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Active Solders and Active Soldering

Shih-Ying Chang, Yan-Hua Huang and Lung-Chuan Tsao

Abstract

Due to the relatively high stability of ceramic surfaces, ceramics, graphite, and alloys that easily form an oxide passivation layer by natural oxidation, such as aluminum alloys, titanium alloys, and magnesium alloys, are not wetted by common solders and brazing fillers. Moreover, in most applications, the brazing temperature is so high that it causes hot cracking or functional degradation of the difficult-to-wet materials. Active filler metals containing active elements have been developed, which can successfully join the nonwetting materials at low temperatures ($<250^{\circ}\text{C}$) in air. The active elements, such as titanium, magnesium, and rare earth elements, in active solders play an important role in wettability and reactivity between filler metals and difficult-to-wet materials. Solders with active element content have been shown to provide excellent wettability. Hence, direct active soldering has been developed to simplify the manufacturing of difficult-to-wet material joints. A practical understanding of the design and characterization of low melting point active solders and active soldering processes is elaborated in this chapter. The effects of active elements, active solder characteristics, mechanism of active soldering, active soldering techniques, and specific applications are introduced. The influence of the thermal and mechanical activation on the interfacial reactions between filler metals and difficult-to-wet materials during the active soldering process is also discussed.

Keywords: active soldering, difficult-to-wet materials, rare earth elements, titanium, magnesium, wetting, mechanical agitation, ultrasonic-assisted soldering

1. Introduction

Due to functional, structure, or property needs, joining of dissimilar materials is increasingly used to achieve components with improved or tailor-engineered properties. For example, ceramic-metal joints have found wide application in electrical engineering and electronics for their combination of ceramic insulating properties and metallic conductivity. Moreover, ceramic-metal seals are used extensively in applications such as engine ignitors, vacuum tubes, high-voltage feedthroughs, magnetic recorder heads, synthetic colorless sapphire-metal windows, and ceramic sputtering targets [1]. Most ceramics have very high melting temperatures, so the applicability of conventional fusion welding methods to the bonding of ceramic-metal is not feasible in cases of extremely high power requirements. During the fusion welding process, the high temperature can cause severe property degradation or fracture in surrounding heat-affected areas. Furthermore, the great thermal expansion coefficient mismatch between ceramics and metals can cause serious residual stresses at the interface of the ceramic and

metal [2]. In lightweight construction, the bonding of difficult-to-wet materials such as aluminum alloys, magnesium alloys, or titanium alloys, which easily forms an oxide passivation layer by natural oxidation, entails numerous difficulties. Brazing and soldering with fillers as interlayers are considered to be more feasible ways to bond dissimilar materials such as ceramics and difficult-to-wet metals. However, because ceramics provide mostly covalent or ionic bonding, have a very stable electron configuration, and are chemically inert, most brazing or soldering fillers cannot be wetted on their surfaces [3]. Thus, the filler metal is the most important key factor in determining wettability. Direct bonding has been developed to simplify wetting of difficult-to-wet materials by using active fillers containing active elements that improve the wettability of the filler on the difficult-to-wet material surface and eliminate the need for pre-metallization during the joining process [4].

2. Active solders

Both brazing and soldering are joining processes that use the principle of capillary action to distribute a molten filler metal between the surfaces of base materials [5]. In all cases, filler metal melting temperatures are below the melting temperatures of the base materials. Brazing filler metals melt completely at temperatures above 450°C, while soldering filler metals melt below that temperature [5]. A variety of alloys are used as filler metals for brazing, depending on the workpieces and the intended use or application method. In general, braze alloys are made up of Cu, Ag, Ni, or precious metals [6]. Low melting point metals such as Pb, Sn, Zn, Sb, and In are usually used for soldering filler [7]. Filler metals can be divided into three types according to their melting points, namely, high melting point, medium melting point, and low melting point fillers, as shown in **Figure 1** [8].

Chemical bonding at the interfaces of the filler metal and base materials is evaluated by wettability, defined as the ability of the molten filler metal to spread uniformly onto the surface of a base material. The molten filler metals must be able to be wetted on the surface of the base materials during the joining process, whether it is brazing or soldering. Ceramics and some materials, which easily form an oxide passivation layer by natural oxidation, such as aluminum alloys, magnesium alloys, titanium alloys and stainless steels, have surfaces of extreme physical and chemical stability that prevent filler metals from wetting the surface.

One critical parameter of wettability is the contact angle between the drop of molten filler and the wetting surface, as shown in **Figure 2a** and **2b** [2]. The contact angle can be calculated by Young's equation [9]:

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (1)$$

where θ is the contact angle, γ_{SV} is the solid-vapor interfacial energy, γ_{LV} is the liquid-vapor interfacial energy, and γ_{SL} is the solid-liquid interfacial energy.

