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FUNDAMENTAL METALLURGICAL CONSIDERATIONS IN BRAZING AND SOLDERING[a]

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Introduction

The practice of joining materials by brazing and soldering techniques dates to ancient times [1], but a cursory inspection of the inner workings of nearly any piece of consumer electronics equipment should be enough to convince anyone of the technological importance of these processes even today. The fact that these processes can be done easily by manual techniques, or can just as easily be automated have helped make them into well-established commercial practices that are used for applications from household plumbing to high-performance aerospace and outerspace structures.

Brazing and soldering are materials joining processes that rely on the melting, flow, and solidification of a filler metal to form leaktight seals or strong, structural bonds. According to the American Welding Society [2], the features common to both processes are that: (1) only the filler metals and not the parts being joined are melted during processing; and, (2) the filler metals must wet the base materials and be drawn into or held in the joint by capillary attraction. The AWS definition further states that the term "brazing" is used when the joining process is performed above 450°C, while the term "soldering" is used below that temperature. This distinction is somewhat arbitrary, and, in reality, there is no fundamental difference between the two processes.

Because brazing and soldering do not involve melting of the joint component materials and they can be accomplished over a wide range of temperatures depending on filler metal composition. These processes have some significant advantages compared to fusion welding. For instance, alloys which are susceptible to solidification cracking or subsolidus cracking due to limited ductility may be easily joined by brazing, even for high temperature applications. Also, brazing and soldering can be used for making dissimilar material joints which would otherwise be impossible, e.g. metals joined to ceramics or graphites. Other desirable attributes of these processes are that: thermally induced stresses can be minimized by heating components uniformly in a furnace; and, flexibility in selecting a heating process and filler metal permits close assembly and finish tolerances to be maintained, and can reduce the need for costly secondary operations.

Many variations of brazing and soldering exist, but, in their traditional, and perhaps most common, form they are accomplished by uniformly raising the temperature of an assembly to a point where the filler metal and flux (if used) become molten. Ideally, a liquid filler metal fills a capillary gap between the base materials as illustrated in Fig. 1, and a bond is achieved when the assembly is cooled from the joining temperature. Although Fig. 1 is a fairly simple representation, brazing and soldering result in and depend on some rather complicated processes occurring on the surfaces of the materials involved. Wetting of the base materials by the filler metal is required to develop useful bonding. Once wetting conditions are established, capilliary forces produce flow of the liquid filler metal, and act to fill the joint gap. Both wetting and flow are strongly influenced by the existing surface conditions, the chemical reactions occurring at the interfaces and within the bulk phases, and the geometry of the joint. In turn, the extent and nature of wetting and flow, as well as joint geometry directly affect the final properties of the joint. The basic phenomena of wetting and flow are major concerns in brazing and soldering operations, and, therefore, will be emphasized in this brief review.

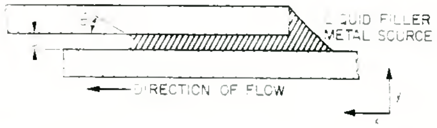

Figure 1. Schematic representation of filler metal flow into a braze or solder joint of gap D.

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Wetting in Brazing and Soldering

Wetting under conditions of chemical equilibrium

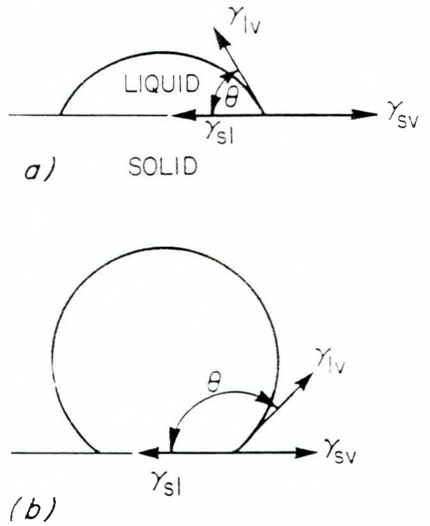

Figure 2. Equilibrium configuration of a liquid droplet on a solid substrate for conditions of (a) wetting, and (b) nonwetting.

