *et al.*, Ed., 1990. *Aluminum Brazing Handbook*, 4th ed., The Aluminum Association Inc.
- J.C. Ambrose and M.G. Nicholas, 1986. Alloys for Vacuum Brazing Aluminum, *Brazing Soldering*, Vol 11 (No. 3), p 374–379
- C.E. Birchenall, 1959. *Physical Metallurgy*, Metallurgy and Metallurgical Engineering Series, McGraw-Hill
- J.D. Boughton and M.H. Sloboda, 1970. Embrittling Effects of Trace Quantities of Aluminum and Phosphorus on Brazed Joints in Steel, *Weld. Met. Fabr.*, Vol 8, p 335–339
- R.C. Bowen and D.M. Peterson, 1987. A Comparison of Rapid Solidification Cast Versus Conventional Die Attach Soft Solders, *IEEE Trans. on Components Hybrids and Manufacturing Technology*, Vol 10 (No. 3), p 341–345 doi: [10.1109/TCHMT.1987.1134764](https://doi.org/10.1109/TCHMT.1987.1134764)
- C. Brukl, H. Nowotny, and F. Benesovsky, 1961. Untersuchungen in der Dreistoffsystemen: V-Al-Si, Nb-Al-Si, Cr-Al-Si Mo-Al-Si bzw. Cr(Mo)-Al-Si, *Monatsh. Chem.*, Vol 92, p 967–980 doi: [10.1007/BF00924762](https://doi.org/10.1007/BF00924762)
- D.A. Canonico, N.C. Cole, and G.M. Slaughter, 1977. Direct Brazing of Ceramics, Graphite and Refractory Metals, *Weld. J. Res. Suppl.*, Vol 56 (No. 8), p 31s–38s doi: [10.2172/4051634](https://doi.org/10.2172/4051634)
- S.K. Chatterjee and Z. Mingxi, 1990. Tin-Containing Brazing Alloys, *Weld. J. Res. Suppl.*, Vol 69 (No. 10), p 37s–42s
- T.H. Chuang *et al.*, 2000. Development of a Low Melting Point Filler Metal for Brazing Aluminum Alloys, *Metall. Mater. Trans. A*, Vol 31A, p 2239–2245 doi: [10.1007/s11661-000-0141-z](https://doi.org/10.1007/s11661-000-0141-z)
- N. DeCristofaro and D. Bose, 1986. Brazing and Soldering with Rapidly Solidified Filler Metals, *Proc. Conf. Rapidly Solidified Materials*, February 3– 5 (San Diego, CA), p 415–424
- N. DeCristofaro and C. Henschel, 1978. Metglass Brazing Foil, *Weld. J. Res. Suppl.*, Vol 57 (No. 7), p 33s–38s

- S.C. Dev *et al.*, 1992. A Copper-Based Brazing Alloy for Electronics Industries, *J. Mater. Sci.*, Vol 27 (No. 24), p 6646–6652 doi: [10.1007/BF01165949](https://doi.org/10.1007/BF01165949)
- A.M. Eagles, S.C. Mitchell, and M. Rebbeck, 1995. Investigation of the Suitability of New High Manganese, Low-Silver Braze Alloys for Joining Steels, *British Association of Brazing and Soldering*, Vol 13, p 8–12
- R.D. Eng, E.J. Ryan, and J.R. Doyle, 1977. Nickel-Base Brazing Filler Metals for Aircraft Gas Turbine Application, *Weld. J. Res. Suppl.*, Vol 56 (No. 10), p 15s–19s
- N. Eustathopoulos, M.G. Nicholas, and B. Drevet, 1999. *Wettability at High Temperatures*, Pergamon
- E.B. Gempler, 1976. Parameters Evaluated in Long Cycle Aluminum Vacuum Brazing, *Weld. J. Res. Suppl.*, Vol 55 (No. 10), p 293s–301s
- M. Hagiwara *et al.*, 1988. Aluminum Brazing Material for use in Aluminum Heat Exchanger, U.S. Patent 4,781,888
- B. Heine and K.F. Sahm, 1993. Flussmittelfrei Hartloten Luftfahrtrelevanter Aluminiumlegierungen mit Niedrigschmelzendem Lot, *Schweissen Schneiden*, Vol 45, p 429–430 (in German)
- A. Hellawell, 1979. The Growth and Structure of Eutectics with Silicon and Germanium, *Progress in Materials Science*, A. Chalmers, J.W. Christian, and T.B. Massalski, Ed., Pergamon Press
- F.M. Hosking *et al.*, 2000. Microstructural and Mechanical Characterisation of Actively Brazed Alumina Tensile Specimens, *Weld. J. Res. Suppl.*, Vol 81 (No. 8), p 222s–230s
- G. Humpston *et al.* 1992. Recent Developments in Silicon/Heat-Sink Assemblies for High Power Applications, *GEC J. Res.*, Vol 9, p 67–78
- G. Humpston and D.M. Jacobson, 1993. *Principles of Soldering and Brazing*, ASM International
- G. Humpston, D.M. Jacobson, and S.P.S. Sangha, 1995. New Filler Metals and Processes for Fluxless Brazing of Aluminum Engineering Alloys, *Mater. Sci. Technol.*, Vol 11, p 1161–1167 doi: [10.1179/mst.1995.11.11.1161](https://doi.org/10.1179/mst.1995.11.11.1161)
- L. Illgen *et al.*, 1991. Preparation of Ductile Al-Ge Soldering Foils by PFC Technique, *Mater. Sci. Eng. A*, Vol 133, p 738–741 doi: [10.1016/0921-5093\(91\)90175-M](https://doi.org/10.1016/0921-5093(91)90175-M)
- K. Ishida and T. Nishizawa, 1990. Co-Cr (Cobalt-Chromium), *Binary Alloy Phase Diagrams*, 2nd ed., T.D. Massalski, Ed., ASM International, p 1180



- D.M., Jacobson *et al.*, 2002, The Development of New Silver-Free Brazing Alloys for Steel Tubular Assembly, *Weld. J. Res. Suppl.*, Vol 81 (No. 8), p 149s–155s
- D.M. Jacobson and G. Humpston, 1995. Lowering the Melting Point of Solders and Brazes by Eutectic Alloying, *GEC J. Res.*, Vol 12, p 112–121
- D.M. Jacobson, G. Humpston, and S.P.S. Sangha, 1996. A New Low Melting Point Aluminum Braze, *Weld. J. Res. Suppl.*, Vol 75 (No. 8), p 243s–249s
- A. Johnson, 1990. Evidence for Au-Si Bonding in Liquid Gold-Silicon Alloys from Electrical Resistivity Measurements, *Solid State Commun.*, Vol 76 (No. 6), p 733–775 doi: [10.1016/0038-1098\(90\)90625-L](https://doi.org/10.1016/0038-1098(90)90625-L)
- S. Kang and H.J. Kim, 1995. Design of High Temperature Brazing Alloys for Ceramic-Metal Joints, *Weld. J. Res. Suppl.*, Vol 74 (No. 9), p 289s–295s
- J.H. Kayamoto *et al.*, 1994. *Proc. Conf. Workshop of the Japanese Welding Society*, Vol 12, p 495–501 (in Japanese) doi: [10.2207/qjjws.12.495](https://doi.org/10.2207/qjjws.12.495)
- T. Kayamoto *et al.*, 1996. Vacuum Brazing 2017 Aluminum Alloy Using Al-Ge-Cu Based Fillers, *J. Jap. Weld. Soc.*, Vol 14 (No. 1), p 63–68 doi: [10.2207/qjjws.14.63](https://doi.org/10.2207/qjjws.14.63)
- A.M. Korol'kov 1956. Effect of Added Elements on the Surface Tension of Aluminum at 700 to 740°C, *Otdelenie Tekhnicheskik Nauk*, Vol 2, p 35–42
- K.J. Lee and P. Nash, 1990. Ni-P (Nickel-Phosphorus), *Binary Alloy Phase Diagrams*, 2nd ed., T.D. Massalski, Ed., ASM International, p 2835
- Y. Liu, G. Shao, and P. Tsakiroopoulos, 2000. Thermodynamic Reassessment of the Mo-Si and Al-Mo-Si Systems, *Intermetallics*, Vol 8 (No. 8), p 953–962 doi: [10.1016/S0966-9795\(00\)00068-6](https://doi.org/10.1016/S0966-9795(00)00068-6)
- E. Lugscheider and Th. Schittny, 1988. Wide Gap Brazing of Stainless Steel and Carbon Steel, *Brazing Soldering*, Vol 14 (No. 1), p 27–29
- E. Lugscheider and W. Tillmann, 1991. Development of New Active Filler Metals for Joining Silicon Carbide and Nitride, Paper 11, *Proc. Conf. British Association for Brazing and Soldering*, September 3– 5 (Stratford-upon-Avon, U.K.)
- C.J. Miller 1969. Fluxless Aluminum Brazing furnace, U.S. Patent 3,460,816
- V.R. Miller and A.E. Schwaneke, 1978. Interfacial Compositions of Silver Filler Metals on Copper, Brass and Steel, *Weld. J. Res. Suppl.*, Vol 57 (No. 10), p 303s–310s
- H. Mizuhara and K. Mally, 1985. Ceramic-to-Metal Joining with Active Brazing Filler Metal, *Weld. J. Res. Suppl.*, Vol 64 (No. 10), p 27s–32s

