Automatic systems supporting research on modern materials and industrial bonding technologies

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Abstract. Industrial bonding technologies, including soldering and brazing, operate on solid-liquid phase boundaries. Commonly applied in many areas of industry (such as electronics, metallurgy or aviation), these bonding processes rely on the wetting of joining surfaces using a liquid bonding material. Understanding the wetting process and quantitative description of its parameters enables the design of new materials and joining technologies, as well as the optimization of existing methods. From the primary interfacial impact parameters, i.e. the contact angle and surface tension, the dynamics of the wetting process can be determined, including adhesive tension. This article investigates two independent measurement systems for wetting parameters in industrial brazing technologies: the sessile drop method and the Wilhelmy plate method. Both methods can be applied effectively in research on wetting processes. The measurement systems are compared in an example study.

1. Introduction

Phenomena occurring on interphase surfaces can be described using primary capillarity equations. These formulate the relationships between phase surface energies and capillary pressure, wettability, interphase adhesion and adsorption. The wetting process of joining surfaces using a liquid bonding material is affected by primary interfacial impact parameters, i.e. the contact angle and surface tension. Knowledge of these parameters enables technological aspects of the dynamics of the wetting process to be determined, including adhesive tension. Surface tension denotes a force tending to minimize the area of the surface. It is caused by asymmetries in the intermolecular forces between surface molecules. In the equilibrium state, the tension forces (liquid \(\sigma_{LV}\), solid \(\sigma_{SV}\) and interphase \(\sigma_{SL}\)) at each point of contact between the three phases, between the liquid drop and the flat solid surface, are balanced. When a liquid comes into contact with a solid in a bulk, gaseous phase, an interface between the surface of the liquid and the outline of the contact surface is created. This is known as the contact angle. When the value of the contact angle is less than 90°, the solid is wetted by the fluid. When it is greater than 90°, the fluid does not wet the substrate surface (figure 1). When one phase is wetted by another, the surface separation disappears and energy is released, due to the respective surface tensions. The relationship between the wetting angle \(\theta\) and the surface energies \(\omega\) is described by the Young equation [1, 2, 3, 4, 5, 6].

The contact angle and surface tension are common parameters of wettability. However, knowledge of adhesive tension enables more adequate analysis of the technological processes involved. Adhesive tension describes the difference between the surface energies when a fluid in a bulk, gaseous phase
spreads over a solid surface and becomes a solid-fluid surface. In industrial bonding, the dynamics of the wetting process can be changed to customize the bonding process by modifying adhesive tension over time.

**Figure 1.** Liquid drop shapes in contact with: a), b) non-wettable (wetting angle $\theta \geq 90^\circ$) and c), d) wettable (wetting angle $\theta < 90^\circ$) substrates.

2. **Measurement of wetting parameters**

The sessile drop method is a general measurement procedure, which may be used to determine common parameters of wettability, including surface tension and contact angles, on the interface between liquid and solid surfaces. This method relies on geometrical traits analysis of a stationary liquid drop on a substrate. Drop shape analysis and geometrical properties extraction are performed using image processing algorithms. The accuracy of the method depends primarily on the quality of the images grabbed during the experimental process. The theoretical geometry of a liquid drop on a non-wettable substrate is presented in figure 2 a. The spreading of a liquid material along a wettable substrate is shown in figure 2 b [7, 8, 9, 10, 11].

**Figure 2.** Theoretical geometry of a liquid drop: a) on a non-wettable substrate, b) spreading along a wettable substrate.

Surface tension can be described based on the Bashforth-Adams and Dorsey equations:

$$\sigma = g \cdot \Delta \rho \cdot \alpha^2$$  \hspace{1cm} (1)

where $\sigma$ is surface tension, $g$ the gravity acceleration, $\Delta \rho$ the difference in density between the metallic liquid phase and gaseous bulk phase and $\alpha$ is an empirical parameter calculated using Dorsey’s or Porter’s formulas. For small drop measurements, the preferred method of estimating $\alpha$ is Porter’s formula, which for the theoretical geometry of a liquid drop on a non-wettable substrate (figure 2 a) is formulated as follows [7, 8, 9, 10, 11]:
The braze spread on a wettable substrate can be measured to determine the extreme wetting angles $\theta_1$ and $\theta_2$ (figure 2 b). In terms of technological analysis, verification and optimization of the process can be achieved based on knowledge of the adhesive tension and its variability with regard to process duration. A strict correlation exists between the parameter of adhesive tension and common parameters of wettability. Adhesive tension depends on the surface tension of the braze material and the current wetting angle, which converges over time with the extreme wetting angles. The Wilhelmy plate method is a measurement procedure which enables determination of adhesive tension. This method requires real-time observation of the forces acting on the specimen during its immersion in a fluid braze bath (gravity, capillary and buoyancy forces according to the experiment phase). In the case of immersion in a liquid braze, the adhesive tension is denoted by the formula [2, 12, 13, 14, 15]:

$$\sigma_A = \sigma \cdot \cos \theta$$

where $\sigma$ is the surface tension of the liquid braze and $\theta$ is the current wetting angle. Including the distribution of forces,

$$\sigma_A = \frac{1}{P_s} \cdot (F_{m2} - F_{m1} + C_s \cdot \rho \cdot g \cdot h)$$

where $F_{m1}, F_{m2}$ are the resultant forces measured before and after immersion of the specimen in the fluid braze, $\rho$ is the density of the specimen, $g$ is gravity acceleration, $h$ is immersion depth, $P_s$ is the specimen perimeter and $C_s$ is the cross-section of the specimen.

3. Laboratory stands for measuring wetting parameters

ThermoWet is an automatic laboratory stand, which enables accurate measurement of surface tension and wetting angles using the sessile drop method, at temperatures of up to 1800° in the presence of a protective gas atmosphere. The main part of the measurement system is a custom-build resistance furnace, in which the specimen and a solid substrate are placed during the experiment. The temperature is measured and controlled precisely using a Eurotherm process PID controller. This enables temperature control accuracy of 0.5 K [18]. Images of the specimen are registered during the experiment by a vision system composed of a Watec camera with set of vision protection filters. They are then submitted to further analysis using dedicated image processing algorithms in an external application, a component of the ThermoWet system [16, 19]. A PC computer communicates with all of the components of the device using USB and serial ports, allowing planning of the experiment (temperature set points, camera settings), operation of the PID temperature controller, monitoring of system behaviour and registering of the camera images. The system produces good quality images, features an automatic measurement cycle and provides accurate temperature control. Figure 4 presents an overview of the ThermoWet measurement system, with close-ups of the vision- and specimen loading subsystems. Figure 5 shows the system architecture [7, 16].

$$\frac{\sigma^2}{X^2} = \left( \frac{Z}{X} \right)^2 - 0.66 \left( \frac{Z}{X} \right)^3 \cdot \left[ 1 - 4.05 \cdot \left( \frac{Z}{X} \right)^2 \right]$$ (2)
Figure 3. Overview of Thermo-Wet measurement system with close-ups of the vision- and specimen loading subsystems.

The measurement procedure is based on the sessile drop method. While the specimen is heated up and melting, the measurement system registers images of the specimen. The grabbed images are analyzed, with the main goal of extracting the geometrical properties of the drop against the base surface. The geometrical dimensions of the drop of material are determined analytically, based on approximation of its shape (polynomial, elliptical). The contact angles are computed at points of contact between the drop and the substrate base for each of the three phases (solid-, gas- and liquid). The accuracy of the analysis depends primarily on image quality. The measurement system should enable precise determination of the borders between the drop, the surface of the base and the background. Its accuracy can be reduced, however, by phenomena associated with high-temperatures, such as glare or auroras. Using vision protection filters can improve the results [7, 16].

WAST is an autonomous measurement laboratory system, which enables complex research into the dynamic properties of brazing processes. Adhesive tension can be analyzed at temperatures of up to 1000 °C under various technological gas atmospheres. This measurement system is principally composed of a movable cylindrical resistance furnace, in which the specimen immersed in a braze bath is placed, connected by scales. Figure 5 provides an overview of the WAST measurement system, with
close-ups of the PLC control- MFCs- and driver sub-systems and of the entrance to the furnace, with optical sensors and a gas protection atmosphere gate. The measurement procedure is based on the Wilhelmy plate method. In the main part of the experiment, the specimen is immersed and remains in a fluid braze bath. The weighing module registers resultant forces acting on the specimen. A state diagram of the measurement experiment is presented in figure 6.

Figure 5. Overview of the WAST measurement system, with close-ups of the PLC control-, MFCs and driver sub-systems and the furnace entrance with gas protection atmosphere gate and optical sensors.

![State diagram of measurement experiment](image)

Figure 6. State diagram of measurement experiment.

Knowledge of the weight, geometrical specimen parameters and braze surface tension enables determination of the technological parameters – wetting force, adhesive tension or wetting angle. These in turn permit analysis of the wetting dynamics (e.g. advancing and receding angles, observation of the
wetting changes as the specimen remains static in the fluid braze). To understand the results, this research should be supplemented by additional studies, such as analysis of the microstructure of the specimen and its resistance against oxides, or of specific phases generated in the process [12, 17].

