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Wetting and laser brazing of Zn-coated steel products by Cu–Si filler metal

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Abstract Laser brazing is an effective process for joining of steel products widely applied in automobile industry on exposed parts, especially on two following targeted applications: roofs and hatchbacks. The obtaining of good quality joints requires an adequate understanding of interaction phenomena of the brazing filler with the steel surface. This study concerns the investigation of wetting and interfacial reactivity in Cu–Si brazing alloy/Zn-coated steel systems in order to identify how the coating influences the wettability and, consequently, the brazability of steel products. The wetting experiments are performed on hot-dip-galvanized and electro-galvanized coatings, as well as on bare steel. The morphology and chemistry of interfacial reaction products are characterized by SEM-FEG and X-microanalysis.

Introduction

Laser brazing was introduced in the automotive industry for car body joining at the end of the nineties, thanks to productivity and cost efficiency reasons. This process is nowadays standard in Europe for such applications as roofs and hatchbacks. Currently, this technology is extensively used within the Volkswagen group [1]. Other car manufacturers as General Motors Europe [2], BMW [3], Ford [4] have launched in production their first mass production application on vehicles (Fig. 1a).

The principle of laser brazing consists to fill a gap between two steel materials by fusion of a filler wire provided by a defocused laser beam (Fig. 1b). Pure Ar is injected during brazing process for the seam protection from oxidation. By adjusting the laser power, the brazing speed and the filler wire speed, sufficient braze material can be deposited to completely fill the joint (Fig. 1a). The quality of the brazed joints depends on the process parameters during brazing operation, but also on the wetting and interfacial reactivity phenomena when a liquid braze contacts a steel product surface.

Numerous studies have been performed on the wettability of iron or steel substrates by low and moderate melting point metals for different applications [5–12]. The molten Pb [5–8] and molten Ag [5, 9] on solid Fe present non-reactive couples due to very low solubility of Fe (few ppm) in these liquids at the temperature close to its melting point. The alloying of silver with high surface energy elements as Cu or Ni leads to a significant increase of wetting [9]. Some studies have investigated the reactive wetting of iron or steel by molten metals as Sn [5, 7], Al [5, 10] and Zn [11, 12]. In these systems the measured contact angle is the one on intermetallic compound formed at the molten metal/iron interface. For clean metallic surfaces the formation of intermetallic compounds at the interface has beneficial but rather limited effect on wetting [5, 7]. However, for iron or steel surface covered at low temperatures by thin oxide film the interfacial reaction improves strongly the wetting due to elimination of the oxide film and formation of the intermetallic compound at the interface [5, 7].

The aim of this study is to identify mechanisms involved during liquid Cu–Si braze interaction with different steel

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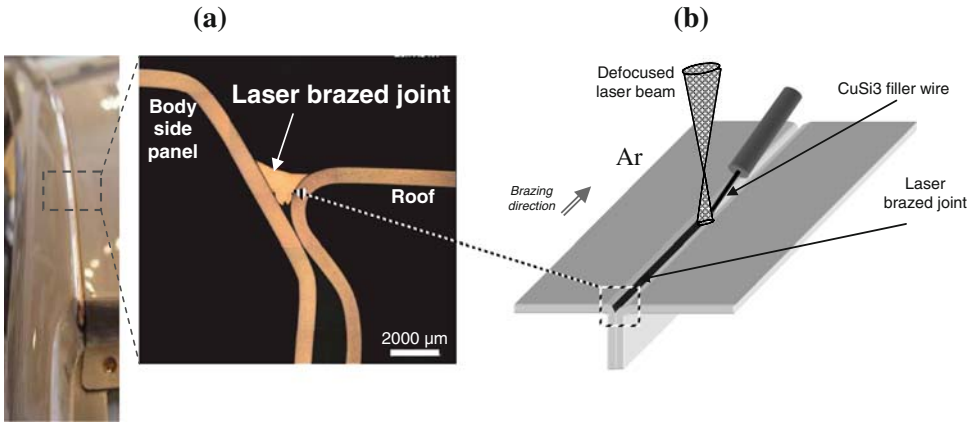

Fig. 1 **a** Typical applications of laser brazing in the automotive industry: roof/body side panel laser joining; **b** Principle of laser brazing

products developed for the automotive market, i.e. to understand the effect of Zn coating on steel on wetting and interfacial reactivity phenomena. The wetting experiments are performed on bare steel, electro-galvanized and hot-dip-galvanized steel products by dispensed-drop technique in the optimal conditions to simulate the interfacial processes taking place during brazing operation.