If the solid-vapor interfacial energy (γ_{SV}) is higher than the solid-liquid interfacial energy (γ_{SL}), the right side of Young's equation will be positive, so $\cos\theta$ must be positive and the contact angle will be less than 90° [9]. Small contact angles correspond to high wettability, as shown in **Figure 2a**. A contact angle of less than 90° indicates that wetting of the surface is favorable, and most strong chemical bonds can be formed at the interface. To improve the wettability of the filler, it is necessary to reduce the surface tension between the bonding material and the filler, usually by forming a chemical reaction between the filler and the bonded material surface, as shown in **Figure 3** [9].

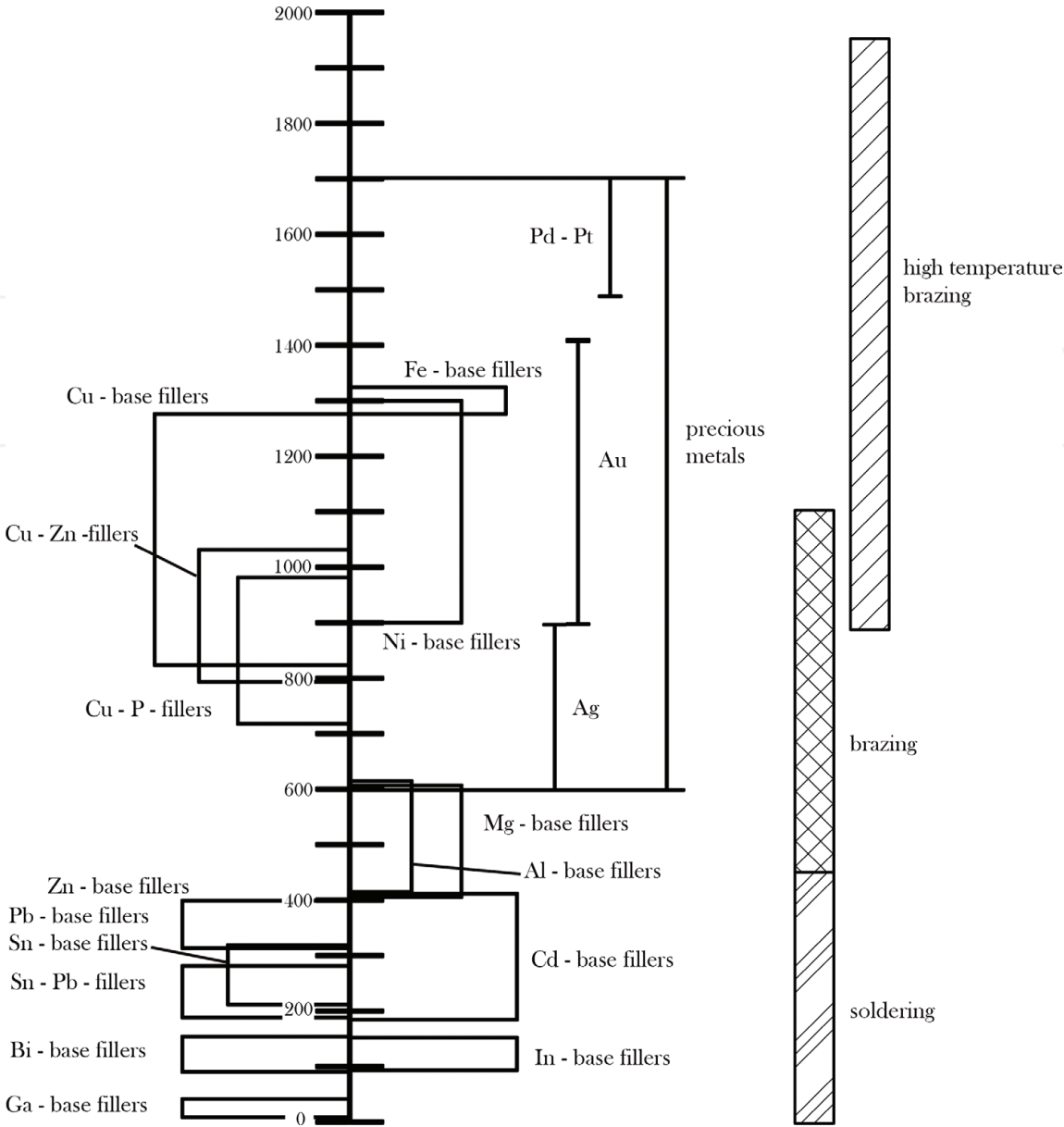


Figure 1.
The melting ranges of some typical solder and braze materials [8].