- W. Muller and D. Ruhlicke, 1991. Microcrystalline Aluminum-Germanium Solder Foil for Chip Bonding, *Metallwissenschaft und Technik*, Vol 45 (No. 1), p 41–45
- M.G. Nicholas, 1998. *Joining Processes: Introduction to Brazing and Diffusion Bonding*, Kluwer Academic
- J.T. Niemann and G.W. Wille, 1978. Fluxless Diffusion Brazing of Aluminum Castings, *Weld. J. Res. Suppl.*, Vol 57 (No. 10), p 285s–291s
- G. Petzow and F. Aldinger, 1968. Nonvariante Gleichgewichte und Schmelzraume im System Silber-Kupfer-Zink-Kadmium, *Z. Metallkd.*, Vol 59 (No. 2), p 145–153; Vol 59 (No. 5), p 390–395; Vol 59 (No. 7), p 583–589 doi: [10.1515/ijmr-1968-590508](https://doi.org/10.1515/ijmr-1968-590508)
- A. Rabinkin, 1998. Stability to Aging of Copper-to-Copper Joints Brazed with Metglas MBF-2005 and BCuP-5 Filler Metals, *Weld. J. Res. Suppl.*, Vol 77 (No. 10), p 29s–30s
- A. Rabinkin and H.H. Liebermann, 1993. Brazing and Soldering with Rapidly Solidified Alloys, *Rapid Solidified Alloys, Processes, Structures, Properties and Applications*, H.H. Liebermann, Ed., Dekker doi: [10.1201/9781482233995](https://doi.org/10.1201/9781482233995)
- A. Rabinkin, E. Wenski, and A. Ribaud, 1998. Brazing Stainless Steel Using a New MBF-Series of Ni-Cr-B-S-Amorphous Brazing Foils, *Weld. J. Res. Suppl.*, Vol 77 (No. 2), p 66s–75s
- N.N. Samsonova and P.D. Budberg, 1995. Cr-Ti-V, *Handbook of Ternary Alloy Phase Diagrams*, Vol 7, Villars, Prince, and Okamoto, Ed., ASM International, p 9261
- W. Schultze and H. Schoer, 1973. Fluxless Brazing of Aluminum Using Protective Gas, *Weld. J. Res. Suppl.*, Vol 52 (No. 10), p 644–651
- M.M. Schwartz, 2003. *Brazing*, ASM International
- M.H. Sloboda, 1961. Design and Strength of Brazed Joints, *Weld. Met. Fabr.*, Vol 6, p 291–296
- M.H. Sloboda, 1971. Industrial Gold Brazing Alloys, *Gold Bull.*, Vol 4 (No. 1), p 2–8 doi: [10.1007/BF03215128](https://doi.org/10.1007/BF03215128)
- J.J. Stephens and F.A. Greulich, 1995. Elevated Temperature Creep and Fracture Properties of the 62Cu-35Au-3Ni Braze Alloy, *Met. Mater. Trans. A*, Vol 26 (No. 6), p 1471–1482 doi: [10.1007/BF02647598](https://doi.org/10.1007/BF02647598)
- K. Suzuki, M. Kagayama, and Y. Takeucji 1993. *J. Jap. Institute Light Met.*, Vol 43 (No. 10), p 533–538 (in Japanese) doi: [10.2464/jilm.43.533](https://doi.org/10.2464/jilm.43.533)
- P.D. Taylor, 1992. *Thyristor Design and Realisation*, John Wiley and Sons

- P.F. Timmins, 1994. The Development of Non-Toxic Ag-Based Brazing Alloys, *Weld. J. Res. Suppl.*, Vol 73 (No. 9), p 31s–33s
- I. Tuah-Poku, M. Dollar, and T.B. Massalski, 1988. A Study of the Transient Liquid Phase Bonding Process Applied to a Ag/Cu/Ag Sandwich Joint, *Metall. Trans. A*, Vol 19A (No. 3), p 675–686 doi: [10.1007/BF02649282](https://doi.org/10.1007/BF02649282)
- P. Villars *et al.*, 2001. Binary, Ternary and Quaternary Compounds Former/Nonformer Prediction via Mendeleev Number, *J. Alloy. Compd.*, Vol 317– 318, April 12, p 26–38 doi: [10.1016/S0925-8388\(00\)01410-9](https://doi.org/10.1016/S0925-8388(00)01410-9)
- J. Werner, G.M. Slaughter, and F.B. Gurtner, 1972. Development of Filler Metals and Procedures for Vacuum Brazing of Aluminum, *Weld. J. Res. Suppl.*, Vol 53 (No. 2), p 64s–70s

# Chapter 3: The Joining Environment

## References

- *Aluminum Brazing Handbook*, 1990. The Aluminum Association, Inc.
- J.C. Ambrose and M.G. Nicholas, 1986. Alloys for Vacuum Brazing Aluminium, *Brazing Soldering*, Vol 11 (No. 3), p 374–379
- W.A. Anderson, 1977. The Effects of Metallurgical Structure on the Brazing of Aluminum, *Proc. Symp. Physical Metallurgy of Joining Metals*, Warrendale, Pennsylvania, p 222–243
- J.N. Antonevich, 1976. Fundamentals of Ultrasonic Soldering, *Weld. J. Res. Suppl.*, Vol 55 (No. 7), p 200s–207s
- A.J. Ashby, 1993. Equipment Used in the Controlled Atmosphere Brazing of Aluminium Heat Exchangers, *Proc. Conf. Advances in Brazing and Soldering Technology*, Solihull, October 20, 1993
- Z. Bangwei *et al.*, 1993. Fundamental Research for Cu-P Based Amorphous Filler Alloys, *China Weld.*, Vol 2 (No. 2), p 95–103
- T.S. Bannos, 1984. The Effect of Atmosphere Composition on Braze Flow, *Heat Treatment*, Vol 16, (No. 4), p 26–31
- J.B. Boughton and M.H. Sloboda, 1970. Embrittling Effects of Trace Quantities of Aluminium and Phosphorus on Brazed Joints in Steel, *Weld. Met. Fabr.*, Vol 8, p 335–339
- S.K. Chatterjee and Z. Mingxi, 1990. Tin-Containing Brazing Alloys, *Weld. J. Res. Suppl.*, Vol 69 (No. 10), p 37s–42s
- W.E. Cooke, T.E. Wright, and J.A. Hirschfield, 1978. Furnace Brazing of Aluminum with a Non-Corrosive Flux, *SAE Technical Paper Series No. 780300*, Society of Automotive Engineers doi: [10.4271/780300](https://doi.org/10.4271/780300)
- A. Datta, A. Rabinkin, and D. Bose, 1984. Rapidly Solidified Copper-Phosphorus Base Brazing Foils, *Weld. J. Res. Suppl.*, Vol 63 (No. 10), p 14s–21s
- E.N. Dorofeeva, 1993. Modifying Copper-Phosphorus Alloys for Brazing Alloys, *Paton Weld. J.*, Vol 46 (No. 2), p 101–105 (Translated from *Avtomaticheskaya Svarka*, 1993, Vol 46 (No. 2), p 24–27)

- A.E. Esquivel and E. Chavez, 1992. Benefits of Using Carbonic Gas in the Soldering Process and Curing Oven for Electronic Assemblies, *Proc. Conf., NEPCON West '92*, February 23–27, (Anaheim, CA), p 219–227
- N. Eustathopoulos, M.G. Nicholas, and B. Drevet, 1999. *Wettability at High Temperatures*, Pergamon Press
- E.B. Gempler, 1983. Parameters Evaluated in Long Cycle Aluminum Vacuum Brazing, *Weld. J. Res. Suppl.*, Vol 49 (No. 11), p 843s–849s
- H.K. Herr, 1983. *Aluminum Fluxless Vacuum Brazing*, The Aluminum Association Inc.
- D.M. Jacobson, G. Humpston, and S.P.S. Sangha 1996. A New Low-Melting-Point Aluminum Braze, *Weld. J. Res. Suppl.*, Vol 75 (No. 8), p 243s–250s
- J.B. Jones and J.G. Thomas, 1956. Ultrasonic Soldering of Aluminum, *Proc. Symp. Symposium on Solder*, American Society for Testing and Materials, June 19–20, Atlantic City, p 15–29
- M.F. Jordan and D.R. Milner, 1951. The Removal of Oxide from Aluminium by Brazing Fluxes, *J. Inst. Met.*, Vol 85, p 33–40
- M. Martin and E. Fromm, 1977. Low-Temperature Oxidation of Metal Surfaces, *J. Alloy. Compd.*, Vol 258, p 7–16
- B. McGurran and M.G. Nicholas, 1984. A Study of Aluminum Brazing Filler Metals Using Hot Stage Scanning Electron Microscopy, *Weld. J. Res. Suppl.*, Vol 64 (No. 10), p 295s–299s.
- D.R. Milner, 1958. A Survey of the Scientific Principles Related to Wetting and Spreading, *Br. Weld. J.*, Vol 6, p 90–105
- R.D. Mottram, A.S. Wronski, and A.C. Chilton, 1986. Brazing Copper to Mild Steel and Stainless Steels Using Copper-Phosphorus-Tin Pastes, *Weld. J. Res. Suppl.*, Vol 65 (No. 4), p 43s–46s
- H. Scheffer *et al.*, 1962. How to Ultrasonically Seal Hermetic Ceramic Transistor Packages, *Ceram. Ind.*, Vol 79 (No. 6), 50–64
- W. Schultze and H. Schoer, 1973. Fluxless Brazing of Aluminium Using Protective Gas, *Weld. J. Res. Suppl.*, Vol 52 (No. 9), p 644s–651s
- M.M. Schwartz, 2003. *Brazing*, ASM International
- O.R. Singleton, 1970. A Look at the Brazing of Aluminum—Particularly Fluxless Brazing, *Weld. J. Res. Suppl.*, Vol 49 (No. 11), p 843s–849s