Experimental procedure

Wetting experiments were carried out by the dispensed-drop technique in a vertical furnace under Ar atmosphere at normal pressure. The furnace is composed of an alumina crucible with a controlled atmosphere (argon/hydrogen mix) in which a few grams of Cu-3 wt% Si alloy are induction melted (Fig. 2a). The braze temperature inside the crucible is monitored by a pyrometer. In order to simulate brazing process conditions, a controlled amount of Cu-3 wt% Si liquid (0.8 ± 0.1 g) heated at $T_i = 1300$ °C or $T_i = 1400$ °C is dropped from the 6 cm height onto a water-cooled substrate. The use of optimized initial drop temperatures (T_i) and liquid drop mass allows obtaining almost the same interfacial reactivity that on industrially brazed samples (see "Laser brazing" section).

The spreading of liquid drops on the substrate surface is filmed by a CCD camera at an acquisition speed of 125 frames/s (250 frames/s for experiments on bare steel). From the image analyses, the characteristic dimensions of the drop (drop base radius R and contact angle θ) are measured with an accuracy of ±2° for θ and ±2% for R (Fig. 2b).

The temperature in the central parts of brazing alloy drop during spreading is captured by a photodiode through a small hole in the centre of the substrate (Fig. 2a). The experimentally obtained cooling curves for brazing alloy drops of 0.8 ± 0.1 g deposited at different temperatures are shown in the Fig. 3. The increase of the drop-deposition temperature on ~100 °C leads to the important variation of cooling kinetics, i.e. the Cu-3 wt% Si alloy liquidus temperature [13] is attained in 0.5 s after drop deposition at 1300 °C and only in 1 s after drop deposition at 1400 °C. In such non-isothermal wetting experiments the temperature in the zones of the drop near the triple line presenting relatively minor metallic mass can decrease faster than at the drop centre. However, as it will be explained in the "Wetting" section, the deposition of the brazing alloy drop on galvanized materials leads to the formation at the triple line of the liquid alloy rich in Zn. In view that the solidus temperature of the brazing alloy

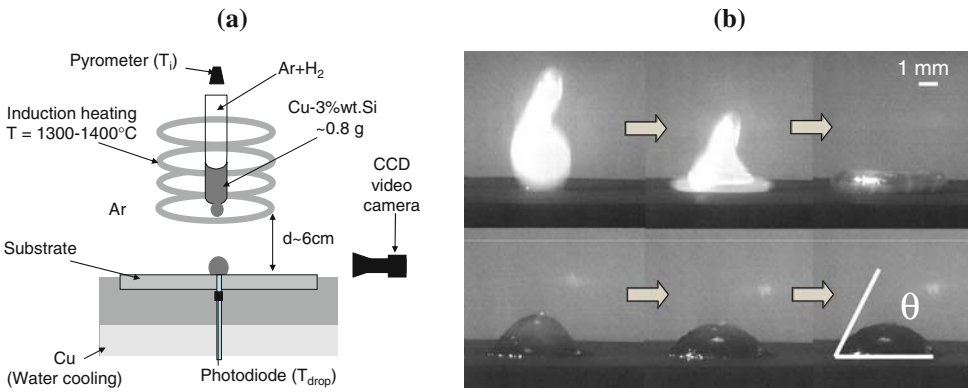

Fig. 2 **a** Schematic representation of the experimental apparatus used for wettability experiments (dispensed-drop technique); **b** Droplet profiles during spreading

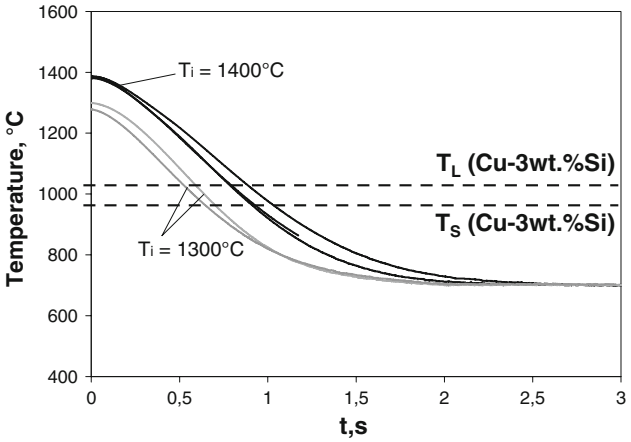

Fig. 3 Cooling curves of brazing alloy droplets of 0.8 ± 0.1 g deposited on Zn-coated materials at different temperatures. T_i—initial drop deposition temperature. T_L and T_S are, respectively, liquidus and solidus temperatures of Cu-3 wt% Si alloy [12]

deposited at 1300 or 1400 °C is about 970 °C [13] (Cu-3 wt% Si alloy) and the melting temperature of Zn is about 420 °C we can suppose that these Zn rich areas near the triple line are liquid at least until the braze-drop solidification. This assumption was experimentally confirmed by (i) the presence of small movements of liquid front near the triple line on the wetting experiment video before drop solidification, (ii) the formation near the triple line of areas with locally improved wetting in the case of relatively thick Zn coating ("Influence of the type of steel product on wetting properties" section).

