Enhancement of mechanical properties of Copper Brazed by laser surface modification

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Abstract. Nowadays, laser surface modification (LSM) has become the most advance technique for improving the surface properties for joining methods. This is due to its advantages such as cleaner, precise, more reliable and provides exact control compare to other surface modification techniques. This technique also applicable on wide range of materials, such as metal/alloy, ceramic and polymer. Brazing is a metal-joining process in which two or more metal items are joint together by melting and flowing a filler metal into the joint, the filler metal having a lower melting point than the base materials. The brazing process performed under a controlled atmosphere in vacuum tube furnace. Microscopic observations were made by use of both optical and electron microscopes. Fibre laser surface modification-brazing of 2 mm thick 99% pure copper plate in the lap joint configuration performing with Cu-based filler metal. There are three microgrooves were produced with three different laser power apply 15 watt, 21 watt and 27 watt. It found that successful brazing and wetting can be achieved by modified the surface for the base metal. The result of shear tensile test indicated that the highest shear strength was achieve in groove by using 27. This is because of its excellent of its excellent spreading behaviour of molten filler metal, largest bonding interface area and suitable intermetallic compound (IMC) distribution.

Keywords. Laser surface modification; Brazing; Vacuum brazing; Microgroove; IMC

1. Introduction

The latest development of surface modification technology is the establishment of laser surface modification (LSM) technique [1,2]. This technique involves materials removal, ablation from material surface by radiating laser energy. Compare with others surface modification techniques, LSM not involve in harmful consumables and applicable on wide range of materials. Moreover, by being a non-contact, this technique is clean, simple and provide exact on control. For many years, studies have been conducted to enhance the surface properties of materials to better endure high temperature, wear resistance, improved coating adhesion and friction through coating or surface modification. There has been a heightened demand for surface engineered structure such as micro/Nano texture or surface modification to achieve desirable surface properties that are different from those origin materials for applications. Material surface properties for such applications are crucial as they involved contact of two material surfaces [3].
The laser surface modification has huge advantages compared with other surface modification technique. Thorough previous studies reported on the effect of surface roughness on the brazing and soldering metal [4]. Regardless of the great industrial importance of brazing process [5], in order to achieve further improvement in brazing process, a proper parameter control of LSM process is vital procedures that need to be undertake. Certain adjustment of laser beam (power, wavelength) is possible according to the nature of substrate and various adaptations of patterns created by means of certain adjustment [7]. Another effect represents visual features of textile surface, which becomes wrinkled and three-dimensional by means of deformation as well as designing on leather. The same mechanism used for the purpose of cutting and creating designs through cutting [6,7]. Lasers allow precise modification of properties of a small surface area without affecting the properties of the inner layer [8]. Laser modification process is simple, provide exact controlled and environmentally safe. Depending on purpose of surface modification (physical or chemical), type of laser, modification conditions and type of the modified material, the process of laser modification can take place in different ways [9-11]. Laser treated materials including polymers used in many applications including electronics, sensors or for biocompatibility enhancement [12-14]. Various kinds of joining methods have been carried out to achieve reliable bonding. Brazing is also the most feasible joining process for small copper parts and when high joint strength is required [15].

The American Welding Society (AWS) defines as a group of joining process that produce coalescence of materials by heating them to the brazing temperature and by using a filler metal having a liquidus above 450°C and below the solidus of the base metals [16,17]. Previous study reported that copper and its alloy able to withstand high temperature brazing process without a substantial loss in strength [18]. Modified surfaces by using laser on the base metal plays an important factor in braze joint strength and spreadability of the filler metal. A modified surface is related to roughness of the surface on base metal as it creates groove on the base metal. Extensive studies have been reported on the effects of surface roughness on the brazing and soldering of metals [5,19-21].

On these two-combination processes there two key factors should be considered: spreadability of the molten filler metal and formation on intermetallic compound (IMC). Many laser parameters, such as laser power, initial temperature of base metal and laser configuration had influence on the spreadability of molten filler metal [22]. Custom adjustment of molten metal wettability is feasible with LSM, and has been proven effective to conduct, improve or stop the flow molten on a metallic surface. Hence, it can enhance the brazing joint.

2. Method and materials
Materials used in this study were (99.99%) pure copper and commercially obtained Cu-based filler. The filler alloy is custom-made from company and the composition of this filler was given in table 1 according to the data provided by the manufacturer. The solidus and liquidus temperature of the Cu-based filler used in this study were 600°C and 640°C respectively. As received 2 mm diameter copper plate were cut sectioned by using wire-cutting machine into 60x19 mm samples. The surface of the samples is grit using 800 grit paper, the purpose of grit process is to remove any coating or dirt on the samples surface. Then the samples were cleaned with acetone prior to process in order to remove any residual oil contamination on the samples surface.