- H.D. Solomon, R.E. Delair, and J. Thyssen, 2003. The High Temperature Wetting Balance and the Influence of Grit Blasting on Brazing of IN718, *Weld. J. Res. Suppl.*, Vol 72 (No. 10), p 278s–287s
- C.A. Stubbington, 1988. Materials Trends in Military Airframes, *Metals and Mater.*, Vol 4 (No. 7), p 424–431
- T. Takemoto and I. Okamoto, 1988. Effects of Magnesium Content in Brazing Sheet Claddings on the Vacuum Brazeability of Aluminum in Relatively Enclosed Volumes, *Brazing Soldering*, Vol 15 (No. 3), p 32–36
- J.T. Terrill *et al.*, 1971. Understanding the Mechanisms of Aluminum Brazing. *Weld. J. Res. Suppl.*, Vol 50 (No. 12), p 833s–839s
- R.S. Timsit and B.J. Janeway, 1994. A Novel Brazing Technique for Aluminum, *Weld. J. Res. Suppl.*, Vol 73 (No. 6), p 119s–128s
- *Welding, Brazing and Soldering*, 1993. *ASM Handbook*, Vol 6, ASM International
- C.E. Wicks and F.E. Block, 1963. “Thermodynamic Properties of 65 Elements – Their Oxides, Halides, Carbides and Nitrides,” U.S. Bureau of Mines, Bull. 605, U.S. Government Printing Office
- D.A. Wigley, P.G. Sandefur, and P.L. Lawing, 1981. Preliminary Results on the Development of Vacuum Brazed Joints for Cryogenic Wind Tunnel Aerofoil Models, Proc. Conf. International Cryogenic Materials Conference, August 10–14, (San Diego, CA) doi: [10.1007/978-1-4613-3542-9\\_90](https://doi.org/10.1007/978-1-4613-3542-9_90)
- W.L. Winterbottom, 1984. Process Control for Brazing Aluminum Under Vacuum, *Weld. J. Res. Suppl.*, Vol 63, p 33s–39s
- W.L. Winterbottom and G.A. Gilmour, 1976. Vacuum Brazing of Aluminum: Auger Studies of Wetting and Flow Characteristics, *J. Vac. Sci. Technol.*, Vol 13 (No. 2), p 634–643 doi: [10.1116/1.569048](https://doi.org/10.1116/1.569048)

# Chapter 4: The Role of Materials in Defining Process Constraints

## References

- M.F. Ashby, 1994. *Materials Selection in Mechanical Design*, Pergamon Press
- *ASM Handbook*, Vol 13A, ASM International. *Corrosion: Fundamentals, Testing, and Protection*, 2003
- J. Barranger, 1989. Critical Parameters of Measurement Using the Wetting Balance, *Solder. Surf. Mt. Technol.*, Vol 1 (No. 2), p 11–13 doi: [10.1108/eb037659](https://doi.org/10.1108/eb037659)
- M.B. Bever, ed., 1986. *Encyclopaedia of Materials Science and Engineering*, Pergamon Press
- *Brazing Handbook*, 4th ed., 1991. American Welding Society
- N. Bredzs, 1954. Investigation of Factors Determining the Tensile Strength of Brazed Joints, *Weld. J. Res. Suppl.*, Vol 43 (No. 11), p 545s–562s
- E.M. Breinan and K.G. Kreider, 1969. Braze Bonding and Joining of Aluminum Boron Composites, *Met. Eng. Quart.*, Vol 9 (No. 11), p 192–202
- J. Cao and D.D.L. Chung, 1992. Carbon Fibre Silver-Copper Brazing Filler Composites for Brazing Ceramics, *Weld. J. Res. Suppl.*, Vol 71 (No. 1), p 21s–24s
- I.P. Chekunov, 1996. A Composite Brazing Alloy for Stainless Steel and Creep Resistant Steels, *Weld. Int.*, Vol 10 (No. 9), p 735–738 doi: [10.1080/09507119609549081](https://doi.org/10.1080/09507119609549081)
- G.E. Dieter, 1976. *Mechanical Metallurgy*, 2nd ed., McGraw-Hill
- A.M. Eagles, S.C. Mitchell, and A.S. Wronski, 1995. Electrodeposition of Copper or Nickel Barrier Layers on Steels to Produce Strong Joints Using a Copper-Phosphorus Brazing Alloy, *British Association for Brazing and Soldering*, (No. 12), p 9–12
- D.D. Eley, 1961. *Adhesion*, Oxford University Press
- N. Eustathopoulos, M.G. Nicholas, and B. Drevet, 1999. *Wettability at High Temperatures*, Pergamon
- J.A. Fernie and K.I. Ironside, 1999. Ceramic Brazing, *Mater. World*, Vol 7 (No. 11), p 686–688

- W.F. Gale *et al.*, 2002. Microstructure and Mechanical Properties of Titanium Aluminide Wide-Gap Transient Liquid Phase Bonds Prepared Using a Slurry-Deposited Composite Interlayer, *Metall. Mater. Trans. A*, Vol 33A (No. 10), p 3205–3214 doi: [10.1007/s11661-002-0306-z](https://doi.org/10.1007/s11661-002-0306-z)
- H.H. Glascock and H.F. Webster, 1983. Structured Copper: A Pliable High Conductance Material for Bonding Silicon Power Devices, *IEEE Components Hybrids and Manufacturing Technology*, Vol 6 (No. 4), p 460–466 doi: [10.1109/TCHMT.1983.1136213](https://doi.org/10.1109/TCHMT.1983.1136213)
- J.P. Hammond and G.M. Slaughter, 1971. Bonding Graphite to Metals with Transition Pieces, *Weld. J. Res. Suppl.*, Vol 50 (No. 1), p 33s–40s
- W. Hanson and J. Fernie, 1994. Ceramics in Turbine Applications, *TWI Bull.*, No. 5, p 103–106
- J.A. Harris and R.D. Adams, 1984. Strength Prediction of Bonded Single Lap Joints by Non-Linear Finite Element Methods, *Int. J. Adhes. Adhes.*, Vol 4 (No. 2), p 65–78 doi: [10.1016/0143-7496\(84\)90103-9](https://doi.org/10.1016/0143-7496(84)90103-9)
- T. Haug, W. Schaefer, and R. Schamm, 1989. Joining Electrochemical High Temperature Components, *Proc. 3rd International Conf. Joining Ceramics, Glass and Metal*, W. Kraft, Ed., April 26–28 (Bad Nauheim, Germany), p 171–178
- C.T. Ho and D.D.L. Chung, 1990. Carbon Fiber Reinforced Tin-Lead Alloy as a Low Thermal Expansion Solder Preform, *J. Mater. Res.*, Vol 5 (No. 6), p 1266–1270 doi: [10.1557/JMR.1990.1266](https://doi.org/10.1557/JMR.1990.1266)
- T. Huchisuka, 1986. Bonding of Sintered Alloys, *Met. Technol.*, Vol 56 (No. 5), p 21–27
- T. Iseki, T. Kameda, and T. Murayama, 1984. Interfacial Reactions Between SiC and Aluminium During Joining of MMCs, *J. Mater. Sci.*, Vol 19, p 1692–1698 doi: [10.1007/BF00563067](https://doi.org/10.1007/BF00563067)
- D.M. Jacobson, G. Humpston, and S.P.S. Sangha, 1996. A New Low Melting Point Aluminium Alloy Braze, *Weld. J. Res. Suppl.*, Vol 75 (No. 8), p 243s–249s
- R.A. Jarman, G.A.B. Linekar, and C.J.L. Booker, 1973. Interfacial Corrosion of Brazed Stainless Steel Joints in Domestic Tap Water, Part II: Metallographic Aspects, *Br. Corros. J.*, Vol 10 (No. 3), p 150–154 doi: [10.1179/000705975798320684](https://doi.org/10.1179/000705975798320684)
- R.A. Jarman, J.W. Myles, and C.J.L. Booker, 1973. Interfacial Corrosion of Brazed Stainless Steel Joints in Domestic Tap Water, *Brit. Corros. J.*, Vol 8 (No. 1), p 33–37 doi: [10.1179/000705973798322567](https://doi.org/10.1179/000705973798322567)
- M.E. Kassner *et al.*, 1992. Recent Advances in Understanding the Mechanical Behaviour of Constrained Thin Metals in Brazes and Solid-State Bonds, *The Metal Science of Joining*, M.J. Cieslak *et al.*, Ed., The Minerals, Metals and Materials Society, p 223–232