Factors important for determining the extent of wetting can be illustrated by the familiar problem of describing the equilibrium configuration of a liquid droplet resting on a flat, horizontal solid surface, shown in Fig. 2 both for conditions of (a) wetting, and (b) nonwetting. The original treatment of this problem is attributed to Young who used mechanical equilibrium to relate the wetting angle, θ, to the horizontal components of the various surface tensions as:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv}\cos\theta \qquad (1)$$

where the surface tensions are γ_{sv} at the solid/vapor interface, γ_{sl} at the solid/liquid interface, and γ_{lv} at the liquid interface. The wetting angle is measured through the liquid phase so that wetting occurs for $\theta < 90°$, and non-wetting is represented by $\theta > 90°$. Spreading is a condition where liquid spontaneously covers the entire solid surface, and this occurs when θ approaches the value of 0°. Alternatively, wetting may be defined as the reduction of the total surface energy of the solid by the liquid, i.e. $\gamma_{sv} > \gamma_{sl}$. The condition of non-wetting can then be defined as $\gamma_{sl} > \gamma_{sv}$, and the quantity $(\gamma_{sv} - \gamma_{sl})$ can be considered the driving force for wetting.

The validity of the Young equation has been questioned over the years, but it has since been derived using rigorous thermodynamic principles. For instance, Johnson [3] considered this problem, showed that Young's equation was correct, and further treated the effects both of curvature on the pressure within the liquid, as well as that of gravity. Another important assumption implicit in this treatment of wetting is that the solid-liquid-vapor system is in chemical equilibrium, i.e. there is no chemical reaction at, or mass transport across the interfaces.

Wetting under conditions of chemical non-equilibrium

In reality, the wetting which occurs in brazing and soldering operations generally is not initiated and may not be completed under conditions of chemical equilibrium. The requirement of chemical equilibrium then can be a drawback in applying the Young equation analysis directly to these processes. The mechanics of wetting under condition of chemical non-equilibrium have been addressed in detail by Aksay el al. [4] and applied to some of the situations which might be encountered in brazing and soldering. According to their analysis, wetting in a solid-liquid-vapor is a dynamic process in which the individual surface tensions and thus the contact angle is continually changing until a state of chemical equilibrium is reached.

Wetting in systems of technological interest is usually accompanied by solution reactions or by the formation of a reaction layer at the solid-liquid interface, and either type of reaction must result in a decrease in the free energy of the solid-liquid-vapor system. Only the interface regions are involved in the initial stages of wetting, so that the initial free energy decrease of the system can be attributed solely to that of the solid-liquid interface. The magnitude of the decrease in the specific interfacial free energy of the solid-liquid interface, Δg^{sl}, then is directly equal to $(-\Delta G^{sl}/A)$, where $-\Delta G^{sl}$ is the free energy change associated with the bulk phases constituting the solid-liquid interface and A is the interfacial area. In this analysis, the surface tension of the solid-liquid interface is a dynamic quantity described by:

$$\gamma_{sl}' = \gamma_{sl}^{0} + \Delta g^{sl} \qquad (2)$$

where γ_{sl}^{0} is the initial solid-liquid interfacial tension. Because the magnitude of $-\Delta G^{sl}$ can be very large for some reactions, the initial surface tension can be reduced substantially from its equilibrium value, resulting in enhanced wetting.

Under chemical equilibrium conditions, however, specific interfacial free energies will always be higher than the free energy associated with the reacted bulk phases. Consequently, as reactions continue to completion at the solid-liquid interface, the equilibrium interfacial tension value must be approached. Therefore, after an initial decrease, γ_{sl}' increases as it gradually approaches the equilibrium value representative of the reacted bulk phases, γ_{sl}. This general process is shown schematically in Fig. 3.

