CHAPTER 2

Brazing Fundamentals

BRAZING does not involve any melting or plastic state of the base metal. Brazing comprises a group of joining processes in which coalescence is produced by heating to suitable temperatures above 450 °C (840 °F) and by using a ferrous and/or nonferrous filler metal that must have a liquidus temperature above 450 °C and below the solidus temperature(s) of the base metal(s). The filler metal is distributed between the closely fitted surfaces of the joint by capillary attraction. Brazing is distinguished from soldering in that soldering employs a filler metal having a liquidus below 450 °C.

Brazing has four distinct characteristics:

- The coalescence, joining, or uniting of an assembly of two or more parts into one structure is achieved by heating the assembly or the region of the parts to be joined to a temperature of 450 °C or above.
- Assembled parts and filler metal are heated to a temperature high enough to melt the filler metal but not the parts.
- The molten filler metal spreads into the joint and must wet the base-metal surfaces.
- The parts are cooled to freeze the filler metal, which is held in the joint by capillary attraction and anchors the part together.

Adhesion, Wetting, Spreading, and Capillary Attraction

Metals

More than 195 years ago, Thomas Young (Ref 1) proposed treating the contact angle (θ) of a liquid as the result of the mechanical equilibrium of a drop resting on a plain, solid surface under the action of three surface tensions (Fig. 2.1). The surface tensions are γ_{lv} at the interface of the liquid in equilibrium with its saturated vapor, γ_{sl} at the interface between the solid and the liquid, and γ_{sv} at the interface of the solid in equilibrium with the saturated vapor of the liquid. Hence:

\[ \gamma_{sv} = \gamma_{lv} \cos \theta + \gamma_{sl} \]  
(Eq 1)

It is important to keep in mind that phases are supposed to be mutually in equilibrium. The designation γ_{sv} is a reminder that the solid surface near the liquid should have an equilibrium film of vapor due to the film pressure. Young’s equation has been used extensively in literature, which reflects its general acceptance.

However, Eq 1 has never been verified experimentally. The problem is that surface tensions of solids are not easy to measure due to the inevitable presence of the interfacial tension between a solid and its liquid. More importantly, there is the difficulty that any tensile stresses existing in the surface of the solid would prevent the system from being in equilibrium. The surface tension at the solid-vapor interface (γ_{sv}) has a relationship with surface tension of a solid in vacuum (γ_s) as follows:

\[ \gamma_{sv} = \gamma_s - \pi_e \]  
(Eq 2)

where π_e refers to the spreading pressure. Consequently, Young’s equation may be rewritten as:

\[ \gamma_s = \gamma_{lv} \cos \theta + \gamma_{sl} + \pi_e \]  
(Eq 3)

Because most of the solids have a negligible π_e, particularly when the contact angle (θ) is greater than 10°, Young’s equation becomes:

\[ \gamma_s = \gamma_{lv} \cos \theta + \gamma_{sl} \]  
(Eq 4)

A decrease of the contact angle causes an increase of the liquid drop surface area and thus increases the total liquid surface free energy.
The total surface free energy of the solid decreases concurrently. A balance of these two forces results in a steady-state condition represented by an acute contact angle. Mathematically, this balance is expressed as Young’s equation (Eq 1) acting at the periphery of the drop.

The driving force for wetting thus is \( \gamma_{sv} - \gamma_{sl} \). The balancing resisting force is represented by the horizontal component of the surface tension of the liquid \( \gamma_{lv} \cos \theta \), as shown in Fig. 2.1. A balance of vertical forces also exists, but vertical forces do not play a role in this problem.

When \( \gamma_{sv} < \gamma_{lv} \) and \( \gamma_{sv} < \gamma_{sl} < \gamma_{lv} \) (again, in the absence of a reaction), a steady-state condition results with \( \theta > 90^\circ \). With a decrease of the obtuse contact angle, the liquid drop surface area (and thus the total liquid surface free energy) also decreases.

Young’s equation (Eq 1) represents a steady-state condition for a solid-liquid interface in stable or metastable thermodynamic equilibrium. However, there is no definite indication of whether chemical or van der Waals bonding exists, other than that the contact angle is generally smaller with chemical bonding versus van der Waals bonding (because when \( \gamma_{sl} \) is smaller, the driving force for wetting is greater).