To obtain better bonding integrity, difficult-to-wet materials, especially ceramics, are usually metallized prior to brazing or soldering. To overcome the non-wetting of common filler metals on the surfaces of difficult-to-wet materials, pre-metallization by molybdenum-manganese method, electroless plating, physical vapor deposition (PVD), chemical vapor deposition (CVD), thermal spraying, or ion implantation can be used to increase the wettability [10]. The indirect joining process includes two steps and is costly; thus, it is difficult to implement. Recently, direct active brazing has been developed to join difficult-to-wet materials such as ceramic and graphite. The direct brazing process, without the need for pre-metallizing, is simpler than the indirect brazing. Active brazing fillers that include an active element, such as Ti, Zr, Ta, Nb, or Hf, are used to promote wetting [11–14]. It is believed that the addition of an active element to filler metals can effectively improve the wettability of difficult-to-wet materials by reducing the solid-liquid interfacial free energy and allowing chemical reactions in the interfaces between filler metals and substrates [15]. Due to its high chemical activity, titanium is often chosen as the active element in filler metals to improve the wetting on ceramic surfaces. For example, Ag–Cu–Ti active filler has been used widely to join ceramics because of its wettability and good bond strength [16–20]. However, the active filler metals for ceramic brazing have a high

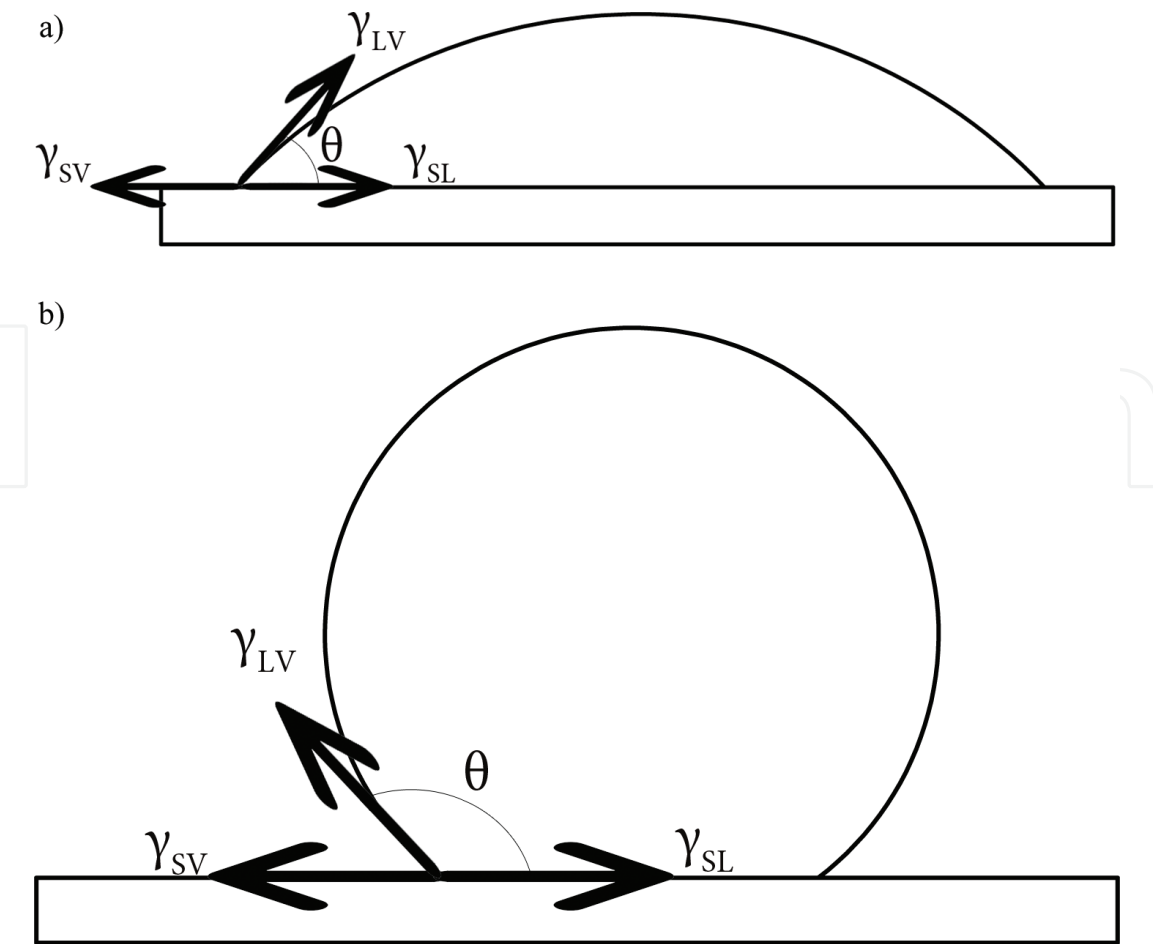


Figure 2. Contact angle of sessile drop configurations (a) wetting and (b) nonwetting [2], where θ is the contact angle, γ_{SV} is the solid-vapor interfacial energy, γ_{LV} is the liquid-vapor interfacial energy, and γ_{SL} is the solid-liquid interfacial energy.