Aksay et al. [4] defined four possible wetting situations assuming that chemical equilibrium is maintained between the vapor and the condensed phases, but not between the solid and liquid: (1) only the solid is not saturated with some or all of the components of the liquid, (2) only the liquid is not saturated with some or all of the

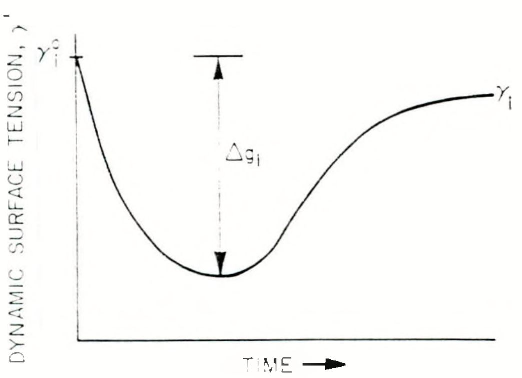

Figure 3. Variation of interfacial tension (denoted by the subscript i) with time for a system which is not initially at chemical equilibrium. (After Aksay el al. [4])

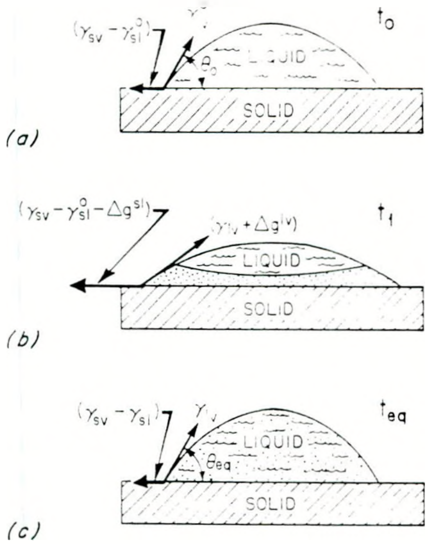

Figure 4. Schematic representation of the dynamic stages of wetting for a system where only the liquid is not saturated with some of the elements of the solid. Dissolution of solid in liquid is indicated by shading in (b) and (c). (After Aksay el al. [4])

components of the solid, (3) both phases are unsaturated with respect to the other, and (4) a compound forms at the solid-liquid interface. The stages associated with wetting where only the liquid is not saturated with the solid are illustrated schematically in Fig. 4. At time t = 0, Young's equation can be used to describe the mechanical equilibrium of liquid contact with the solid in terms of the surface tensions of the unreacted solid and liquid phases. These surface tensions are defined as γ_{sv}, γ_{sl}, and γ_{lv} where the latter two terms are for liquid phase of the original, unreacted composition. As the liquid phase becomes saturated with the components of the solid γ_{sl}^0 and γ_{lv}^0 decrease because of the free-energy contribution of the reaction, as indicated at time t_1. As time progresses, diffusion permits the liquid composition to equilibrate, the dynamic surface tensions approach the values consistent with chemical equilibrium, γ_{sl} and γ_{lv} as indicated for time t_{eq} in Fig. 4. One result of this process is that the initial reductions in surface tensions may produce transient spreading, followed by a pull-back of the droplet as the equilibrium contact angle is attained. The extent to which the configurational changes indicated in Fig. 4 occur will depend on the liquid viscosity, diffusion rate in the liquid, and the magnitude of the initial free energy of reaction, Δg's.

The third and fourth cases proposed by Aksay et al. [4] are more relevant to brazing and soldering but are also more difficult to describe using simple concepts. However, in the case of compound formation at the solid-liquid interface it can be seen that an initial decrease of contact angle is very likely, and that compound may completely isolate the solid surface from the liquid. The equilibrium contact angle then will be determined by the surface tension of the compound. If the surface tension of the compound is lower than that of the solid metal, as might be expected, then pull-back, or de-wetting, of the droplet should occur. The phenomenon of de-wetting is often observed, for instance, in the soldering or coating of Cu with Sn-Pb alloys, [5] and is attributed to the formation of Cu-Sn intermetallic phases at solid-liquid interfaces.