In either wetting \( \gamma_{sv} > \gamma_{lv} \) or nonwetting \( \gamma_{lv} > \gamma_{sv} \), if an intimate interface does not form between the phases to be bonded (as with contaminated solid surfaces, such as absorbed carbonaceous layers), \( \gamma_{sl} \) is larger than \( \gamma_{sv} \) and also \( \gamma_{lv} \). Then, a large, obtuse contact angle forms and approaches 180° with decreasing attractive forces, as indicated by the absence of reduction of either the solid or liquid surface free energy and very weak adherence. An optimal 180° angle would indicate no attractive forces between the two phases.

Technologically, a nonwetting liquid is highly unfavorable with regard to the formation of an intimate interface, due to its lack of capability of penetration of surface and grain-boundary irregularities because of the lack of capillary behavior. Also, the liquid does not distribute itself uniformly.

In either case of a starting acute or obtuse contact angle, the characteristic of wetting can be achieved and enhanced by a reaction at the interface at an elevated temperature.

Young’s equation (Eq 1) can be modified to represent a spreading coefficient, \( S \) (Ref 2), or a work of spreading, \( W_s \), by taking the extreme case of wetting when the contact angle approaches 0 and \( \cos \theta \) approaches 1. The resisting force to the extension of the drop then is \( \gamma_{lv} \), as discussed earlier. Young’s equation can then be expressed as:

\[
W_s = \gamma_{sv} - \gamma_{sl} - \gamma_{lv} \tag{Eq 5}
\]

In order to have spreading occur, \( W_s \) has to be positive. Under these conditions, the driving force for wetting \( \gamma_{sv} - \gamma_{sl} \) is greater than \( \gamma_{lv} \). If the \( W_s \) is negative, then the driving force for wetting is smaller, and spreading does not occur, but an acute angle forms. If a reaction occurs in which the substrate is an active participant, then the free energy of the reaction, \( \Delta G_R/\text{d}A/\text{d}t \), contributes to the driving force for wetting, which practically always exceeds \( \gamma_{lv} \). Spreading thus occurs.

Young’s equation (Eq 1) for a nonreacting steady-state sessile drop can be modified to include the contribution of the free energy of reaction:

\[
\gamma_{sv} - \left( \frac{\gamma_{sl} + G_R}{\text{d}A/\text{d}t} \right) \geq \gamma_{lv} \cos \theta \tag{Eq 6}
\]

The free energy required for the increase of the surface area of the drop as the perimeter expands provides the only resisting force to the
expansion. It can be shown thermodynamically that in the absence of a reaction, the driving force for wetting does not exceed $\gamma_{lv}$, resulting in a steady-state contact angle (Ref 3). The driving force with the contribution of the free energy of reaction in most cases exceeds the resisting force represented by $\gamma_{lv}$, because $\theta$ is $0^\circ$ during spreading. A condition of an expanding drop during a reaction is defined as spreading. It can be seen that the free energy of a reaction in which the substrate is a passive participant does not contribute to the driving force for wetting; thus, spreading does not occur. The contact angle, however, adjusts to conform with the surface-energy changes of the liquid caused by composition changes due to the reaction.

**Example: Copper-Silver System.** The equilibrium phase diagram for the copper-silver binary system (Fig. 2.2) can be used to illustrate examples of wetting and spreading (Ref 3). The system has a eutectic at 780 °C (1430 °F), with 72 wt% Ag. At 900 °C (1650 °F), the solid-solution limit is 5 wt% Ag in copper and 8 wt% Cu in silver.

Several compositions are identified in the phase diagram by the letters A to D. When a drop of liquid C is placed on solid B at 900 °C (1650 °F), wetting occurs, with a contact angle of 11° and no chemical reaction, because the phases are in chemical equilibrium. This behavior corresponds to $\gamma_{sv} > \gamma_{lv}$, because, in a given system, the surface free energy of a liquid is less than that of a solid, due to its lack of long-range order. The liquid thus has the opportunity to rearrange its surface structure to a lower free-energy state. However, when liquid C is placed on solid A, spreading occurs, because substrate A (as an active participant in the reaction) changes its surface composition toward B. The third equation in Fig. 2.1 applies in this case.

Another example is that of liquid D on solid B. Liquid D is not in equilibrium with B and dissolves some of the substrate to change its composition to C. Even though a reaction occurs, there is no spreading, because B is a passive participant with no change in composition, even though it is being dissolved. However, with liquid D on solid A, spreading occurs, because both are active participants as they change to equilibrium compositions C and B, respectively. In both of the latter examples, liquid D is an active participant, because it dissolves some of the substrate to reach equilibrium compositions. It does not, however, contribute to spreading, which is controlled by the active participation of the substrate.