melting point of about 750–850°C. Brazing is conducted at temperatures generally higher than 800°C. For some applications, the brazing temperature is so high that it causes hot cracking or functional degradation of the ceramics. Moreover, due to the difference in the thermal expansion coefficients of the metal and ceramic materials, high residual stress will develop upon cooling from the elevated temperature. Hence, the bonding temperature should be as low as possible to minimize the residual stresses. To solve this problem, low melting point filler metals containing titanium, such as $\text{Sn}_{10}\text{Ag}_4\text{Ti}$ and $\text{Pb}_4\text{In}_4\text{Ti}$, have been developed, and they exhibit excellent wettability on ceramic substrates at 850°C. Unlike the widely used Ag–Cu-based active filler metals, the low melting point filler metals possess a melting range below 300°C. However, brazing ceramics with low melting point active filler metals is always conducted above 850°C, such as the Ag–Cu–Ti brazing temperature, owing to the decent thermodynamic activation [21–23]. Although the act of brazing with low melting point filler metals must be conducted at elevated temperatures far above

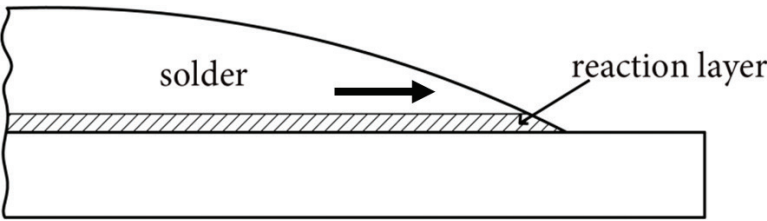


Figure 3. Schematic of the spreading process of solder with the formation of reaction layer [9].

Solder	Sn	Zn	Ag	Al	Cu	Ti	In	Cr	Ni	Ce, Ga	Melting range, °C
Sn ₄ Ag ₄ Ti	Bal.	—	4	—	—	4	—	—	—	<0.5	220–232
Sn ₃ Ag ₃ Cu ₄ Ti	Bal.	—	3	—	1	4	—	—	—	<0.5	220–232
Sn ₅ In ₄ Ti	Bal.	—	—	—	—	4	5	—	—	<0.5	220–232
Zn ₆ Al ₆ Ag	—	Bal.	6	6	—	—	—	—	—	<0.5	140–220
Zn ₄ Ag ₄ TiCr _{0.7}	—	Bal.	4	—	—	4	—	0.7	—	<0.5	220–232
Zn ₄ Ag ₄ TiNi _{0.3}	—	Bal.	4	—	—	4	—	—	0.3	<0.5	180–220

Table 1.
Active solders developed by Hillen et al. [4].

their melting points, their lower solidification temperature can alleviate the thermal stresses in the ceramic-metal joint. Active soldering techniques, which provide for bonding of various ceramics and difficult-to-wet materials at low temperature, have also been developed [4]. The solders used for active soldering consist of a low melting point metal such as tin or zinc with active elements such as titanium and rare earth elements. There have been reports of active solders developed by adding rare earth elements (Ce, La) and a wetting promoter (Ga) into Sn–Ag–Ti, Zn–Ag–Ti, Sn–Bi–Ti, and In–Sn–Ti alloys [4, 24]. Hillen et al. initially developed active solders for soldering difficult-to-wet materials, as listed in **Table 1**. With these active solders, the joining process of ceramics can be performed at temperatures lower than 450°C without flux and without the need for premetallization or a protective atmosphere.

3. Effects of active elements

A number of active soldering filler metals for direct soldering of difficult-to-wet materials have been reported. S-Bond technologies LLC has developed a series of active solder metals and an active soldering process [25]. In a prior study, the active filler metallic alloy Sn–Ag–Ti(Ce, Ga) was successfully used to join indium tin oxide (ITO) targets with Cu backing plates at 250°C in air [26]. Moreover, a lower-melting-point-active-filler metal $\text{Sn}_{56}\text{Bi}_{4}\text{Ti}(\text{Ce}, \text{Ga})$ with a low bonding temperature of 180°C was used to join ZnS– SiO_2 targets with Cu backing plates [27]. Due to the high chemical activity of Ti, it can easily form the required subsequent chemical reaction between filler metal and substrate. Fu et al. [28] studied the effect of Ti content on the wetting behavior of the $\text{Sn}_{0.3}\text{Ag}_{0.7}\text{Cu}/\text{AlN}$ system. They demonstrated that the addition of Ti to Sn–Ag–Cu filler resulted in a significant enhancement of wettability for Ti content of 4–10%. Chang et al. [24, 26, 29, 30] have shown that the affinity of rare earth elements to oxygen gives rise to the reaction of Ti with some difficult-to-wet materials at a low temperature. Moreover, rare earth elements have a very strong affinity for oxygen, nitrogen, carbon, or almost all metals and hence create chemical reactions at the interface [31]. Qu et al. [32] investigated the effect of Ti content and Y additions on the oxidation behavior of Sn–Ag–Ti solder. Their results indicated that the addition of Y significantly improved the oxidation resistance of Sn–Ag–Ti solder. Due to the higher affinity of Y for oxygen than Ti, the Y added to the solder efficiently inhibited the oxidation of Ti during the soldering process. Many researchers have demonstrated that rare earth element dopants can significantly enhance solder bonding with difficult-to-wet materials [33–36]. The addition of Ti and rare earth elements to Sn or In alloys improves the solderability by increasing the wettability on difficult-to-wet materials. Furthermore, the oxidation resistances of these soldering filler metals are somewhat limited. For example, the addition of the rare earth element Ce to $\text{Sn}_{3.5}\text{Ag}_4\text{Ti}$ solder protects Ti from oxidation and enhances the activity of Ti [26, 28, 32]. Magnesium is also very chemically active and has good electric and thermal conductivity. It is also a suitable additive active element for Sn or In alloys used to increase the wetting in some applications of electronic packaging [37, 38]. Chang et al. [39, 40] have also developed a series of magnesium-containing active solders, as listed in **Tables 2–4**. $\text{Sn}_{3.5}\text{Ag}_{0.5}\text{Cu}_1\text{Mg}$ filler metal was used for joining alumina with alumina at 250°C in air. The microstructure of the bonding interface of $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ joint is shown in **Figure 4**, which demonstrates a good wettability of the filler metal on the alumina. Hence, a satisfactory joint can be obtained using the magnesium-containing active filler. A good bonding strength of 6.54 MPa can be achieved using the $\text{Sn}_{3.5}\text{Ag}_{0.5}\text{Cu}_1\text{Mg}$ filler metal.