The surface of both copper samples modified into periodic surface groove structures fabricated by fibre laser marking machine. This fibre laser had 1064 nm wavelength, 300 KHz frequency with precision of 0.001 mm and was focused by a 186 mm-focal-length lens. The grooving experiments were carried out in air. The distance between the grooves are constant with 0.1mm (100μm) as shown in figure 1. During laser surface modification process, a constant flow of argon gas at 0.1 MPa (1 bar) pressure was maintained to reduce oxidation occur on the sample surfaces. The parameters that used in this study are shows in table 2.
Figure 1. Schematic diagram for Laser surface modification.

Table 1. Parameter for laser surface modification.

| Laser specifications          | Parameters       |
|------------------------------|------------------|
| Power (W)                    | 15, 21 and 27    |
| Speed (mm/s)                 | 500              |
| Operational mode             | Loop : 3         |
| Frequency (KHz)              | 20               |
| Focus length (mm)            | 186              |

The joints were brazed with consistent brazing parameters in a vacuum furnace under 7.0x10^1 Pa. The temperature profile was: heating to 700 °C at 23 °C/min and holding for 30 minutes; cooling down to 500 °C at 23 °C/min and finally furnace cooling to room temperature as illustrated in figure 2. The joint strength was examined by tensile testing with a constant speed of 3 mm/min at room temperature. Each data set point was an average of 6 samples. Figure 3 illustrates the configuration for brazed joint and the schematic diagram of tensile test. The fracture surface was examine using an optical microscope.

Table 2. Parameter for laser surface modification.

| Filler Metal | Cu (wt.% ) | Ni (wt.% ) | Sn (wt.% ) | P (wt.% ) |
|--------------|------------|------------|------------|-----------|
| VZ2250       | 77.4       | 7.0        | 9.3        | 6.3       |
Figure 2. Temperature profile for brazing.

Figure 3. (i) Schematic for lap joint, (ii) Schematic of shear stress.
3. Results and discussions

3.1. Modified Geometry

The surface modifications were produced using one scanning pattern through fibre laser by the same
separation distance (array) between each scan. The distance between each parallel groove was set as a
constant value, 200\mu m. According to figure 3, the modified surface was smoother than the unmodified
surface, and the size each of the groove are precise accordingly. It is well known that a fibre laser has
a good beam quality and the possibility to deliver several kilowatts of power with extended lifetime
[22]. The depths for each pattern are different depending on its power usage. The different between
high laser power usage and low are 0.010\mu m. Therefore, it shows that there are significant different on
depth of the groove as summarised in table 3. The higher laser power usage, the deeper the groove
produced on the surface material. The length opening each of the grooves measured. The depth and
opening length were measure using ImageJ software.

| Laser Power (W) | 15   | 21   | 27   |
|----------------|------|------|------|
| Depth groove (\mu m) | 16   | 22   | 26   |
| Length groove (\mu m) | 29.2 | 32.4 | 36.2 |

Figure 4 illustrates the relation between laser power, depth and length of the groove.

Figure 4 illustrates the relation between laser power and depth of microgroove. The depth of
microgroove is directly proportional to the laser power. As the power of the laser increase the depth of
the microgroove also increase and become deeper. The microgroove also will produce surface
roughness as illustrates in figure 5. The surface roughness can be adjusted by controlling the spacing
between the grooves [23].
3.2. Mechanical Properties of brazed joint

The shear strength of brazed joint at different laser power is shown in figure 6. For the normal brazing, in the graph indicate on 0 laser power usage. The brazed joint has the higher shear strength at laser power 27 watt. The pattern of the graph illustrates the shear strength of joint sharply increases when laser power increase to 27 watt. Compare with the shear strength of brazed joint with normal brazing, the brazed joint with surface modified using laser power present higher shear strength starting from 15 watt, which further verifies that the bonding strength of brazed interface is strong. From figure 4, it shows that increases approximately 26% on shear strength in laser surface modification on least laser power which is 15 watt. As for the high laser power, which is 27 watt, it displays around 30% increases on shear strength.

The spreading of the filler and fracture of brazed joint is shown in figure 7. For figure 7(a) it indicates that the fracture or necking occur at base metal due to high shear strength. Plus, the spreading area on figure 7(a) of the filler is much larger, which is 23 μm², compare to spreading area on figure 7(b), which is 18.3 μm². If the filler material is not filling the whole joining area, joint strength will be lower than expected. Besides that, if there is no modified surface, the wettability becomes poor, and then the filler metal could not spread on the surface during brazing. This led to the very short brazed length of the interface layer and produce very low shear strength. The spreading of the filler metal on brazed area is one of the vital factors that contribute on mechanical joint strength.