- A.J. Kinloch, 1982. The Science of Adhesion Part 2: Mechanics and Mechanisms of Failure, *J. Mater. Sci.*, Vol 17, p 617–651 doi: [10.1007/BF00540361](https://doi.org/10.1007/BF00540361)
- S. Kon-ya *et al.*, 1990. New Metallising Process of Alumina Ceramics for Hermetic Sealing, *Proc. Conf. 3rd Electronic Materials and Processing Congress*, Aug 20– 23 (San Francisco, CA), p 19–24
- A.T. Kuhn, R.D. Rawlings, and R. May, 1984. A Potentiometric and Microstructural Study of the Corrosion of Silver-Brazed Stainless Steel Joints, *Brazing Soldering*, Vol 6 (No. 1), p 14–20
- J.F. Lancaster, 1965. *The Metallurgy of Welding, Brazing and Soldering*, George Allen and Unwin Ltd.
- C. Lea, 1991. Quantitative Solderability Measurement of Electronic Components, Part 5: Wetting Balance Instrumental Parameters and Procedures, *Solder. Surf. Mt. Technol.*, Vol 7 (No. 1), p 10–13. doi: [10.1108/eb037739](https://doi.org/10.1108/eb037739)
- G. Levi and W.D. Kaplan, 2002. Oxygen Induced Interfacial Phenomena during Wetting of Alumina by Liquid Aluminum, *Acta Mater.*, Vol 50, p 75–88 doi: [10.1016/S1359-6454\(01\)00333-0](https://doi.org/10.1016/S1359-6454(01)00333-0)
- C.H. Li, 1993. Dynamic Mismatch between Bonded Dissimilar Materials, *JOM*, Vol 45 (No. 6), p 43–46 doi: [10.1007/BF03223310](https://doi.org/10.1007/BF03223310)
- J. Li and V. Krsulich, 1996. “Metal Alloy Applied in Ceramic Package Lids Reduces Stress,” *Semiconductor International*, Feb, p 105–110
- L.C. Lim, W.Y. Lee, and M.O. Lai, 1995. Nickel-Base Wide Gap Brazing with Pre-Placement Technique, *Mater. Sci. Technol.*, Vol 11 (No. 9), p 1041–1045 doi: [10.1179/mst.1995.11.10.1041](https://doi.org/10.1179/mst.1995.11.10.1041)
- P.S. Liu and K.M. Liang, 2000. Preparation and Corresponding Structure of Nickel Foam, *Mater. Sci. Technol.*, Vol 16 (No. 5), p 575–578 doi: [10.1179/026708300101508108](https://doi.org/10.1179/026708300101508108)
- R.W. Messler Jr., M. Jou, and T.T. Orling, 1995. A Model for Designing Functionally Graded Material Joints, *Weld. J. Res. Suppl.*, Vol 74 (No. 5), p 160s–167s
- Y. Miyazawa *et al.*, 1989. Effect of Precompression on the Strength of Ceramic/Steel Joints, *Proc. Conf. Materials Research Society International Meeting on Advanced Materials* (Tokyo, Japan), Vol 8, Metal-Ceramic Joints, p 131–137
- H. Mizuhara and K. Mally, 1985. Ceramic-to-Metal Joining with Active Braze Filler Metal, *Weld. J. Res. Suppl.*, Vol 64 (No. 10), p 27s–32s

- A.J. Moorhead, W.H. Elliott, and H.E. Kim, 1993. Brazing of Ceramics and Ceramic-to-Metal Joints, *Welding, Brazing, and Soldering*, Vol 6, *ASM Handbook*, ASM International doi: [10.31399/asm.hb.v06.a0001457](https://doi.org/10.31399/asm.hb.v06.a0001457)
- K. Nielsen, 1984. Corrosion of Soldered and Brazed Joints in Tap Water, *Brit. Corros. J.*, Vol 19 (No. 2), p 57–63 doi: [10.1179/000705984798273353](https://doi.org/10.1179/000705984798273353)
- H.J. Nolte, 1954a. Method of Metallising Ceramic Member, U.S. Patent 2,667,427
- H.J. Nolte 1954b. Metallised Ceramic, U.S. Patent 2,667,432
- M.G. Norton, 1993. Indirect Bonded Metal-lisation of Aluminum Nitride, *Proc. Symp. Materials Research Society*, Vol 314, p 223–234 doi: [10.1557/PROC-314-223](https://doi.org/10.1557/PROC-314-223)
- C.S. Pershall, 1949. New Brazing Methods for Joining Non-Metallic Materials to Metals, *Mater. Methods*, Vol 30 (No. 6), p 61–62
- A.G. Pincus, 1953. Metallographic Examination of Ceramic Metal Seals, *J. Am. Ceram. Soc.*, Vol 36 (No. 50), p 152–58 doi: [10.1111/j.1151-2916.1953.tb12856.x](https://doi.org/10.1111/j.1151-2916.1953.tb12856.x)
- W.N. Radsijewski, 1992. High Temperature Brazing of Large-Sized Constructions at Wide Joint Clearance, *Proc. Conf. Brazing, High Temperature Brazing and Diffusion Welding*, Aachen, Nov 24– 26, (DVS-Berichte Band 148, Dusseldorf), p 35–37
- M.M. Schwartz, 2003. *Brazing*, 2nd ed., ASM International
- M.H. Sloboda, 1961. Design and Strength of Brazed Joints, *Weld. Met. Fabr.*, Vol 29 (No. 7), p 291–296
- H.D. Solomon, R.E. Delair, and J. Thyssen, 2003. The High Temperature Wetting Balance and the Influence of Grit Blasting on Brazing of IN718, *Weld. J. Res. Suppl.*, Vol 72 (No. 10), p 278s–287s
- F. Thamm, 1976. Stress Distribution in Lap Joints with Partially Thinned Adherends, *J. Adhes.*, Vol 7, p 301–309 doi: [10.1080/00218467608075061](https://doi.org/10.1080/00218467608075061)
- S. Timoshenko, 1925. Analysis of Bi-Metal Thermostats, *J. Optical Society of America and Review of Scientific Instruments*, Vol 11 (No. 9), p 233–255 doi: [10.1364/JOSA.11.000233](https://doi.org/10.1364/JOSA.11.000233)
- D.R. Totty, 1979. Brazing Cast Iron—No Longer a Problem?, Paper 7, Proc. Conf. 3rd International Brazing and Soldering Conference, London, UK
- S.K. Tung and L.C. Lim, 1994. Void Formation in the Wide Gap Brazing Using Pre-Packs of the Nickel Base Braze Mixes, *Mater. Sci. Technol.*, Vol 10 (No. 5), p 364–369 doi: [10.1179/mst.1994.10.5.364](https://doi.org/10.1179/mst.1994.10.5.364)

- S.K. Tung and L.C. Lim, 1995. Wide Gap Brazing with Prepacks of Nickel Base Braze Mixes, *Mater. Sci. Technol.*, Vol 11 (No. 9), p 949–954 doi: [10.1179/mst.1995.11.9.949](https://doi.org/10.1179/mst.1995.11.9.949)
- M.E. Twentyman, 1975. High-Temperature Metallizing, Part I: The Mechanism of Glass Migration in the Production of Metal-Ceramic Seals, *J. Mater. Sci.*, Vol 10, p 765–776 doi: [10.1007/BF01163071](https://doi.org/10.1007/BF01163071)
- M.E. Twentyman and P. Popper, 1975a. High-Temperature Metallizing, Part II: The Effects of Experimental Variables on the Structure of Seals to Debased Aluminas, *J. Mater. Sci.*, Vol 10, p 777–790 doi: [10.1007/BF01163072](https://doi.org/10.1007/BF01163072)
- M.E. Twentyman and P. Popper, 1975b. High-Temperature Metallizing, Part III: The Use of Metallizing Paints Containing Glass or Other Inorganic Bonding Agents, *J. Mater. Sci.*, Vol 10, p 791–798 doi: [10.1007/BF01163073](https://doi.org/10.1007/BF01163073)
- W.J. Werner and G.M. Slaughter, 1968. Brazing Graphite to Hastelloy N for Nuclear Reactors, *Weld. Engineer*, Vol 53, p 65
- X.W. Wu *et al.*, 2001. Wide Gap Brazing of Stainless Steel to Nickel-Based Superalloy, *J. Mater. Process. Technol.*, Vol 113, p 215–221 doi: [10.1016/S0924-0136\(01\)00596-9](https://doi.org/10.1016/S0924-0136(01)00596-9)
- A. Xian and Z. Si, 1992. Interlayer Design for Joining Pressureless Sintered Sialon Ceramic and 40Cr Steel Brazing with Ag57Cu38Ti5 Filler Metal, *J. Mater. Sci.*, Vol 27 (No. 3), p 1560–1566 doi: [10.1007/BF00542918](https://doi.org/10.1007/BF00542918)
- X.F. Yang and X.M. Xi, 1995. Critical Wetting Angle for Spontaneous Liquid Infiltration into Orderly Packed Fibres and Spheres, *J. Mater. Sci.*, Vol 30, p 5099–5102 doi: [10.1007/BF00356055](https://doi.org/10.1007/BF00356055)
- Y.H. Yu and M.O. Lai, 1995. Effects of Gap Filler and Brazing Temperature on Fracture and Fatigue of Wide-Gap Brazed Joints, *J. Mater. Sci.*, Vol 30, p 2101–2107 doi: [10.1007/BF00353041](https://doi.org/10.1007/BF00353041)
- M. Zhu and D.D.L. Chung, 1997. Improving the Strength of Brazed Joints to Alumina by Adding Carbon Fibres, *J. Mater. Sci.*, Vol 32, p 5321–5333 doi: [10.1023/A:1018666827969](https://doi.org/10.1023/A:1018666827969)