**Ceramics**

Joining dissimilar materials invariably results in high interfacial energy; that is, the work of

![Fig. 2.2 Stable phase equilibrium diagram for the copper-silver system](image-url)
adhesion is not sufficient to maintain the joint integrity. Most structural ceramic-metal interfaces are no exceptions; the liquid metal does not readily wet the ceramic surface. Therefore, the first challenge in metal-to-ceramic joining is to alter the interfacial thermodynamics to render the ceramic surface wettable. There are two approaches available today (Ref 4) to accomplish this task: metallization of the ceramic surface and reaction wetting. A thin layer of metal alloy is deposited on the ceramic by vapor deposition or sputtering. Brazing is then carried out by appropriate filler material or by simply melting the deposited layer (Ref 5). This two-step approach is not as enthusiastically embraced by industry as is direct reaction brazing.

In reaction brazing, the filler metal is carefully chosen so as to facilitate compound formation at the interface. A small percentage of reactive metals, such as aluminum and titanium, are added to the otherwise inert base alloys (Ref 6, 7). The compounds that form are commonly spinels for the oxide ceramics and complex nitrides for the ceramic nitrides (Ref 8, 9).

It is important to realize that wetting in such systems is time dependent. Successful bond formation relies on rapid transport of the reactive metal to the interface and a rapid rate of compound formation. Reaction wetting may not be the solution to all metal-ceramic joining problems, because interfacial compound formation could create fragile layers (Ref 9), further complicating the development of good joint efficiency. The weakest among the adhesive strength at the ceramic-compound boundary, the cohesive strength of the compound, or the adhesive strength between compound and metal would determine the final joint strength.

Table 2.1 (Ref 10) summarizes the various reaction products that have been identified in literature for the common metal-ceramic systems. Many researchers have concentrated their study on alumina surfaces, because it is one of the very few ceramics for which essential thermodynamic data are available. One of the first commercial applications of metal-to-ceramic brazed components is the turbocharger rotor (Ref 8), where a silicon nitride turbine blade is brazed to a stainless steel shaft. Other ceramics of interest to brazers are silicon carbide and zirconia.

Ceramics exhibit very different thermal expansion behavior compared to metals; hence, considerable residual stress can build up during cooling. This thermal expansion mismatch more or less dictates the use of a ductile filler material. Most commercial brazing systems are therefore silver and copper base. The soft interlayer might not be sufficient to compensate for large differences in thermal expansion coeffi-

<table>
<thead>
<tr>
<th>System</th>
<th>Temperature, K</th>
<th>Load, MPa (ksi)</th>
<th>Time, h</th>
<th>Atmosphere</th>
<th>Reaction products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al2O3(a)-Nb(a)</td>
<td>1925</td>
<td>20 (3)</td>
<td>0.1</td>
<td>Argon</td>
<td>(Al)Nb</td>
</tr>
<tr>
<td>Al2O3(b)-Nb(c)</td>
<td>1973</td>
<td>10 (1.5)</td>
<td>2</td>
<td>Vacuum 10^-3 Pa</td>
<td>(O)Nb</td>
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<tr>
<td>Al2O3(d)-Nb(a)</td>
<td>1973</td>
<td>6.4 (1.0)</td>
<td>1</td>
<td>Vacuum 10^-3 Pa</td>
<td>NbO, (Al,O)Nb</td>
</tr>
<tr>
<td>Al2O3(b)-Nb(a)</td>
<td>1973</td>
<td>6.4 (1.0)</td>
<td>1</td>
<td>Vacuum 10^-3 Pa</td>
<td>NbO, (Al,O)Nb</td>
</tr>
<tr>
<td>SiC(b)-Ti(a)</td>
<td>1250</td>
<td>...</td>
<td>60</td>
<td>Vacuum 10^-3 Pa</td>
<td>TiAl, TiO, (AlO)Ti</td>
</tr>
<tr>
<td>SiC(b)-Zr(a)</td>
<td>1773</td>
<td>0.34 (0.05)</td>
<td>1</td>
<td>Vacuum 10^-3 Pa</td>
<td>Ti5SiC2, Ti5Si(C), TiSi2</td>
</tr>
<tr>
<td>SiC(a)-AlTi4Al(a)</td>
<td>1273</td>
<td>0.56 (0.08)</td>
<td>1</td>
<td>Vacuum 10^-3 Pa</td>
<td>ZrSi, ZrC + (Si)Zr</td>
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<tr>
<td>SiN4(a)-Fe(a)</td>
<td>1683</td>
<td>3000 (435)</td>
<td>1</td>
<td>Argon</td>
<td>FeSi, (Si)Fe</td>
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<td>Si2O2-Al(a)</td>
<td>875</td>
<td>10 (1.5)</td>
<td>10^-4</td>
<td>75N2/25H2</td>
<td>Not observed</td>
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<td>Si2O2-Al(a)</td>
<td>...</td>
<td>...</td>
<td>24</td>
<td>(H2/H2O = 10^3)</td>
<td>α-Al2O3, (Si)Al</td>
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<tr>
<td>Al2O3(b)-Cu(a)</td>
<td>1270</td>
<td>20 (3)</td>
<td>0.25</td>
<td>H2/H2O = 2 x 10^3</td>
<td>None</td>
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<tr>
<td>Al2O3(b)-Pt(a)</td>
<td>1773</td>
<td>20 (3)</td>
<td>0.25</td>
<td>H2/H2O = 10^5</td>
<td>None. After 6 h, (Al)Pt; after 1000 h, Pt,Al</td>
</tr>
<tr>
<td>Al2O3(b)-Pt(a)</td>
<td>1773</td>
<td>20 (3)</td>
<td>0.25</td>
<td>H2/H2O = 5 x 10^5</td>
<td>PtAl, (Al)Pt</td>
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<tr>
<td>SiO2-Pr(a)</td>
<td>1473</td>
<td>1 (0.15)</td>
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<td>ZrO2(a)-Pt</td>
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<td>0 (0)</td>
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<td>H2</td>
<td>(Zr)Pt</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
<td>8</td>
<td>H2</td>
<td>Pt, Zr, (Zr)Pt</td>
</tr>
</tbody>
</table>