In aim to respond to the needs of automotive market, in our study the experiments were performed on four types of steel products (Fig. 4): (i) electro-galvanized steel (EG) with coating thickness of 8 μm, (ii) hot-dip-galvanized steel (GI) with coating thickness of 8 μm, (iii) GI steel with coating thickness of 20 μm and (iv) non-coated steel (bare steel). For experiments on non-coated steel substrates, the Zn coating was removed mechanically and then the substrates were polished using diamond paste 6 μm up to mirror surface.

After cooling, the specimens were cut perpendicular to the interface, embedded in resin and polished for optical and SEM-FEG observation on the cross-section and X-microanalysis.

Results and discussion

Wetting

Description of a typical experiment

Figure 5a gives the variation of the contact angle θ and drop base radius R vs. time for two identical experiments carried out in the same conditions on EG 8 μm substrate for brazing alloy droplets deposited at 1400 °C. The reproducibility of results is satisfactory even at very short contact times where deposited drop is deformed due to its high kinetic energy. At the first contact of the liquid alloy with the substrate the observed initial contact angle θ_0 is about 135° which is typical for noble metal/ionocovalent oxide systems [5] and can be related to the contact angle of the metallic non-reactive liquid on nanometric layer of zinc oxide covering EG material surface. Then, the braze drop spreads on the substrate surface in the first 20 ms under gravitational forces until the maximum R value. The contact angle at this time rests steady and equal to its initial value. In the following 30 ms an important decrease in the contact angle from $\sim$135° to $\sim$35° is observed due to interfacial reaction, that blocks the liquid receding. After 60 ms of the experiment, the contact angle remains almost steady until the drop solidification. The drop-spreading rate is higher than its cooling rate, i.e. after drop deposition at 1400 °C the final contact angle is attained in 0.06 s whereas the alloy liquidus and solidus temperatures at the drop centre—only in $\sim$1 s (Fig. 3).

The following drop spreading rates could be measured on the kinetic curves (Fig. 5a):

(i) dR/dt on the linear part of the R–t curve from the first drop contact with the substrate and until the spreading to its maximum diameter. At this spreading stage, the drop radius increases at the steady θ corresponding to

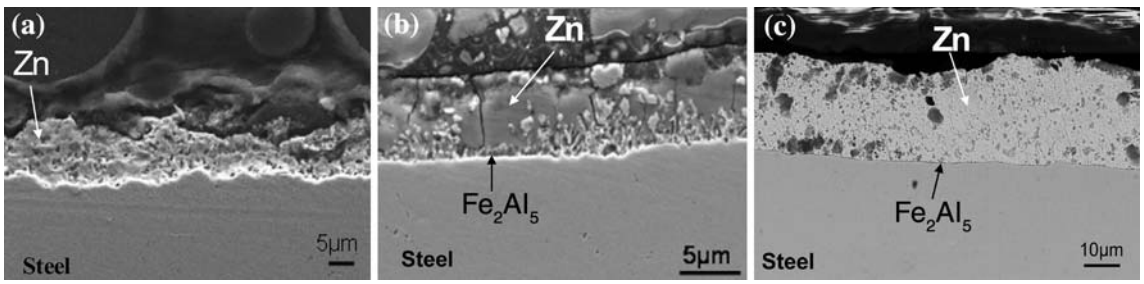

Fig. 4 SEM micrographs of a cross-section of electro-galvanized 8 μm product (**a**), hot-dip galvanized 8 μm product (**b**) and hot-dip galvanized 20 μm product (**c**)