# Chapter 5: Filler Metals for Carat Gold and Hallmark Silver Jewelry

## References

- *Alloy Phase Diagrams*, 1992. Vol 3, *ASM Handbook*, ASM International, p 3.5
- C.W. Corti, 2001. Strong 24 Carat Golds: the Metallurgy of Microalloying, *Gold Technology* (No. 33), p 27–36
- C.W. Corti, 2002. Micro-Alloying of 24 Carat Golds: Update, *Gold Technology* (No. 36), p 34
- C.W. Corti, 2004. Blue, Black and Purple! The Special Colours of Gold, *Proc. Conf. 18th Annual Santa Fe Symposium*, May 23– 26 (Albuquerque, NM)
- V. Faccenda, 1999. *Handbook on Finishing in Gold Jewellery Manufacture*, World Gold Council
- M.F. Grimwade, 2002. *Handbook on Soldering and Other Joining Techniques in Gold Jewellery Manufacture*, World Gold Council
- Gold Alloy Data, 1991. Au 990–Ti 10 (“990 gold”), *Gold Bull.*, Vol 24 (No. 1), p 15–19 doi: [10.1007/BF03214715](https://doi.org/10.1007/BF03214715)
- H.H. Hilderbrand, 1993. Gold Solder Pastes, *Gold Technology* (No. 9), p 8–12
- G. Humpston and D.M. Jacobson, 1994. Do 18 Carat Gold Solders Exist?, *Gold Bull.*, Vol 27 (No. 4), p 110–116 doi: [10.1007/BF03214731](https://doi.org/10.1007/BF03214731)
- D.M. Jacobson, 2000. Corinthian Bronze and the Gold of the Alchemists, *Gold Bull.*, Vol 33 (No. 2), p 60–66 doi: [10.1007/BF03216582](https://doi.org/10.1007/BF03216582)
- D.M. Jacobson and S.P.S. Sangha, 1996. A Low Melting Point Solder for 22 Carat Yellow Gold, *Gold Bull.*, Vol 29 (No. 1), p 3–9 doi: [10.1007/BF03214735](https://doi.org/10.1007/BF03214735)
- A.A. Johnson and D.N. Johnson, 1983. The Room Temperature Dissociation of Au<sub>3</sub>Si in Hypereutectic Au-Si Alloys, *Mater. Sci. Eng.*, Vol 61 (No. 3), p 231–235 doi: [10.1016/0025-5416\(83\)90105-2](https://doi.org/10.1016/0025-5416(83)90105-2)
- T.B. Massalski, Ed., *Binary Alloy Phase Diagrams*, 2nd ed., Vol 1, ASM International, 1990

- G. Normandeau, 1992. White Golds: A Review of Commercial Material Characteristics and Alloy Design Alternatives, *Gold Bull.*, Vol 25 (No. 3), p 94–103 doi: [10.1007/BF03214721](https://doi.org/10.1007/BF03214721)
- G. Normandeau, 1996. Cadmium-Free Gold Solder Alloys, *Gold Technology* (No. 18), p 20–24
- D. Ott, 1996. Development of 21 Carat Cadmium-Free Gold Solders, *Gold Technology* (No. 19), p 2–6
- W.S. Rapson, 1990. The Metallurgy of the Coloured Carat Gold Alloys, *Gold Bull.* Vol 23 (No. 4), p 125–133 doi: [10.1007/BF03214713](https://doi.org/10.1007/BF03214713)
- W.S. Rapson and T. Groenewald, 1978. *Gold Useage*, Academic Press
- P. Raw, 2002. Hollow Carat Gold Jewellery from Strip and Tube, *Gold Technology* (No. 35), p 3–10
- M. du Toit *et al.*, 2002. The Development of a Novel Gold Alloy with 995 Fineness and Increased Hardness, *Gold Bull.* Vol 35 (No. 2), p 46–52 doi: [10.1007/BF03214837](https://doi.org/10.1007/BF03214837)

# Chapter 6: Diffusion Brazing

## References

- O.M. Askelsen, 1992. Diffusion Bonding of Ceramics, *J. Mater. Sci.*, Vol 27, p 569–579 doi: [10.1007/BF00554019](https://doi.org/10.1007/BF00554019)
- C. Bocking *et al.*, 1997. Rapid Prototype Tools Using Layer Manufacturing Technology, *GEC J. Technol.*, Vol 14, p 110–14
- C. Bocking, D. Jacobson, and G. Bennett, 2000. Layer Manufacturing of Heat Exchange Elements Using Photochemical Machining, Electroplating and Diffusion Brazing, *Trans IMF*, Vol 78 (No. 6), p 243–246 doi: [10.1080/00202967.2000.11871349](https://doi.org/10.1080/00202967.2000.11871349)
- E.A. Brandes and G.B. Brook, Ed., 1992. *Metals Reference Book*, Butterworth-Heinemann
- R.S. Bushby and V.D. Scott, 1995. Liquid Phase Bonding of Aluminium and Aluminium/Nicalon Composite Using Interlayers of Cu-Ag Alloy, *Mater. Sci. Technol.*, Vol 11 (No. 7), p 643–649 doi: [10.1179/026708395790165336](https://doi.org/10.1179/026708395790165336)
- D.S. Duvall, W.A. Owczarski, and D.F. Paulonis, 1974. TLP Bonding: A New Method for Joining Heat Resistant Alloys, *Weld. J. Res. Suppl.*, Vol 53 (No. 4), p 203s–214s
- M. Elahi and R. Fenn, 1981. The Joining of a Titanium Alloy Using a Copper/Silver Intermediate Layer, *Proc. Conf. Joining of Metals: Practice and Performance*, April 10 (Coventry, UK), p 137–144
- W.F. Gale, 1999. Applying TLP Bonding to the Joining of Structural Intermetallic Compounds, *JOM*, Vol 51 (No. 2), p 49–52 doi: [10.1007/s11837-999-0210-8](https://doi.org/10.1007/s11837-999-0210-8)
- W.F. Gale and S.V. Orel, 1996. A Microstructural Investigation of NiAl/Ni-Si-B/NiAl Transient Liquid Phase Bonds, *J. Mater. Sci.*, Vol 31, p 345–349 doi: [10.1007/BF01139150](https://doi.org/10.1007/BF01139150)
- W.F. Gale *et al.*, 2002. Microstructure and Mechanical Properties of Titanium Aluminide Wide-Gap, Transient Liquid-Phase Bonds Prepared Using a Slurry-Deposited Composite Interlayer, *Met. Mat. Trans. A*, Vol 33A, p 3205–3214 doi: [10.1007/s11661-002-0306-z](https://doi.org/10.1007/s11661-002-0306-z)
- H. Ikawa, Y. Nakao, and T. Isai, 1979. Theoretical Considerations on the Metallurgical Processes in TLP Bonding of Nickel-Based Superalloys, *Trans. Jpn. Weld. Soc.*, Vol 10 (No. 1), p 24–29

- T.I. Khan and E.R. Wallach, 1995. Transient Liquid-Phase Bonding of Ferritic Oxide Dispersion Strengthened Superalloy MA957 Using a Conventional Nickel Braze and a Novel Iron-Base Foil, *J. Mater. Sci.*, Vol 30, p 5151–5160 doi: [10.1007/BF00356063](https://doi.org/10.1007/BF00356063)
- P.H. Khanna *et al.* 2000. Novel Ni/Al/Ni Diffusion Soldered Joints for High Temperature Applications, *Proc. Conf. EuroMat 2000*, Sept 27– 30 1999 (Munich, Germany) p 1–6
- J. Li and P. Xiao, 2001. Joining Ceramic to Metal Using a Powder Metallurgy Method for High Temperature Applications, *J. Mater. Sci.*, Vol 36 (No. 6), p 1383–1387
- W.D. MacDonald and T.W. Eagar, 1992. Transient Liquid Phase Bonding Processes, in M.J. Cieslak *et al.*, Ed., *The Metal Science of Joining*, TMS, p 93–100
- W.D. MacDonald and T.W. Eagar, 1998. Isothermal Solidification Kinetics of Diffusion Brazing, *Met. and Mater. Trans. A*, Vol 29A, p 315–325 doi: [10.1007/s11661-998-0183-1](https://doi.org/10.1007/s11661-998-0183-1)
- H. Nakagawa, C.H. Lee, and T.H. North, 1991. Modelling of Base Metal Dissolution Behavior during Transient Liquid-Phase Brazing, *Metall. Trans. A*, Vol 22A (No. 2), p 543–555 doi: [10.1007/BF02656822](https://doi.org/10.1007/BF02656822)
- M. Nakahashi *et al.*, 1985. Transient Liquid Phase Bonding for Heat Resistant Steels, *J. Jpn. Inst. Met.*, Vol 49 (No. 4), p 285–290 doi: [10.2320/jinstmet1952.49.4\\_285](https://doi.org/10.2320/jinstmet1952.49.4_285)
- M.G. Nicholas, 1998. *Joining Processes, Introduction to Brazing and Diffusion Bonding*, Kluwer Academic
- J.T. Niemann and G.W. Wille, 1978. Fluxless Brazing of Aluminum Castings, *Weld. J. Res. Suppl.*, Vol 57 (No. 10), p 2855s–2915s
- B. Norris, 1986. Liquid Interface Diffusion (LID) Bonding of Titanium Structures, *Proc. Conf. Designing With Titanium*, July 7– 9 (Bristol, UK), p 83–86
- K. Ohsasa, T. Shinmura, and T. Narita, 1999. Numerical Modeling of the Transient Liquid Phase Bonding Process of Ni Using Ni-B-Cr Ternary Filler Metal, *J. Phase Equilibria*, Vol 20 (No. 3), p 199–206 doi: [10.1361/105497199770335721](https://doi.org/10.1361/105497199770335721)
- D.L. Ornellas and E. Catalano, 1974. Diffusion Bonding of Gold to Gold, *Rev. Sci. Instrum.*, Vol 45 (No. 7), p 955 doi: [10.1063/1.1686778](https://doi.org/10.1063/1.1686778)
- W.A. Owczarski, 1962. Eutectic Brazing of Zircaloy 2 to Type 304 Stainless Steel, *Weld. J. Res. Suppl.*, Vol 41 (No. 2), p 78s–83s
- G.J. Qiao, C.G. Zhang, and Z.H. Jin, 2003. Thermal Cyclic Test of Alumina/Kovar Joint Brazed by Ni-Ti Active Filler, *Ceram. Industry*, Vol 29, p 7–11 doi: [10.1016/S0272-8842\(02\)00081-0](https://doi.org/10.1016/S0272-8842(02)00081-0)