Flow in Brazing and Soldering

Horizontal Joints

While the theories of wetting provide insight into the driving force for the flow of liquids during brazing and soldering, fluid mechanics must be applied to determine the resistance against which the driving force must work, and how flow is influenced by material properties. Fluid mechanics is too complicated a subject for a detailed discussion here, but the application of some simple principles to brazing and soldering, based largely on the works of Milner [6], and Funk and Udin [7] will be presented.

The advancing front of a liquid metal in a capillary consisting of two horizontal plates is shown schematically in Fig. 1. If the plates are spaced so closely that gravitational effects can be ignored, then the pressure across the liquid-vapor surface is given by the familiar expression:

$$\Delta P = \frac{-2\gamma_{lv}\cos\theta}{D} \qquad (3)$$

where D is the separation between the plates.

According to Milner [6], fluid flow under the conditions shown in Fig. 1 are approximately laminar. Based on the assumption of laminar flow, the velocity v of the advancing liquid metal front as a function of distance y in the joint gap is given by:

$$v = \left(\frac{1}{2\eta}\right)\left(\frac{dP}{dx}\right)(y^2 - yD) \qquad (4)$$

where η is the liquid metal viscosity, and P is the pressure. Assuming that the plates are uniformly spaced, so that $dP/dx = \Delta P/x$, then the average fluid velocity is:

$$\bar{v} = \frac{1}{6}\left(\frac{\gamma_{lv}\cos\theta}{\eta}\right)\left(\frac{D}{x}\right) \qquad (5)$$

Simple integration can then be used to determine the time required to flow a distance x as:

$$t = \frac{3\eta x^2}{D\gamma_{lv}\cos\theta} \qquad (6)$$

and rearranging this gives the distance flowed in any length of time:

$$x = \sqrt{\frac{Dt\cos\theta}{3\eta}} \qquad (7)$$

This last expression then relates the distance a liquid metal flows in a joint gap to the height of the gap, the time allowed for filling, and the physical properties of the alloy. The distance flowed in a given amount of time, an important practical consideration, can be increased by increasing D, and by chosing a filler metal alloy with a high γ/η ratio. However, the joint gap cannot usually be increased substantially, but will be limited by factors such as the affect of gravity on the ability of the liquid filler metal to retain a well defined meniscus, manufacturing details such as fixturing, and mechanical property requirements of the joint. Increasing the joining temperature is the most effective way of increasing the distance flowed, and this is primarily because of the dependence of viscosity on temperature. The surface tension of liquid metals decreases with increasing temperature by a weak linear dependence. However, the viscosity of liquid metals decreases exponentially with temperature, which results in γ/η increasing with temperature. Two other important points regarding Equation 7 are that: (1) doubling the joining time increases the distance flowed by a factor of only 1.4; and, (2) theoretically and provided the liquid filler metal is available in sufficient supply, it can flow an indefinite distance between two flat plates.

Vertical Joints

For the case of vertical plates, the liquid metal will still be driven to rise in the joint gap, but because the weight of the liquid must be supported by the pressure differential there is a maximum height *h* that can be attained. Ignoring the weight of the vapor phase, the pressure across the liquid-vapor interface for vertical plates is given by:

$$\Delta P = -\frac{2\gamma_{lv}\cos\theta}{D} + \rho g y \qquad (8)$$

where ρ is the density of the liquid metal, g is the gravitational constant, and y is the liquid height. Eventually the weight of the liquid stops its rise, and $\Delta P = 0$. Then, from equation 8 the familiar expression for capillary rise is obtained:

$$h = \frac{2\gamma_{lv}\cos\theta}{D\rho g} \qquad (9)$$

The velocity distribution in the joint gap, the average velocity of the liquid metal, as well as the relationship between distance flowed and time can be calculated just as for the horizontal case, [7] but the need to account for the weight of the liquid in the expressions for a vertical configuration makes them somewhat more complicated. For instance, the relationship between distance flowed and time is:

$$t = \frac{12\eta\gamma_{lv}\cos\theta}{\rho^2 g^2 D^3}[-2R - 2\ln(1 - R)] \qquad (10)$$

where $R = y/h$.