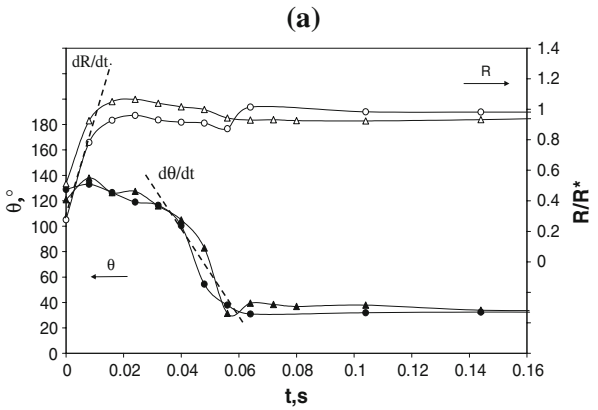

Fig. 5 **a** Spreading curves of 0.87 ± 0.07 g brazing alloy droplets deposited on EG material at 1400 °C. $t = 0$ is taken to be the first contact of the liquid droplet with the substrate surface. The drop base radius R is normalized using $R^* = \left(\frac{3 \cdot V^*}{4\pi}\right)^{1/3}$, where V^* is the volume of the drop. **b** SEM micrograph of a cross-section at the centre of the EG steel/brazing alloy interface for braze drops deposited at 1400 °C

the wetting of superficial oxide layer. Therefore, no reactivity is observed: the drop spreads the substrate surface because of its high kinetic energy.

(ii) dθ/dt related to the contact angle decrease while the drop radius is constant that illustrates more properly the rate of the chemical interaction of the liquid braze with the substrate coating.

The Fig. 5b represents the SEM micrograph at the centre of the braze/substrate interface for EG 8 μm system at 1400 °C. It can be seen that initial Zn coating is removed and a reaction layer of 2 μm thick of iron silicide is formed at the interface. Due to the Zn coating dissolution the brazing alloy near the interface contains about 25 at.% of Zn. The reaction layer is not continuous: it contains the areas of the brazing alloy imprisoned between the iron silicide grains. It shows that the layer formation mechanism consists in the dissolution of iron in the liquid alloy and in following precipitation of the iron silicide phase, but not in the solid state diffusion of Si in the steel. In view that the iron silicide layer is in contact with copper liquid alloy, it can be slightly alloyed by Cu. Similar layers of iron silicide have been observed on industrially brazed joints (see "Laser brazing" section). We can then assume that the thermodynamic conditions of real scale laser brazing and of the dispensed-drop test are relatively similar, and that the phenomena observed in the drop test can be considered as representative of the real application on cars.

Influence of the type of steel product on wetting properties

Spreading curves of Cu-3 wt% Si brazing alloy deposited at 1400 °C onto bare steel, hot-dip galvanized GI 8 μm and GI 20 μm and electro-galvanized EG 8 μm steels are presented on the Fig. 6.

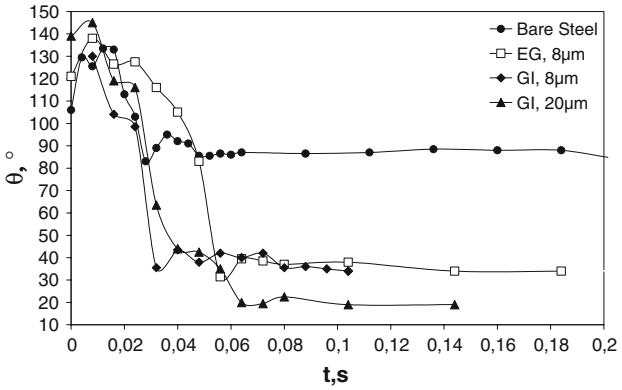

Fig. 6 Spreading curves of 0.9 ± 0.1 g brazing alloy droplets deposited on bare steel, EG 8 μm, GI 8 μm and GI 20 μm materials at 1400 °C. $t = 0$ is taken to be the first contact of the liquid droplet with the substrate surface

As in the case of EG material, at the contact of liquid braze with GI substrates the first observed contact angle θ_0 is 120–140°, which corresponds to the θ on nanometric layer of Zn and Al oxides [14, 15]. θ remains steady during 10–20 ms depending on material (non-reactive wetting [5, 16]), then it decreases significantly to the steady value of 34 ± 2° on GI 8 μm and 22 ± 4° on GI 20 μm. This wetting improvement is attributed firstly to suppression of the nanometric zinc and aluminium oxide layers, then to the melting of Zn coating, its removal and formation at the interface a micrometric layer of iron silicide similar to that observed in the case of EG material (Fig. 7). After solidification, brazing alloy near the interface contains about 20 at.% of Zn in the case of GI 8 μm substrate and about 30 at.% of Zn in the case of GI 20 μm substrate. It indicates that during spreading the melted Zn coating dissolves in the brazing alloy. According to Cu–Zn phase diagram