Solder	Sn	In	Ag	Cu	Zn	Pb	Bi	Mg	Melting range, °C
M-S	Bal.	0	0	0	0	0	0	0.1-5	220-232
M-SA	Bal.	0	0.5-5	0	0	0	0	0.1-5	220-232
M-SAC	Bal.	0	0.5-5	0.1-2	0	0	0	0.1-5	220-232
M-SB	Bal.	0	0	0	0	0	10-60	0.1-5	140-220
M-SC	Bal.	0	0	0.1-2	0	0	0	0.1-5	220-232
M-SP	Bal.	0	0	0	0	10-50	0	0.1-5	180-220
M-SZ	Bal.	0	0	0	1-15	0	0	0.1-5	180-232

Table 2.
Magnesium-containing Sn-based active solders and melting ranges.

M-I	0	Bal.	0	0	0	0	0	0.1-5	150-160
M-IA	0	Bal.	0.5-5	0	0	0	0	0.1-5	144-160
M-IAC	0	Bal.	0.5-5	0.1-2	0	0	0	0.1-5	145-160
M-IC	0	Bal.	0	0.1-2	0	0	0	0.1-5	150-160
M-IS	30-60	Bal.	0	0	0	0	0	0.1-5	120-150
M-ISB	10-30	Bal.	0	0	0	0	10-40	0.1-5	60-100
M-IZ	0	Bal.	0	0	1-15	0	0	0.1-5	145-156

Table 3.
Magnesium-containing In-based active solders and melting ranges.

Solder	Sn	Zn	Bi	In	Ag	Cu	Mg
M-SZB	Bal.	5–15	0.1–10	0	0	0	0.1–5
M-SZI	Bal.	5–15	0	0.1–10	0	0	0.1–5
M-SZA	Bal.	5–15	0	0	0.1–10	0	0.1–5
M-SZBI	Bal.	5–15	0.1–10	0.1–10	0	0	0.1–5
M-SZBA	Bal.	5–15	0.1–10	0	0.1–10	0	0.1–5
M-SZBC	Bal.	5–15	0.1–10	0	0	0.1–5	0.1–5
M-SZIA	Bal.	5–15	0	0.1–10	0.1–10	0	0.1–5
M-SZIC	Bal.	5–15	0	0.1–10	0	0.1–5	0.1–5

Table 4.
Magnesium-containing SnZn-based active solders.

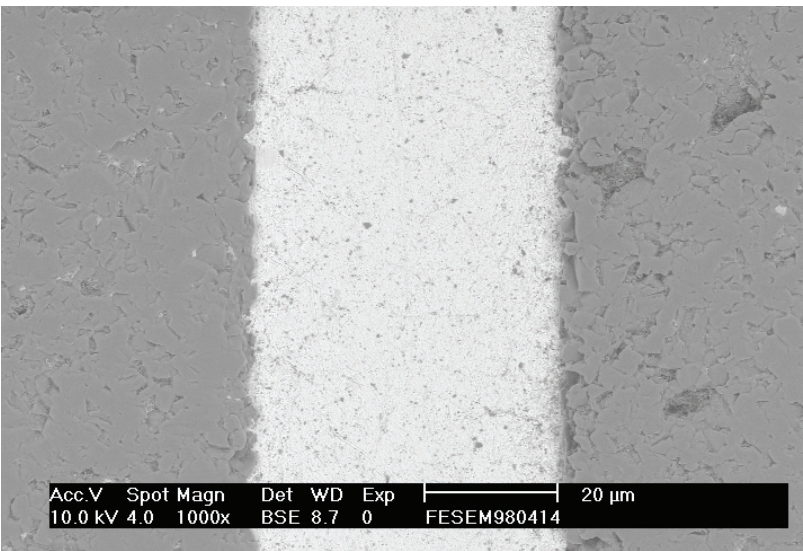


Figure 4.
Microstructure of the bonding interface of Al₂O₃/Al₂O₃ joint with Sn_{3.5}Ag_{0.5}Cu₄Mg filler metal.

