Wetting of Non-Reactive and Reactive Metallic Substrates by Brazing Liquids

Z Weltsch
John von Neumann University, GAMF Faculty of Engineering and Computer Science, Department of Materials Technology, Kecskemét, Hungary

E-mail: weltsch.zoltan@gamf.uni-neumann.hu

Abstract. A survey of wetting as central phenomenon in soldering and brazing technologies are presented in this paper. The wettability is expressed by the magnitude of wetting angle. The equilibrium condition is widely investigated in the case of non-reactive partners. The phenomenon is less documented in the case of reactive partners, when chemical reaction (hence, local compositional change) also occur between the contacting phases. The brazing process belongs to this category. The mutual wettability is basic requirement for the formation of strong and durable bonding between the machine parts. Therefore, the correlation between the wetting angle (Θ) and the strength of the resulting bonding will be investigated. Not only the chemical concentration change, but phase transformations may also occur in such brazing procedure, when the contacting partners are reactive. As the chemical potential of components are also change in this cases, the phase transformations has also impact on the evaluation of wetting angle between the brazing pool and alloy pieces to be joined. This phenomena will also be demonstrated in the case of non-reactive and reactive partners as well.

1. Introduction

The huge importance of wetting phenomena between liquids and solid phases is well known in the soldering and brazing technologies [1-3]. This phenomenon has gained recently increasing interest also in the development of steel production and in non-ferrous metallurgy. Accordingly, the simultaneous study of influence of metal-gas interactions on the surface tension (hence, on the mutual wettability between metallic liquids and solid phases at high temperatures) become of high technical importance [4].

The knowledge of surfaces and interfaces have also of outstanding significance due to the intensive progress in material science (the nature of interfaces between the constituent phases in various composites, or, understanding of alloying effects in ultrafine (nano-crystalline) grain assemble [5]. The complex application of high-resolution structural investigations is inevitable in this field. Similar, complex investigation is required in studying the bonding mechanism during the brazing process structural elements of electronics and also in modern body elements (dual phase steels).

The basic description of wetting phenomena between condensed phases (liquid-liquid, liquid-solid) together with the theoretical background have been elaborated in early nineteen century [6-7]. The wetting is often characterized by the sessile drop method by the measuring of equilibrium contact angle (Θ) according to Fig. 1.
Figure 1. The real illustration of contact angle for a liquid drop on solids, with contact

In earlier study, method and equipment for the observation of the wetting angle ($\Theta$) between non-reactive alloy melts and solid ceramics have been developed, using the sessile drop method. An instrument is also designed and built, making possible the observation $\Theta(T)$ dependence at high temperature range up to $-1200^\circ$C. The essential part of equipment is the double wall thermal isolation system, for the elimination of oxygen traces in the surrounding atmosphere.

In the present article, we focus mainly on the study of wetting phenomena between reactive, metallic partners [7], including dual phase steels [9] and some appropriate brazing alloy liquids. Such systems have outstanding technical significance in the modern car-industry (brazing techniques for body elements). Subsequently the melting of protecting flux, the chemical reaction has started between the melt pool of filler alloy and the contacting solid partner alloy. Hence, the solid–liquid interface turns to lens-shaped, so the melt pool can be characterized by two ($\Theta_1$ and $\Theta_2$) contact angles [11-13].

As it is mentioned, one of the essential requirement for the successful brazing of machine parts is the mutual, perfect wettability between the liquid pool of the brazing alloy, and the solid metallic parts to be joined, which can also be expressed by the appropriate wetting angle. In addition, the actual wettability is strongly influenced by the atmospheric circumstances, therefore the wettability is enhanced by flux addition [5, 10, 16-17].

2. Experimental conditions

The wetting experiments were performed in home-made equipment developed for sessile drop measurements. The substrate and the solder pieces were positioned into the middle of furnace at ambient conditions. The pressure was then reduced to 0.1 Pa at room temperature in the chamber. The vacuum was replaced by a $10^5$ Pa 99.999 % Ar gas. This procedure was repeated 3 times. Subsequently, the temperature was raised to melting point using a heating rate of 4 K/s. Since only a small part of the gas chamber is heated, no pressure change could be detected in the chamber ($10^5$ Pa) during the measuring run. The heating power has stopped around the measuring temperature. Two minutes holding time was applied before the measurement. The contact angle was determined by measuring directly the profile of the drop. Self-made automatic software in the Matlab environment is used for fixing and processing the data. Though the uncertainty of this software is below 1 degree, the total uncertainty of the measured values is higher: $\pm 3^\circ$. At the end of measuring process, the furnace was switched off and cooled slowly to the ambient temperature (the whole cooling time is around 40 minutes). Subsequently the furnace was opened and the solidified sample was removed.

For the experiments, high-purity tin and copper were used to make the CuSn alloys, and DC01 and DP600 type steel plates were used, the chemical composition of which is shown in Table 1. and Table 2.
Table 1. Chemical composition of the DC01 sheet material

|   | Fe (wt%) | C (wt%) | Si (wt%) | Mn (wt%) | P (wt%) | S (wt%) | Cr (wt%) | Ni (wt%) | Al (wt%) | Cu (wt%) |
|---|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
|   | 99.5    | 0.050   | 0.023   | 0.233   | 0.012   | 0.009   | 0.014   | 0.027   | 0.041   | 0.024   |

Table 2. Chemical composition of the DP600 sheet material

|       | Fe (wt%) | C (wt%) | Si (wt%) | Mn (wt%) | P (wt%) | S (wt%) |
|-------|----------|---------|----------|----------|---------|---------|
| DP600 | 98.6     | 0.085   | 0.171    | 0.87     | 0.013   | 0.005   |

The brazing experiments were performed with a 1.2 mm diameter CuSi3 wire, the composition of which is shown in Table 3.