As in the case of wetting theory, the simplest treatment of fluid flow assumes the solid-liquid-vapor system is in a state of chemical equilibrium. Alloying can influence filler metal flow by altering surface tensions and the contact angle, as discussed above. Alloying can also alter the viscosity and melting characteristics of the liquid. For instance, if a eutectic alloy is used for a soldering operation and if it dissolves an element contained in the solid substrate, then its composition could change such that it no longer melts congruently. Instead of being completely molten the filler metal now will contain a fraction of solid phase which will increase its viscosity. An example of this behavior is the dissolution of gold into In-50Pb wt% which results in the solder becoming pasty through the formation of $AuIn_2$ precipitates in the molten alloy.[8] The formation of reaction layers at the solid-liquid interface can also influence liquid flow. Formation of a reaction layer means that the composition of the liquid changes, which can then alter its melting characteristics and viscosity. Reaction layers also can have beneficial effects as in the case of the reaction of In-48Sn wt% solder with Au.[9] A $AuIn_2$ reaction layer forms in this system and acts to prevent continued dissolution of the Au and thereby permits adqueate flow properties to be maintained.

Discussion

The ability to obtain braze or solder joints which are free of defects and have properties suitable for their intended applications depends directly on the phenomena of wetting and flow of liquid filler metals. The ideal treatments of wetting and flow assume that the solid, liquid, and vapor phases are in a state of chemical equilibrium. In real materials systems, chemical reactions which occur during brazing and soldering can influence both wetting and flow characteristics. The extent of the effects of alloying on these phenomena depends on factors such as the initial compositions of the various phases, the solubility of elements in them, diffusion kinetics, and the exact phase relations in the appropriate systems. These effects can be complicated and difficult to predict.

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References

1. P. M. Roberts, "Gold Brazing in Antiquity," Gold Bulletin, 6(4)(1973), 112-119.

2. "Brazing Manual," Fourth Edition, (American Welding Society, Inc., Miami, Florida, 1991).

3. R. E. Johnson, "Conflicts between Gibbsian Thermodynamics and Recent Treatments of Interfacial Energies in Solid-Liquid-Vapor Systems," Journal of Physical Chemistry 63(10)(1959), 1655-1658.

4. I. A. Aksay, C. E. Hoge, and J. A. Pask, "Wetting under Chemical Equilibrium and Nonequilibrium Conditions," Journal of Physical Chemistry 78(12)(1974), 1178-1183.

5. G. L. J. Bailey and H. C. Watkins, "The Flow of Liquid Metals on Solid Metal Surfaces and its Relation to Soldering, Brazing, and Hot-Dip Coating," Journal of the Institute of Metals 80(1951), 57-76.

6. D. R. Milner, "A Survey of the Scientific Principles Related to Wetting and Spreading," British Welding Journal 5(3)(1958), 90-105.

7. E. R. Funk and H. Udin, "Brazing Hydromechanics," Welding Journal 31(6)(1952) 310-s-316-s.

8. M. M. Karnowsky and F. G. Yost, "The Au-In-Pb system: The $AuIn_2$-In-Pb portion," Metallurgical Transactions A 7A(1976) 1149-1156.

9. D. M. Jacobson and G. Humpston, "Gold coatings for fluxless soldering," Gold Bulletin 22(1)(1989) 9-18.