4. Active soldering

Active soldering is a flux-free soldering process. The active solders can be activated by exposure to high temperature or mechanical agitation [41, 42]. Joining with low melting point active solders such as Sn₁₀Ag₄Ti and Pb₄In₄Ti is always conducted at elevated temperatures above 700°C, owing to the decent thermodynamic activation. Chai et al. [22] investigated the wettability of Sn₁₀Ag₄Ti on SiC and Al₂O₃ substrates. They indicated that the contact angles decreased with increases in temperature and heating time. The contact angle of the Sn₁₀Ag₄Ti filler metal on SiC decreased almost to 0° when the temperature was raised above 680°C. Ti aggregated strongly in the Sn₁₀Ag₄Ti/SiC and Sn₁₀Ag₄Ti/Al₂O₃ interfaces after brazing at 700°C. Kolečák et al. [43] indicated that the wettability of Sn_{3.5}Ag₄Ti(Ce, Ga) solder depended on temperature and wetting time. Wettability of the Sn_{3.5}Ag₄Ti(Ce, Ga) solder on Al₂O₃ was achieved with heating at 850°C for 43 min [42]. The schematic in **Figure 5** illustrates the wetting process of low melting point filler metal with high-temperature activation [43].

This soldering process, normally implemented under low temperature, requires mechanical activation to destruct the oxide layer forming on the liquid molten filler, after which the active elements Ti and rare earth elements can allow metallurgical

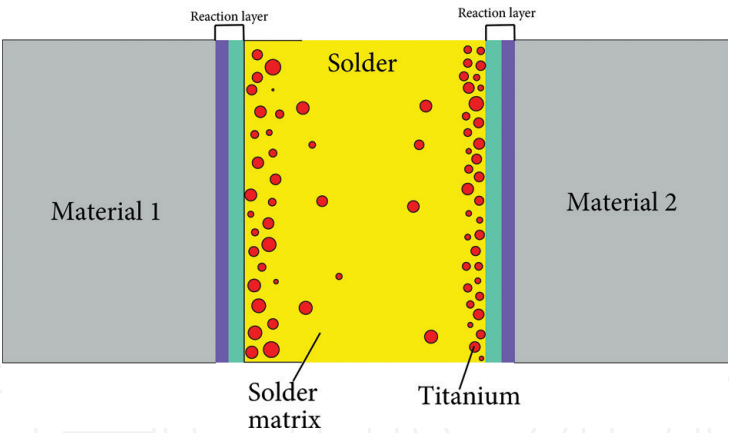


Figure 5.
Schematic of the wetting process of low melting point filler metal with high-temperature activation [44].

reaction with the substrate. Smith [41] has reported that mechanical agitation such as edge abrasion, brushing, vibration, and ultrasonic pressure can disrupt the molten active solder’s surface oxide, thus permitting metallurgical interaction between the active elements, Ti and rare earth elements, and substrate. **Figure 6** illustrates mechanical agitation to disrupt the oxide layer to activate the molten active solder [41].