- R.A. Ricks *et al.*, 1989. Transient Liquid Phase Bonding of Aluminum-Lithium Base Alloy AA8090 Using Roll-Clad Zn Based Interlayers, *Proc. Conf. Aluminum Lithium Alloys*, March 27– 31 (Williamsburg, VA), p 441–449
- S.P.S. Sangha, D.M. Jacobson, and A.T. Peacock, 1998. Development of the Copper-Tin Diffusion-Brazing Process, *Weld. J. Res. Suppl.*, Vol 77 (No. 10), p 432s–438s
- N. Saunders and A.P. Miodownik, 1990. Cu-Sn (Copper-Tin) *Binary Alloy Phase Diagrams* 2nd Edition, T.D. Massalski ed. ASM International, 1990, p 1482
- M.M. Schwartz, 1987. *Brazing*, ASM International
- M.M. Schwartz, 2003. *Brazing*, 2nd ed., ASM International
- M.L. Shalz *et al.*, 1994. Ceramic Joining II: Partial Transient Liquid-Phase Bonding of Alumina via Cu/Ni/Cu Multilayer Interlayers, *J. Mater. Sci.*, Vol 29, p 3200–3208 doi: [10.1007/BF00356663](https://doi.org/10.1007/BF00356663)
- T Shelley, 1998. Aluminium Alloys Can Get it Together, *Eureka*, Vol 18 (No. 6), p 51
- C.W. Sinclair, G.R. Purdy, and J.E. Morral, 2000. Transient Liquid-Phase Bonding in Two-Phase Ternary Systems, *Met. and Mater. Trans. A*, Vol 31A, p 1187–1192 doi: [10.1007/s11661-000-0114-2](https://doi.org/10.1007/s11661-000-0114-2)
- R.S. Timisit and B.J. Janeway, 1994. A Novel Brazing Technique for Aluminum and Other Metals, *Weld. J. Res. Suppl.*, Vol 73 (No. 6), p 119s–128s
- I. Tuah-Poku, M. Dollar, and T.B. Massalski, 1988. A Study of the Transient Liquid Phase Bonding Process Applied to a Ag/Cu/Ag Sandwich Joint, *Metall. Trans. A*, Vol 19A (No. 3), p 675–686 doi: [10.1007/BF02649282](https://doi.org/10.1007/BF02649282)
- A. Urena *et al.*, 1996. Diffusion Bonding of an Aluminium-Lithium Alloy (AA8090) Using Aluminium Copper Alloy Interlayers, Part 1: Microstructure, *J. Mater. Sci.*, Vol 31, p 807–818 doi: [10.1007/BF00367902](https://doi.org/10.1007/BF00367902)
- X.W. Wu, R.S. Chandel, and H. Li, 2001. Evaluation of Transient Liquid Phase Bonding between Nickel-Based Superalloys, *J. Mater. Sci.* Vol 36, p 1539–1546 doi: [10.1023/A:1017513200502](https://doi.org/10.1023/A:1017513200502)
- C.G. Zhang, G.J. Qiao, and Z.H. Jin, 2002. Active Brazing of Pure Alumina to Kovar Alloy Based on the Partial Transient Liquid Phase (PTLP) Technique with Ni-Ti Interlayer, *J. European Ceram. Soc.* Vol 22, p 2181–2186 doi: [10.1016/S0955-2219\(02\)00011-0](https://doi.org/10.1016/S0955-2219(02)00011-0)
- Y. Zhou, W.F. Gale, and T.H. North, 1995. Modelling of Transient Liquid Phase Bonding, *Int. Mater. Rev.*, Vol 50 (No. 5), p 181–196 doi: [10.1179/imr.1995.40.5.181](https://doi.org/10.1179/imr.1995.40.5.181)



- W.D. Zhuang and T.W. Eagar, 1997. Transient Liquid-Phase Bonding Using Coated Metal Powders, *Weld. J. Res. Suppl.*, Vol 76 (No. 4), p 157s–162s
- B. Zorc and L. Kosec, 2000. A New Approach to Improving the Properties of Brazed Joints, *Weld. J. Res. Suppl.*, Vol 79 (No. 1), p 24s–31s

# Chapter 7: Direct Brazing of Nonmetals

## References

- O.M. Akselsen, 1992. Review—Advances in Brazing of Ceramics, *J. Mater. Sci.*, Vol 27, p 1989–2000 doi: [10.1007/BF01117909](https://doi.org/10.1007/BF01117909)
- M.F. Ashby, 1997. Material Property Charts, *Material Selection and Design*, Vol 20, *ASM Handbook*, ASM International, 1997
- R. Asthana and N. Sobczak, 2000. Wettability, Spreading, and Interfacial Phenomena in High-Temperature Coatings, *JOM-e*, Vol 52 (No. 1), p 1–18
- K.-S. Bang and S. Liu, 1994. Interfacial Reaction between Alumina and Cu-Ti Filler Metal during Reactive Metal Brazing, *Weld. J. Res. Suppl.*, Vol 73 (No. 3), p 54s–60s
- P.R. Camilo de Camargo, 1995. “Role of Oxygen in the Cu-O-Ti/Sapphire Interfacial Region Formation,” Ph.D. dissertation, T-4726, Colorado School of Mines
- P.R. Chidambaram, G.R. Edwards, and D.L. Olson, 1991. A Thermodynamic Criterion for Predicting Wettability at Metal-Alumina Interfaces, *Metall. Trans. B*, Vol 23B, p 215–222 doi: [10.1007/BF02651856](https://doi.org/10.1007/BF02651856)
- A.A. Chularis, 1994. A Calculation-Graphical Method for Evaluating the Criterion of Selecting a Refractory Metal of the Barrier Metal When Joining Active Metals to Other Metals and Alloys, *Weld. Intl.*, Vol 8 (No. 3), p 236–238 doi: [10.1080/09507119409548582](https://doi.org/10.1080/09507119409548582)
- R.M. Crispin and M. Nicholas, 1976. The Wetting and Bonding Behaviour of Some Nickel Alloy-Alumina Systems, *J. Mater. Sci.*, Vol 11 (No. 1), p 17–21 doi: [10.1007/BF00541069](https://doi.org/10.1007/BF00541069)
- B. Drevet, S. Kalogeropoulou, and N. Eustathopoulos, 1993. Wettability and Interfacial Bonding in the Au-Si/SiC System, *Acta Metall. Mater.*, Vol 41 (No. 11), p 3119–3126 doi: [10.1016/0956-7151\(93\)90041-P](https://doi.org/10.1016/0956-7151(93)90041-P)
- A.H. El Sawy *et al.*, 1993. Direct Brazing of Silicon Nitride Ceramics to Copper Using Active Filler Metal, *Proc. Conf. Trends in Welding Research*, June 1–5 (Gatlinburg, TN), S.A. David and J.M. Vitek, Ed., p 1119–1127
- N. Eustathopoulos, M.G. Nicholas, and B. Drevet, 1999. *Wettability at High Temperatures*, Pergamon Press
- M.W. Finnis, 1996. The Theory of Metal-Ceramic Interfaces, *J. Phys., Condens. Matter*, Vol 8 (No. 32), p 5811–5836 doi: [10.1088/0953-8984/8/32/003](https://doi.org/10.1088/0953-8984/8/32/003)