Figure 5. Microgroove cross section, (a) 15watt, (b) 21watt (c) 27watt.
Figure 6. Relation between shear stress strength and laser power.

Figure 7. Fracture surface, (a) modified surface, (b) unmodified surface.

Basically, the fracture surface was distinguished by visual observation using optical microscope: interfacial fracture along the braze interface, as shown in figure 6(a) and (b), respectively. The figure shows the fracture surface of brazed specimen at 700 °C for 30 minutes after tensile test. It also can be
clearly seen that there are some pores on the fracture surface due to the vaporization of P and Cu₃P. The copper was mostly observed by solid points as shown in figure 6. As for figure 7(a), it shown that there are necking occur on base metal at the fracture surface whereas, for figure 7(b) there is no necking occur.

According to these result for figure 7(a) and (b), the spreading area of the filler are calculated. The filler metal influences by the surface of the base metal. From the figure 7(a), it shows that the modified surface has largest spreading area which is 2.29x10⁷ µm², compare to the unmodified surface from figure 7(b) which has the lowest spreading area, 1.89x10⁷ µm². Thus it display around 20% increases on spreading area of the filler metal.

3.3. Microstructure Analysis
The surface morphology of copper brazed at 700°C for 30 minutes of holding time was investigated under SEM to visualize the structure grain and IMC on the brazed joint. It clearly seen that sound metallurgical bonding between the filler metals and Cu substrate. No micro-pore or crack exist in the braze seams. The interface of the joints in figure 8(a) and (b) displays dark residual filler metals layer and light grey diffusion reaction layer, which can be categorised into five marked point in table 4. Moreover, a quantitative overview of the chemical analysis (EDX) in atomic percentage for different phases is provided in figure 9.

![Figure 8. SEM image for (a) unmodified surface, (b) modified surface.](image)
Figure 9. EDX point analysis for modified surface.

Table 4. Element composition for EDX point analysis.

| Element | Cu  | Sn  | Ni  | P   |
|---------|-----|-----|-----|-----|
| Point 1 | 91.54 | 1.24 | -   | 1.27 |
| Point 2 | 67.43 | 0.36 | -   | 14.87 |
| Point 3 | 47.56 | 15.60 | -   | 2.88 |
| Point 4 | 30.05 | -   | 47.49 | 19.77 |
| Point 5 | 64.97 | -   | -   | 15.06 |

The dominant element at each point in figure 7 detected by EDX are listed in table 4 respectively. Based on EDX point result tabulated in table 4, it illustrates that the point marked as point 1 at bottom base metal was enriched with Cu (91.54 at%) with small amount of Sn (1.24 at%) and P (1.27 at%). Nevertheless, it can be detected that point marked as point 2 and 5 had high amount of P (14.87 at%) and (15.06 at%) which is on the interface of brazed. Thus, it can be identified that the possible IMC for point 2 and 5 are Cu3P. It can be highlighted also that the P is diffusing towards the top and bottom of the interface much faster compare to Sn and Ni. The light grey phase marked as point 3 has possible IMC phase is Cu13.7Sn66.3 (Sn-rich) with Cu (47.56 at%), Sn (15.60 at%) and small amount of P (2.88 at%). The less dark grey on the top of groove marked as point 4 is a possible IMC having the chemical formula (CuNi)2P with enriched of Ni (47.49 at%) and considerable amount of P (19.77 at%).

4. Conclusions
The strength of brazed joints has been significantly enhanced by fiber laser surface modification on the metal. The main conclusion are:

- The dimension of the groove surface structure was tunable by adjusting laser parameters. Due to laser have high precision and accuracy.
- The joint strength was highly related to the surface modification. Its due to the spreading area, as the spreading area increase, the joint strength also increase. It shows also by using LSM to modified surface can increase the spreading area by 20% compare to unmodified.
Custom adjustment of the molten metal wettability is feasible with LSM and it has been proven effective.

LSM also enhance the joint strength of the brazed joint by 32%, this is due to the mechanical interlocking between the surface and its intermetallic compound of the joint.

Perfect brazing joint of pure Cu can be obtained using the amorphous Cu-Sn-Ni-P filler metals. The brazing joints consists of dark residual layer and some light grey diffusion reaction layer, which contain three phases: Cu₃P, Cu₁₃Sn₈₆.₃ (Sn-rich) and (CuNi)₃P.

Acknowledgement
The authors would like to thank to the University Malaysia Pahang for laboratory facilities and financial assistance under Research Grant project RDU180382, RDU192608 and RDU1803171 and Tokyo Braze Co. Ltd for providing brazing filler materials.

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