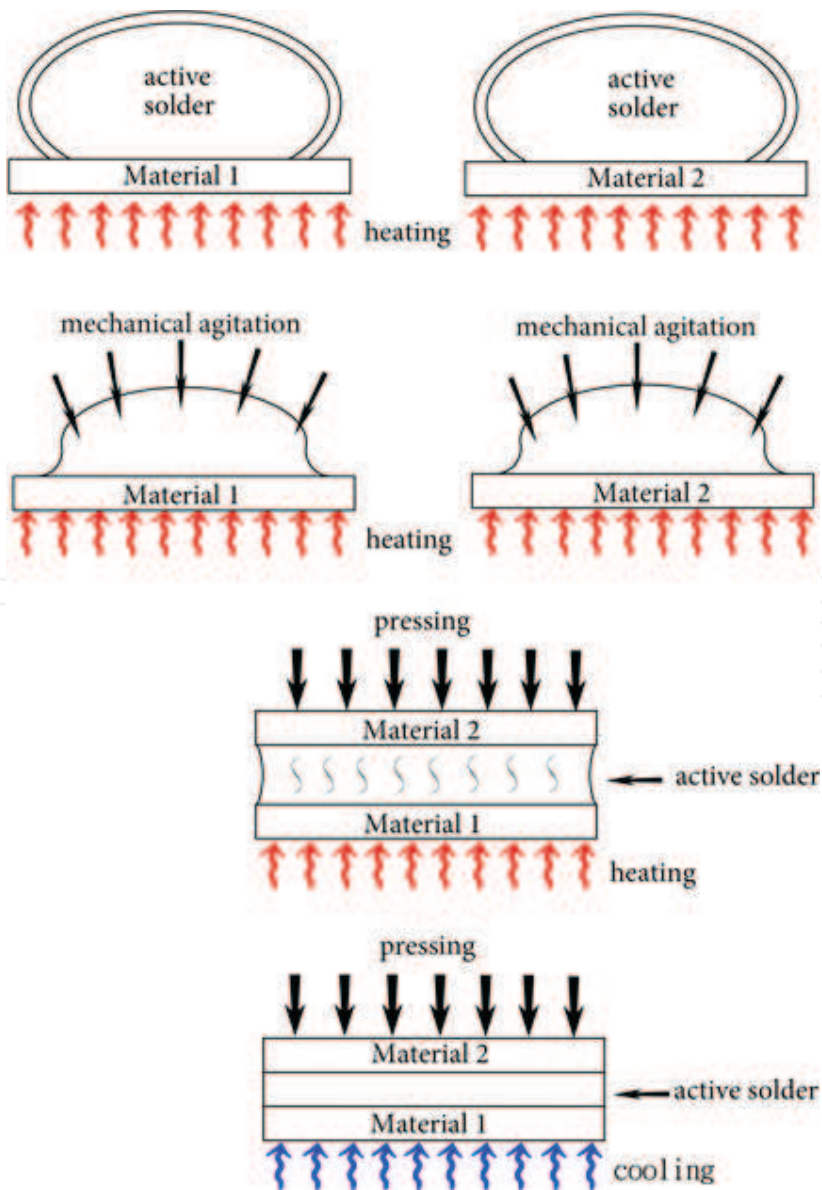


Figure 6.
Schematic of mechanical activation and soldering process [41].

Chang et al. [26, 29, 30] have investigated ITO/Cu, ZnS–SiO₂/Cu, and Al₂O₃/Cu joints using Sn_{3.5}Ag₄Ti(Ce, Ga) and mechanical agitation at 250°C. They have indicated that the affinity of rare earth elements to oxygen gives rise to the reaction of Ti with ITO, ZnS–SiO₂, and Al₂O₃ at a low temperature of 250°C. Their results have also shown a strong tendency of Ti to segregate at the ITO/solder, ZnS–SiO₂/solder, and Al₂O₃/solder interfaces. Cheng et al. [45, 46] investigated the influences of the active element Ti on interfacial reaction and soldering strength between Sn_{3.5}Ag₄Ti(Ce, Ga) alloy filler and Si substrate as well as SiO₂/SiO₂ joints. They also found that Ti played a critical role in obtaining reliable bonds for active soldering. The chemical adsorption of Ti on the substrate and the interfacial reaction between Ti and substrate were the active mechanisms. Similar to the cases in previous studies [24, 27], the joining process of ceramics can be performed using Sn₅₆Bi₄Ti(Ce, Ga) filler at temperatures lower than 180°C. The schematic in **Figure 7** illustrates the wetting process of low melting point filler metal with mechanical activation [47].

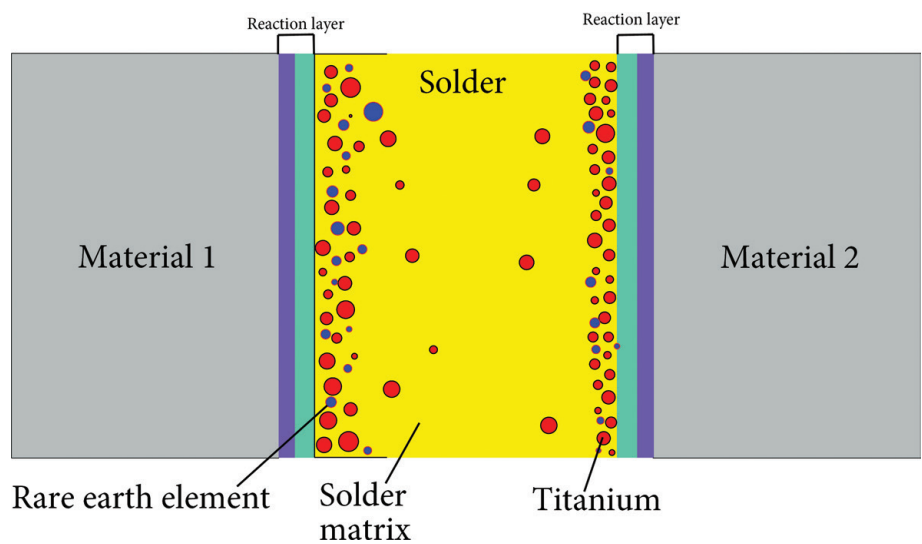


Figure 7.
Schematic of the wetting process of low melting point filler metal with mechanical activation [47].