- N. Frage, N. Froumin, and M.P. Dariel, 2002. Wetting of TiC by Non-Reactive Liquid Metals, *Acta Mater.*, Vol 50 (No. 2), p 237–245 doi: [10.1016/S1359-6454\(01\)00349-4](https://doi.org/10.1016/S1359-6454(01)00349-4)
- N. Froumin *et al.*, 2000. Wetting Phenomena in the TiC/(Cu-Al) System, *Acta Metall. Mater.*, Vol 48 (No. 7), p 1435–1441 doi: [10.1016/S1359-6454\(99\)00452-8](https://doi.org/10.1016/S1359-6454(99)00452-8)
- Granta Design Limited, 2004. Cambridge Engineering Selector v4.5, Cambridge, UK
- H. Hongqi, J. Zhihao, and W. Xiaotian, 1994. The Influence of Brazing Conditions on Joint Strength in Al<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> Bonding, *J. Mater. Sci.*, Vol 29, p 5041–5046 doi: [10.1007/BF01151094](https://doi.org/10.1007/BF01151094)
- J.M. Howe, 1993a. Bonding, Structure and Properties of Metal/Ceramic Interfaces, Part 1: Chemical Bonding, Chemical Reaction and Interfacial Structure, *Intl. Mater. Rev.*, Vol 38 (No. 5), p 233–256 doi: [10.1179/imr.1993.38.5.233](https://doi.org/10.1179/imr.1993.38.5.233)
- J.M. Howe, 1993b. Bonding, Structure and Properties of Metal/Ceramic Interfaces, Part 2: Interfacial Fracture Behaviour and Property Measurement, *Intl. Mater. Rev.*, Vol 38 (No. 5), p 257–271 doi: [10.1179/imr.1993.38.5.257](https://doi.org/10.1179/imr.1993.38.5.257)
- S.T. Kim and C.H. Kim, 1992. Interfacial Reaction Product and its Effect on the Strength of Copper to Alumina Eutectic, *J. Mater. Sci.*, Vol 27, p 2061–2066 doi: [10.1007/BF01117918](https://doi.org/10.1007/BF01117918)
- O. Kubaschewski, 1988. Silver-Copper-Titanium, in Ternary Alloys. *A Comprehensive Compendium of Evaluated Constitutional Data and Phase Diagrams*, Vol 2, G. Petzow and G. Effenberg, Ed., VCH, p 55–59
- T. Kuzumaki, T. Ariga, and Y. Miyamoto, 1990. Effect of Additional Elements in Ag-Cu Based Filler Metal on Brazing of Aluminium Nitride to Metals, *ISIJ Int.*, Vol 30 (No. 12), p 1135–1141 doi: [10.2355/isijinternational.30.1135](https://doi.org/10.2355/isijinternational.30.1135)
- O.T. Lancu and D. Munz, 1990. Residual Stress State of Brazed Ceramic/Metal Compounds, Determined by Analytical Methods and X-Ray Residual Stress Measurements, *J. Am. Ceram. Soc.*, Vol 73 (No. 5), p 1144–1149 doi: [10.1111/j.1151-2916.1990.tb05170.x](https://doi.org/10.1111/j.1151-2916.1990.tb05170.x)
- K. Landry and N. Eustathopoulos, 1996. Dynamics of Wetting in Reactive Metal/Ceramic Systems: Linear spreading, *Acta Mater.*, Vol 44 (No. 10), p 3923–3932 doi: [10.1016/S1359-6454\(96\)00052-3](https://doi.org/10.1016/S1359-6454(96)00052-3)
- C.G., Levi G.J Abbaschian, and R. Mehrabian, 1978. Interface Interactions during Fabrication of Aluminum Alloy-Alumina Fibre Composites, *Metall. Trans. A*, Vol 9A (No. 5), p 697–702 doi: [10.1007/BF02659927](https://doi.org/10.1007/BF02659927)
- G. Levi and W.D. Kaplan., 2002. Oxygen Induced Interfacial Phenomena During Wetting of Alumina by Liquid Aluminum, *Acta Mater.*, Vol 50 (No. 1), p 75–88 doi: [10.1016/S1359-6454\(01\)00333-0](https://doi.org/10.1016/S1359-6454(01)00333-0)

- A. Levy, 1991. Thermal Residual Stresses in Ceramic-to-Metal Brazed Joints, *J. Am. Ceram. Soc.*, Vol 74 (No. 9), p 2141–2147 doi: [10.1111/j.1151-2916.1991.tb08273.x](https://doi.org/10.1111/j.1151-2916.1991.tb08273.x)
- J.G. Li, 1993. Understanding of Wetting, Adhesion and Interfacial Bonding of Metals and Ceramic Oxides, *Proc. Conf 2nd European Colloquium Designing Ceramic Interfaces II: Understanding and Tailoring Interfaces for Coating, Composite and Joining Applications*, Nov 11– 13, 1993 (Petten, Belgium), p 481–498
- R.E. Loehman, 1988. Joining and Bonding Mechanisms in Nitrogen Ceramics, *Proc. Conf. Intl. Meeting on Advanced Materials*, Vol 8, *Metal-Ceramic Joints*, June 2– 3 (Tokyo, Japan), p 49–59
- R.E. Loehman, 1994. Wetting and Joining of Mullite Ceramics by Active-Metal Braze Alloys, *J. Am. Ceram. Soc.*, Vol 77 (No. 1), p 271–274 doi: [10.1111/j.1151-2916.1994.tb06989.x](https://doi.org/10.1111/j.1151-2916.1994.tb06989.x)
- E. Lugscheider, W. Bürger, and U. Broich, 1997. Development and Characterisation of Joining Techniques for Dispersion-Strengthened Alumina, *Weld. J. Res. Suppl.*, Vol 76 (No. 9), p 349s–355s
- E. Lugscheider and W. Tillmann, 1990. Development of New Active Filler Metals in a Ag-Cu-Hf System, *Weld. J. Res. Suppl.*, Vol 69 (No. 11), p 416s–421s
- E. Lugscheider and W. Tillmann, 1991. Development of New Active Filler Metals for Joining Silicon-Carbide and -Nitride, *Proc. Conf. British Association for Brazing and Soldering*, 6th International Conference, Sept 3– 5 (Stratford-upon-Avon), Paper 11
- E. Lugscheider and W. Tillmann, 1993. Interfacial Reactions between New Active Filler Metals and Nonoxide Ceramics, *Proc. Conf 2nd European Colloquium Designing Ceramic Interfaces II, Understanding and Tailoring Interfaces for Coating, Composite and Joining Applications*, Nov 11– 13 (Petten, Belgium), p 499–517
- R.A. Marks *et al.*, 2000. Joining of Alumina via Copper/Niobium/Copper Interlayers, *Acta Mater.*, Vol 48 (No. 18/19), p 4425–4438 doi: [10.1016/S1359-6454\(00\)00229-9](https://doi.org/10.1016/S1359-6454(00)00229-9)
- A. Meier, D.A. Javernick, and G.R. Edwards, 1999. Ceramic-Metal Interfaces and the Spreading of Reactive Liquids, *JOM*, Vol 51 (No. 2), p 44–47 doi: [10.1007/s11837-999-0209-1](https://doi.org/10.1007/s11837-999-0209-1)
- T. Minegishi, T. Sakurai, and S. Morozumi, 1991. Electric Field-Assisted and Field-Depressed Segregation of Reactive Metals to the Bond Interface in Braze Alloy Joining, *J. Mater. Sci.*, Vol 26, p 5473–5480 doi: [10.1007/BF02403945](https://doi.org/10.1007/BF02403945)
- H. Mizuhara and K. Mally, 1985. Ceramic-to-Metal Joining with Active Brazing Filler Metal, *Weld. J. Res. Suppl.*, Vol 64 (No. 10), p 27s–32s
- A.J. Moorhead, H.M. Henson, and T.J. Henson, 1987. In *Ceramic Microstructures '86: Role of Interfaces*, J.A. Pask, and A.G. Evans, Ed., Plenum Press

- R. Morrell, 1985. *Handbook of Properties of Technical and Engineering Ceramics*, Her Majesty's Stationary Office
- Y. Mutoh *et al.* 1993. Strength and Fracture Toughness of Si<sub>3</sub>N<sub>4</sub>-Metal Joints with Phase Transforming Interlayer Metal, Proc. Conf. 9th Biennial Conference on Fracture, Sept 21– 25, 1992 (Varna, Bulgaria), Pub., *Reliability and Structural Integrity of Advanced Materials*, S. Sedmak, A. Sedmak, and D. Ruzic, Ed., Vol 2, p 1043–1048
- M. Naka, M. Kubo, and I. Okamoto, 1989. Brazing of Si<sub>3</sub>N<sub>4</sub> to Metals with Al Filler (Report II), *Trans. JWRI*, Vol 2 (No. 18), p 33–36
- Y. Nakao, K. Nishimoto, and K. Saida, 1989. Bonding of Si<sub>3</sub>N<sub>4</sub> to Metals with Active Filler Metals, *Trans. Jpn. Weld. Soc.*, Vol 20 (No. 1), p 66–76
- Y.V. Naidich, V. Zhuravlev, N. Krasovskaya, 1998. The Wettability of Silicon Carbide by Au–Si Alloys, *Mater. Sci. Eng.*, Vol A245, p 293–299 doi: [10.1016/S0921-5093\(97\)00718-1](https://doi.org/10.1016/S0921-5093(97)00718-1)
- T. Narita, T. Ishikawa, and I. Ishikawa, 1992. Simultaneous Measurements of Stress and Distortion of the Ceramic Metal Joints by Scanning Acoustic Microscopy, *Nondestruct. Test. Eval.*, Vol 8-9, p 709–716 doi: [10.1080/10589759208952744](https://doi.org/10.1080/10589759208952744)
- M.G. Nicholas, 1988. Reactive Brazing of Ceramics, *Proc. Conf. Intl. Meet. Adv. Mater.*, Vol 8, *Metal-Ceramic Joints*, June 2– 3 (Tokyo, Japan), Materials Research Society, p 49–59
- M.G. Nicholas, 1989a. Reactive Metal Brazing, Proc. Conf. 3rd International Conference Joining Ceramics, Glass and Metal April 26– 28 (Bad Nauheim, Germany), W. Kraft, Ed., p 3–6
- M.G. Nicholas, 1989b. In *Surfaces and Interfaces of Ceramic Materials*, Kluwer Academic Press, L.C. Dufour *et al.*, Ed.
- M.G. Nicholas, 1990. *Joining of Ceramics*, The Institute of Ceramics/Chapman and Hall
- M.G. Nicholas, 1993. Fabrication of Ceramic Interfaces and Joints, *Proc. Conf 2nd European Colloquium Designing Ceramic Interfaces II, Understanding and Tailoring Interfaces for Coating, Composite and Joining Applications*, Nov 11– 13 (Petten, Belgium), p 173–189
- M.G. Nicholas and R.M. Crispin, 1986. Copper-Ceramic Materials, *INCRA Report* 383
- M.G. Nicholas and S.D. Peteves, 1991. Reactive Joining of Silicon Nitride Ceramics, Proc. Conf. British Association for Brazing and Soldering, 6th International Conference, Sept 3– 5 (Stratford-upon-Avon), Paper 10
- M.G. Nicholas and S.D. Peteves, 1994. Reactive Joining; Chemical Effects on the Formation and Properties of Brazed and Diffusion Bonded Interfaces, *Scr. Metall. Mater.*, Vol 31 (No. 8), p 1091–1096 doi: [10.1016/0956-716X\(94\)90532-0](https://doi.org/10.1016/0956-716X(94)90532-0)