Plane of interaction: (a) Polycrystal. (b) (0001). (c) (110). (d) (1010). (e) (1100). Source: Ref 10
cients (e.g., Si₃N₄ as compared to stainless steel). In such situations, laminated interlayers that provide a continuous gradient thermal expansion coefficient are used (Ref 6).

Thermodynamic phenomena that occur at the interface can be studied in terms of the contact angle, θ, and the work of adhesion, W. These terms can be related to various surface or interfacial energies. The general case for a liquid metal in contact with a solid ceramic is shown in Eq 1, where a balance of surface tension forces results in the familiar Young's equation.

The Dupree equation is easily derived from Eq 1:

\[ W = \gamma_s (1 + \cos \theta) \quad (\text{Eq 7}) \]

Attempts at understanding the nature of the force of adhesion across the interface have not been very successful. In 1965, researchers (Ref 11) rationalized, on the basis of the work of adhesion data for an alumina-metal interface, that the observed work of adhesion was the sum of two independent contributions arising from the van der Waals forces and a primary chemical bond.

Predicting adhesion data in joining an alumina-metal interface is of great importance in many applications. The objective of proposed research to predict wettability and bond strength from measurable parameters and bridge the gap between a theoretical understanding and technology of observed work was undertaken (Ref 12).

Researchers (Ref 13, 14) attempted to explain the entire work of adhesion across the metal-ceramic boundary in terms of physical forces using the dielectric principle. Such models are not of much use to the brazing industry, because most commercial metal-to-ceramic bonds are based on chemical bond formations.

Effects of Capillary Attraction and Wetting on Brazing

Capillary attraction makes leak-tight joints a simple proposition for brazing. In a properly designed joint, the molten filler metal is normally drawn completely through the joint area without any voids or gaps, and brazed joints remain liquid- and gas-tight under heavy pressures, even when the joint is subjected to shock or vibrational types of loading.

Capillary action results in the phenomenon where surface tension causes molten braze filler metal to be drawn into the area that covers the parallel surfaces that are to be brazed.

Capillarity is a result of surface tension between base metals(s), filler metal, flux, or atmosphere and the contact angle between base metal and filler metal. In actual practice, fillermetal flow characteristics are also influenced by dynamic considerations involving viscosity, vapor pressure, gravity, and metallurgical reactions between filler metal and base metal.

As a matter of fact, present-day brazing practices have evolved as the result of an empirical approach to the phenomena of wetting and spreading, which are of prime importance in the formation of brazed joints. Classical, physical, and chemical principles led to equations governing the shape of liquid surfaces and the rate of filling a capillary gap in systems that do not interreact. However, the extension of theory to practical systems necessitates the consideration of a number of complicating factors, which often arise in everyday practice. A few of these factors include the condition of the solid surface as to the presence of oxide films and their effects on wetting and spreading, surface roughness, alloying between the filler metal and base metal and the extent to which this affects the thermodynamic properties of the liquid and solid surfaces, and the condition and properties of the brazing atmosphere.