Another promising option for solving the problems of oxidation and wetting of the filler metal on substrate is ultrasonic-assisted soldering technology. An ultrasonic vibration soldering system is illustrated in **Figure 8** [32]. The wettability study

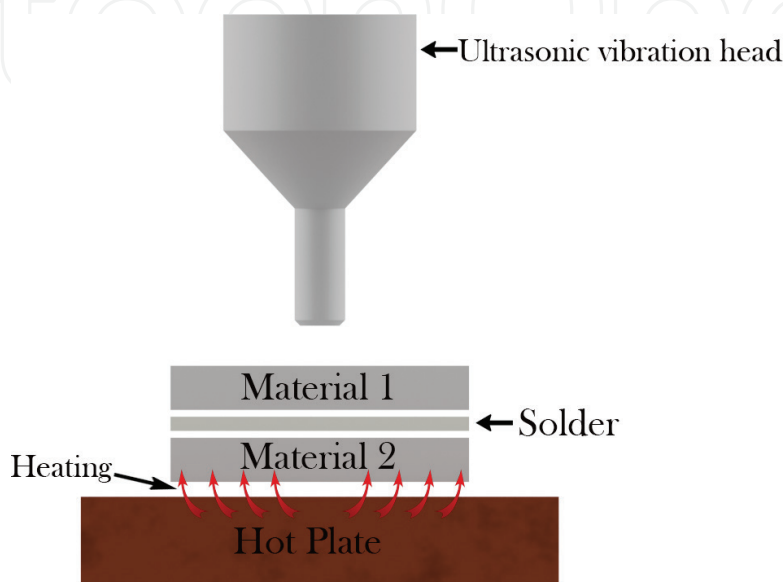


Figure 8.
Schematic of the ultrasonic vibration soldering system [32].

reported by Hillen et al. [4] presented an ultrasonic vibration method using an ultrasonic soldering iron, as shown in **Figure 9**. Ultrasonic vibration can effectively improve the wettability of active solder. Yu et al. [48] have reported that applying ultrasonic vibration during the soldering process causes the active solders Sn–Ag–Ti and Sn–Ag–Ti–Al to spread on the graphite surface at 450°C in air. Kolečák et al. [49] successfully used ultrasonic-assisted soldering to join SiC and copper with $\text{In}_{10}\text{Ag}_4\text{Ti}$ solder at 230°C.

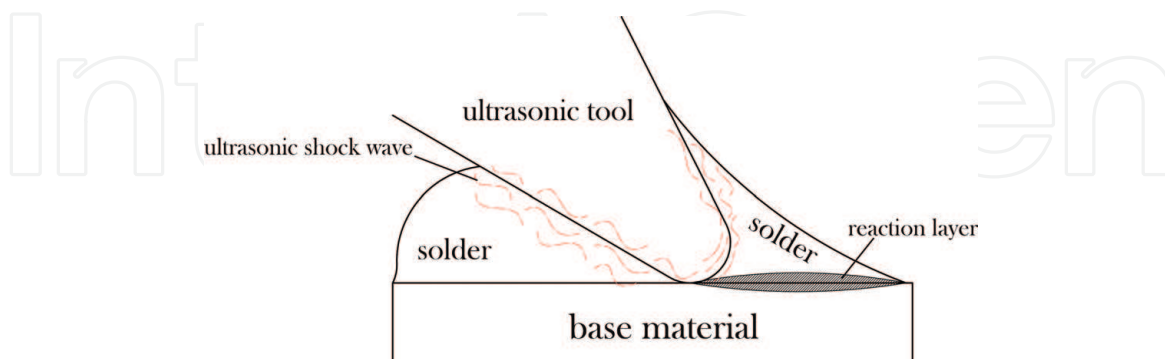


Figure 9.
Schematic of ultrasonic vibration soldering with an ultrasonic soldering iron [4].

5. Conclusion

With the rapid development of new materials and advanced technology in various industries, joining technologies play increasingly important roles. The poor wettability of ceramics for conventional filler metals and the large thermal residual stress make it extremely difficult to obtain sound ceramic/metal joints. Adding active elements such as titanium, rare earth elements, and magnesium to conventional solders provides improved wettability and bonding strength of most metals, glasses, and ceramics. The newly developed low melting point active solders and flux-free active soldering technology can effectively reduce the thermal stress between the ceramic and metal. Moreover, the active soldering process can be performed without the need for premetallization of difficult-to-wet materials and without flux or a protective atmosphere. In a number of cases, fluxless soldering is a necessary condition of optoelectrical devices, glass-to-metal, and ceramic-to-metal sealing. Additionally, active soldering can offer an economic metallization process for high-power ceramic substrates such as direct bonded copper (DBC), direct bonded aluminum (DBA), and active metal bonded (AMB). It has been shown that the active soldering has a great potential to improve the joining properties of difficult-to-wet materials. A gas-tight joint of ceramic/metal can be realized at low temperature (<250°C) in air without the need of premetallization for ceramic. Moreover, the active soldering process can also be applied to metallize the ceramics for electric and heat conduction and electroplating. Thus, this process provides low-cost, high-quality, environmental benefits and convenient joining technology.

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