- H. Ohmura *et al.*, 1994. A Technique for Brazing Graphite/Graphite and Stainless Steel/High-Carbon Steel Joints, *Weld. J. Res. Suppl.*, Vol 73 (No. 10), p 249s–256s
- M. Paulasto, G. Ceccone, and S.D. Peteves, 1997. Joining of Silicon Nitride via a Transient Liquid, *Scr. Mater.*, Vol 26 (No. 10), p 1167–1173 doi: [10.1016/S1359-6462\(97\)00007-9](https://doi.org/10.1016/S1359-6462(97)00007-9)
- M. Paulasto and J. Kivilahti, 1995. Formation of Interfacial Microstructure in Brazing of Si<sub>3</sub>N<sub>4</sub> with Ti-Activated Ag-Cu Filler Alloys, *Scr. Metall. Mater.*, Vol 32 (No. 8), p 1209–1214 doi: [10.1016/0956-716X\(95\)00127-H](https://doi.org/10.1016/0956-716X(95)00127-H)
- M. Paulasto and J. Kivilahti, 1998. Metallurgical Reactions Controlling the Brazing of Al<sub>2</sub>O<sub>3</sub> with Ag-Cu-Ti Filler Alloy, *J. Mater. Res.*, Vol 13 (No. 2), p 343–352 doi: [10.1557/JMR.1998.0046](https://doi.org/10.1557/JMR.1998.0046)
- S.D. Peteves *et al.*, 1996. Joining Silicon Nitride to Itself and to Metals, *JOM*, Vol 48 (No. 1), p 48–77 doi: [10.1007/BF03221363](https://doi.org/10.1007/BF03221363)
- E. Saiz, R.M. Cannon, and A.P. Tomsia, 2001. Reactive Spreading in Ceramic/Metal Systems, *Oil Gas Sci. Technol.—Rev. IFP*, Vol 56 (No. 1), p 89–96 doi: [10.2516/ogst:2001011](https://doi.org/10.2516/ogst:2001011)
- J. Schulz-Harder and P.H. Maier, 1996. DCB Substrates with Reduced Ceramic Thickness in Power Semiconductor Modules, *PCIM Europe*, No. 1, 5 p
- J. Schulz-Harder, 2003. Advantages and New Development of Direct Bonded Copper Substrates, *Microelectron. Reliability*, Vol 43 (No. 3), p 359–365 doi: [10.1016/S0026-2714\(02\)00343-8](https://doi.org/10.1016/S0026-2714(02)00343-8)
- M.M. Schwartz, 1990. *Ceramic Joining*, American Society for Materials
- P.M. Scott, M. Nicholas, and B. Dewar, 1975. The Wetting and Bonding of Diamonds by Copper-Base Binary Alloys, *J. Mater. Sci.* Vol 10 (No. 11), p 1833–1840 doi: [10.1007/BF00754470](https://doi.org/10.1007/BF00754470)
- J.H. Selverian and S. Kang, 1992. Ceramic-to-Metal Joints, Part II: Performance and Strength Prediction, *Am. Ceram. Soc. Bull.*, Vol 71 (No. 10), p 1511–1520
- J. H. Selverian, D. O’Neil, and S. Kang, 1992. Ceramic-to-Metal Joints, Part I: Joint Design, *Am. Ceram. Soc. Bull.*, Vol 71 (No. 9) p 1403–1409
- R.K. Shiue, J.M.O. Wu, and J.Y. Wang, 2000. Microstructural Evolution at the Bonding Interface during the Early-Stage Infrared Active Brazing of Alumina, *Metall. Mater. Trans. A.*, Vol 31A (No. 10), p 2527–2536 doi: [10.1007/s11661-000-0197-9](https://doi.org/10.1007/s11661-000-0197-9)
- T. Suga and G. Elssner, 1989. Structural Features to Relax Thermal Stress at Metal/Ceramic Joined Interfaces, *Proc. Conf. MRS International Meeting on Advanced Materials*, June 2– 3 (Tokyo, Japan), Materials Research Society, M. Doyama *et al.*, Ed., *Metal-Ceramic Joints*, Vol 8

- K. Sukanuma, 1990. Recent Advances in Joining Technology of Ceramics to Metals *ISIJ Int.*, Vol 30 (No. 12), p 1046–1058 doi: [10.2355/isijinternational.30.1046](https://doi.org/10.2355/isijinternational.30.1046)
- T. Torvund *et al.*, 1996. A Process Model for Active Brazing of Ceramics, Part 1: Growth of Reaction Layers, *J. Mater. Sci.*, Vol 31, p 6215–6222 doi: [10.1007/BF00354441](https://doi.org/10.1007/BF00354441)
- P. Villars, A. Prince, and H. Okamoto 1995. *Handbook of Ternary Alloy Phase Diagrams*, Vol 3, American Society for Materials
- Z. Wang and P. Wynblatt, 1998. Study of a Reaction at the Solid Cu/ $\alpha$ -SiC Interface, *J. Mater. Sci.*, Vol 33, p 1177–1181 doi: [10.1023/A:1004317407690](https://doi.org/10.1023/A:1004317407690)
- R. Warren and C.H. Andersson, 1984. Silicon Carbide Fibres and Their Potential for Use in Composite Materials II, *Composites*, Vol 15 (No. 2), p 101–111 doi: [10.1016/0010-4361\(84\)90721-3](https://doi.org/10.1016/0010-4361(84)90721-3)
- N.A. Waterman and M.F. Ashby, 1997. *The Materials Selector*, 2nd ed., Chapman and Hall, p 46
- W. Weise, W. Malinkowski, and H. Krappitz, 1989. Wetting and Strength Properties of Ceramic to Metal Joints Brazed with Active Filler Metals Depending on Brazing Conditions and Joint Geometry, Proc. 3rd International Conference Joining Ceramics, Glass and Metal, W. Kraft, Ed., April 26– 28(Bad Nauheim, Germany), DGM, p 33–42
- H. Xiong, C. Wan, and Z. Zhou, 1998. Development of a New CuNiTiB Brazing Alloy for Joining Si<sub>3</sub>N<sub>4</sub> to Si<sub>3</sub>N<sub>4</sub>, *Metall. and Mater. Trans. A*, Vol 29A (No. 10), p 2591–2596 doi: [10.1007/s11661-998-0231-x](https://doi.org/10.1007/s11661-998-0231-x)
- X.B. Zhou and J.Th.M. De Hosson, 1995. Reactive Wetting of Liquid Metals on Ceramic Substrates, *Acta Metall. Mater.*, Vol 44 (No. 2), p 421–426 doi: [10.1016/1359-6454\(95\)00235-9](https://doi.org/10.1016/1359-6454(95)00235-9)

# Appendix 2: Selected References

## Selected References

- D.G. Brandon, and W.D. Kaplan 1997. *Joining Processes: An Introduction*, John Wiley & Sons
- N. Eustathopoulos, M.G. Nicholas, and B. Drevet, 1999. *Wettability at High Temperatures*, Pergamon Press
- International Organization for Standardization (IOS), 1990. *Welding, Brazing and Soldering Processes: Vocabulary*, (IOS/DIS 857-2) ISO (currently under revision)
- E. Liebermann, 1988. *Modern Soldering and Brazing Techniques*, Business News
- M.G. Nicholas, 1990. *Joining of Ceramics*, The Institute of Ceramics/Chapman and Hall
- D.L. Olson *et al.*, Eds., 1993. *Welding, Brazing and Soldering*, Vol 6, *ASM Handbook*, ASM International, doi: [10.31399/asm.hb.v06.9781627081733](https://doi.org/10.31399/asm.hb.v06.9781627081733)
- M.M. Schwartz, 2003. *Brazing*, 2nd ed., ASM International
- M.M. Schwartz, 1990. *Ceramic Joining*, American Society for Materials
- C.J. Thwaites, 1983. *Capillary Joining: Brazing and Soft-Soldering*, Books Demand UMI