The factors that control the rate at which wetting, spreading, and capillary flow occur are of great practical, as well as theoretical, interest. Studies have indicated profound influences of various kinds of surface activation that cannot be explained in terms of surface energies or alterations in equilibrium contact angle (Ref 15, 16). Some of the most spectacular of these effects have been observed in systems in which a finite contact angle is thermodynamically unstable, because the solid-vapor surface energy exceeds the sum of the liquid-solid surface energies—that is, a system in which thermodynamics would predict complete spreading. In actual fact, spreading may or may not occur in this type of system, and the rate of spreading can be markedly dependent on surface chemistry, although the fundamental mechanisms of this dependence are not all clear.

Wetting is, perhaps, best understood by example. If a solid is immersed in a liquid bath and wetting occurs, a thin, continuous layer of liquid adheres to the solid when it is removed from the liquid. Technically speaking, in the
wetting process, the force of adhesion between the solid and the liquid is greater than the cohesive force of the liquid. In practical terms, with respect to brazing, wetting implies that the liquid filler metal spreads on the solid base metal instead of balling up on its surface (Fig. 2.3). It has been demonstrated that wetting actually depends on a slight surface alloying of the base metal with the filler metal.

A comprehensive theory of the wetting or spreading of liquids on solid surfaces is presented in Ref 17 and 18.

It can be concluded that wetting is the ability of the molten filler metal to adhere to the surface of a metal in the solid state and, when cooled below its solidus temperature, to make a strong bond with that metal.

Wetting is a function not only of the filler metal but also of the nature of the metal or metals to be joined. There is considerable evidence that in order to wet well, a molten metal must be capable of dissolving, or alloying with, some of the metal on which it flows.

Wetting is only one important facet of the brazing process. A very important factor affecting wetting is the cleanliness of the surface to be wetted. Oxide layers inhibit wetting and spreading, as do grease, dirt, and other contaminants that prevent good contact between the filler metal and the base metal. One of the functions of a flux is to remove the oxide layer on the joint area and to expose clean base metal.

Good wetting and spreading of the liquid filler metal on the base metal are necessary in brazing, because the mechanics of the process demand that the filler metal be brought smoothly, rapidly, and continuously to the joint opening. If the conditions within the capillary space of the joint do not promote good wetting, the filler metal is not drawn into the space by capillary attraction.

It all boils down to the fact that, for successful joining of components by brazing, the filler metal selected must have a melting point above 450 °C (840 °F) and must also wet the base metal without melting it. Then, the joint must be designed so that the mating surfaces of the components are parallel and close enough together to cause capillary attraction.

**Practical Experience, Work-Related Tips, and Problem Solving**

In order to braze tungsten carbide (WC) granules or diamonds to 1010 carbon steel wheels with BNi-2 filler metal, avoid the problem of filler metal sagging. Because the wheels must rest flat in the furnace, the diamonds or carbides are then on the vertical surface of the wheel diameter.

Typical brazing takes place at 1040 °C (1900 °F) in a pure dry hydrogen atmosphere. There are a large number of variables that must be taken into consideration. It is much easier and more practical to use temperature as the controlling variable.

Key variables that affect braze quality include:

- The chemistry which is controlled by a specification and as a result the melting and flow characteristics of the filler metal are controlled by the chemistry.
- Partial pressure of nitrogen will affect the melting characteristics of the filler metal.
- A variation in the partial pressure of oxygen will affect the melting and flow characteristics of the filler.
- The length of time in the oxidation range of 540 to 925 °C (1000 to 1700 °F) can also alter the melting and flow characteristics of the filler metal.
- The heating rate, particularly at the high temperature where diffusion takes place, can alter the melting and flow characteristics.
• The maximum brazing temperature is the best variable to control, because any one of the previously mentioned variables can change, requiring a change in the brazing temperature. A better braze filler metal for this type of application would be a very wide-melting-range material and a filler metal of Cr-Ni-B-Si-Fe. This filler metal has a melting range of 970 to 1160 °C (1780 to 2120 °F).
• Therefore, the large number of variables presents a problem, but considering and taking into account the various variables, control of the flow of the filler metal is feasible.

REFERENCES