4. Example analysis
As an example analysis, an investigation was carried out on a sample of L-Ag5P (DIN EN 1044-CP104 composed of 89% Cu, 6% P, 5% Ag) braze. The surface tension was determined using the sessile drop method, by melting the braze on a non-wettable Al2O3 base substrate. The extreme contact angles were calculated using a spreading test, based on the same methodology. The wetting dynamics for the L-Ag5P braze and Cu specimen were also analyzed based on Wilhelmy plate immersion tests. The main aim of the example analysis was to verify and compare the two measurement methods. The parameters of the experiments are shown in table 1.

| Table 1. Parameters of experiments using the sessile drop method and Wilhelmy plate tests. |
|---------------------------------|---------------------------------|
| **Parameter**                   | **Value**                      |
| Laying drop experiment          | Wilhelmy plate experiment       |
| Temperature range [°C]          | Temperature [°C]                |
| Gas reduct. atmosphere          | H2                              |
| Gas protect. atmosphere         | Ar                              |
| Immersion depth [mm]            | Immersion speed [mm s⁻¹]        |
| Activation time [s]             | 30                              |
| Stabilization time [s]          | 100                             |
| Cooling time [s]                | 30                              |
| Gas reduct. atmosphere          | H2 + Ar                         |
| Gas protect. atmosphere         | N2                              |

Figure 7 a shows an image registered by the ThermoWet device of a L-Ag5P drop on a non-wettable Al2O3 substrate. The calculated mean value of the contact angle between the braze drop and base substrate is around 155º and the surface tension of the L-Ag5P braze $\sigma = 0.946$ [N/m]. A spreading test was performed for the same braze material on the copper substrate. The resulting images grabbed during this experiment, illustrating changes in the contact angles over time during the melting / spreading process, are presented in figure 7 b. The extreme contact angle value was approximately 12.5º. Based on (4) and the forces registered during the Wilhelmy plate experiment, characteristic changes in adhesive tension were calculated. From (3) and the value of surface tension determined in the ThermoWet stand, the contact angle dynamics over time were also calculated (figure. 8) At point A, contact between the hanging specimen face and the braze surface was detected by the weighing module. Next, the specimen was immersed in the fluid braze until the specified position of 4 mm depth was reached (points B, B'). During the immersion process, buoyancy and wetting forces began to act on the specimen. At point C,
the wetting angle reached 90°, which implies that the wetting force factor was zero, as the weighing module registers only gravity and buoyancy forces. After point C, the wetting angle reached an acute angle, causing the adhesive tension to rise. At point D, the adhesive tension reached 90% of its maximum value, which is technologically optimal for creating a solid, high quality join. Point E (E’) represents the start of the process of specimen emergence. At point E, the contact angle was approximately 11.8°, which is similar to the value determined in the spreading test.

Figure 7. The laying drop experiment: a) determination of surface tension for L-Ag5P braze on Al₂O₃ base substrate, b) spreading test for L-Ag5P braze on copper substrate.

Figure 8. Changes in adhesive tension and contact angle for L-Ag5P braze and copper specimen material at 750 °C.
5. Conclusions
This article has presented and compared two independent measurement methods: the sessile drop method and the Wilhelmy plate method. The sessile drop method is based on approximation of the drop shape and determination of its geometrical traits, using ThermoWet equipment to grab and process the images. The Wilhelmy plate method consists of analogue measurement of the forces acting on a specimen during immersion in a fluid bath. It employs the WAST laboratory system. In sessile drop experiments, image processing algorithms enable accurate measurement, but this depends primarily on the quality and resolution of the images (allowing effective approximation of the edges of the specimen and the substrate). Phenomena commonly observed in high-temperature processes (such as glare) reduce the quality of the results, but their effect can be limited through use of different vision filters. The experiment is time consuming, but it is important to analyze the interphase reactions accurately and to obtain high-resolution results. The second method described here, the Wilhelmy plate method, provides a relatively rapid method for verifying the suitability of materials to be joined, in different technological environments and using different criteria (conductivity, strength of connection, etc.). Implemented in the WAST system, measurements based on the plate method yield information on changes in adhesive tension over time at a certain temperature. To describe changes in the wetting angle over time, knowledge of surface tension is also needed. For well-known materials, the values for surface tension can be obtained from reference tables in the literature. For new materials, however, additional experiments, such as using ThermoWet, are needed. The energy state of the prepared surface, as well as the assumed process criteria (temperature, gas protection/reduction atmosphere, interphase reaction time, etc.) should be the same for both experimental processes. To verify each of the methods, a comparative analysis was conducted, focusing on the same technological aspects. Based on the convergence of the results, both methods can be used effectively to design new materials and joining technologies, as well as for optimizing already existing materials and technologies. The optimization of production processes using different technological parameters based on knowledge obtained using various measurement methods can significantly reduce overall economic costs and improve the quality of the final product.

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