Table 3. Chemical composition of the CuSi3 brazing wire

|       | Cu (wt%) | Si (wt%) | Mn (wt%) | Zn (wt%) | Sn (wt%) | Fe (wt%) |
|-------|----------|---------|----------|----------|---------|----------|
| CuSi3 | >94      | 3       | 1        | 0.1      | 0.1     | 0.07     |

3. Results and discussions

3.1. Experiments on non-reactive substrates.

The influence of compositional change and the phase relations on the wettability between the brazing pool and non-reactive substrates (wetting study into multiphase substrate alloys) was investigated. The results are summarized in Fig. 2.

![Graph showing wetting angles vs. temperature difference, ΔT (°C)](image)

**Figure 2.** θ(T) for various Cu(Sn) melts on graphite substrate

In Fig. 2, the T-dependence of θ for various composition of Cu(Sn) melts are illustrated (measured on graphite substrate). The wetting angles are plotted versus the relative overheating of the melt drop in
the figures because the higher physical relevance when the possible influence of Eötvös rule is considered [14] (defined as $\Delta T = T_{\text{obs}} - T_{\text{liq}}$, where $T_{\text{obs}}$ is the experimentally measured temperature, $T_{\text{liq}}$ is the liquidus temperature at the alloy composition. The slope of $\Theta(T)$ changes rapidly with Sn-content of the liquid, showing the sensitivity of wetting with the concentration molten phase composition. It is remarkable, that not only the $\Theta$ changes at a given superheating, but the slope of the curves exhibits significant difference. Both curves refer to the concentration range of solid solution in solid state. As the slope of curves differ significantly, one can suspect, that significant structural change (concentration gradient) can be developed as a function of temperature change.

**Figure 3.** Cu-Sn phase diagram [15]

Another remarkable effect is the abrupt change of $\Theta(T)$ curve, when the concentration of melt exceeds the solubility limit of Sn in the terminal $\alpha$ (Sn) solid solution (Fig.3.). As the reaction between the liquid and the substrate is absent, this sudden change (both in the value and also in the slope of $\Theta(T)$ can be the consequence of structural rearrangements in liquid state prior to the solidification. In the case of 3 and 5 at% Sn-content liquid, solidify via primary crystallization of Cu(Sn) solid solutions, in the second case, the crystallization is isotherm, peritectic reaction. One can suspect, therefore, that the slope of the curves can be related with the type of subsequent solidification reaction.

In contrast to the previous cases, the slope of $\Theta(T)$ is negligible in CuSn10% liquid, where the solidification mechanism is peritectic, i.e. the liquid-solus transformation is isothermal process.

### 3.2. Phase relations and wettability on carbon steels

In Fig.4. the temperature dependence of wetting angle on two carbon steel are depicted.

DC01 is single phase ferritic steel, the DP600, originally „dual phase“ (martensitic-ferritic) steel, for which the wettability between CuSi3 brazing melt is better in the investigated temperature region presumably due to the different C-content.
3.3. Mechanical properties

In Fig. 5, the tensile strength of DC and DP in various combinations of joint formation are compared. The difference in tensile strength is obvious, so the double phase character has primary importance in the tensile strength improvement. Especially remarkable, that no sign of deterioration of strength is observed in spite of the presence of heat affected zone caused by the brazing.

Figure 4. Temperature dependence of contact angle of CuSi3 brazing liquid on ferritic and dual phase (ferrite-martensitic) steels

Figure 5. The tensile strength-strain of DC, DP without brazing and DP-DP, DC-DC, DC-DP steels with CuSi3 brazing joint formation.

In Fig. 6. The bending test of various sheets are compared, being previously subjected to brazing-joint formation. Neither the tensile strength, nor the bending strength suffered breakdown due to the joint formation in the case of DP sheets.

It was concluded, that mechanical properties are determined dominantly by the original structure (indirectly by the C-content, making possible the development of dual-phase structure)
Figure 6. The bending test of DC and DP sheets without brazing, DP-DP, DC-DC, DC-DP sheets with CuSi3 brazing.

4. Conclusions
In spite of the promising preliminary results (especially concerning the absent of deterioration of mechanical properties due to the lateral extension of heat affected zone) an extended kinetic study is required at various constant temperatures and atmospheric circumstances. In such experiments continuous monitoring of $\Theta(t)$ is required, comparing the observed phenomena with appropriate non-reactive substrate partners. (i.e. where chemical reactions between the partner substrate, is absent) so the change of $\Theta$ is not expected.

The study of local structural change in the vicinity of solidified filler alloy including also the structural consequence of heat affected zone formation, local phase transformations etc.

It is supposed, that drop-profile monitoring can supply indirect information about the local, mutual compositional changes, within and beyond the melt pool, making also possible the study the mutual relations between the extension of heat affected zone and the diffusion controlled local, compositional changes.

Further widening of knowledge is necessary about the brazing parameters and its relation with real structure of bond, allowing prediction towards the strength and duration of bonds.

Better understanding of the mechanism of brazing joint formation between the body-elements applied in modern car-industry.

Further widening of basic knowledge concerning the relation between shape of phase diagrams and the slope of $\Theta(T)$. (The type of solidification reactions: correlation between the solidification reactions and the necessary superheating of brazing environments)

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