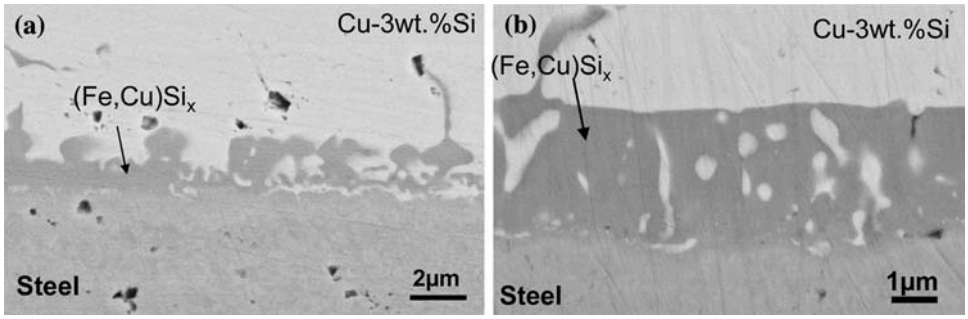

Fig. 7 SEM micrograph of a cross-section at the centre of the steel product/brazing alloy interface for braze drops deposited at 1400 °C on GI 8 μm (**a**) and GI 20 μm (**b**) materials

[13] the presence of 20 at.% of Zn in the brazing alloy liquid decreases the alloy solidus temperature to $T \sim 980$ °C, as well as the presence of 30 at.% of Zn decreases it to $T \sim 915$ °C. Consequently, the presence at the interface of higher Zn content liquid in the case of GI 20 μm coating ensures the local alloy melting temperature decrease. This leads to a longer time presence of liquid phase near the interface before solidification and, thus, a longer time of Fe dissolution and Si diffusion in liquid giving the iron silicide interfacial layer slightly thicker (Fig. 7).

The spreading curves of the brazing alloy droplet on GI 8 μm and GI 20 μm materials are rather similar for the contact times <0.04 s. Nevertheless, some differences can be distinguished for the contact times >0.04 s (Fig. 6). If on the GI 8 μm after 0.04 s of spreading the contact angle is almost steady, on GI 20 μm it can be seen only a slight trend of the contact angle stabilization at $\theta \sim 45°$ followed by its decrease to the steady value of $22 \pm 4°$. However, after 40 ms of spreading on GI 20 μm substrate the profile of the liquid drop presents local spreading areas close to the triple line (Fig. 8a). The SEM analyses of these areas show that at the moment of braze-drop deposition the melted Zn coating is partially dissolved in the brazing alloy and partially rejected to the drop triple line (TL). At the TL the liquid Zn dissolves in the brazing alloy and diffuses to the drop bulk: CuZn compounds are formed after solidification from the TL to the drop centre (Fig. 8b).

For thicker coatings like GI 20 μm at the TL relatively important liquid areas rich in Zn are formed. These areas represent zones of local wetting where a Zn-rich alloy wets better a steel substrate (Fe_2Al_5 intermediary layer at the Zn/steel interface in the case of GI products [17]), than the brazing alloy. Consequently, the final contact angle of $22 \pm 4°$ obtained on GI 20 μm steel product corresponds to the contact angle of a Zn rich alloy on steel substrate. The same effect of Zn on the improvement of wetting of steel by Al-alloy melts has been mentioned by Marder [17] and recently observed near the TL by Agudo et al. [18].

The Fig. 6 shows the brazing alloy reaching the close steady contact angle values on GI 8 μm ($\theta = 34 \pm 2°$) and EG 8 μm ($\theta = 32 \pm 3°$) materials. However, the contact angle decrease on EG 8 μm is slightly retarded comparatively to the GI 8 μm and the average $d\theta/dt$ spreading rate is lower in the case of EG material than of GI one. Assuming the higher spreading rate on GI substrates and the fact that the final θ on GI 8 μm and EG 8 μm substrates is similar, it can be concluded that Fe_2Al_5 intermediary layer at Zn/steel interface in the case of GI materials does not represent a barrier for wetting. It seems to be dissolved in Cu–Si liquid alloy and the iron silicide reaction layer is formed at the Cu–Si alloy/steel interface by Fe dissolution and following iron silicide precipitation mechanism (Figs. 5b, 7a).

In order to verify how the Zn coating influences the spreading of the brazing alloy droplets, some experiments are performed on bare steel. The liquid braze does not wet bare steel (Fig. 6). The initial contact angle θ_0 is $\sim 130°$ corresponding to the contact angle on passive oxide layer [5]. A limited drop spreading observed during first 20 ms can be related to the partial surface deoxidation by reaction between the brazing alloy and the steel that leads to the contact angle value of 90°. Indeed, in the case of the complete deoxidation of the bare steel surface by the reaction with brazing alloy, the formation at the interface of

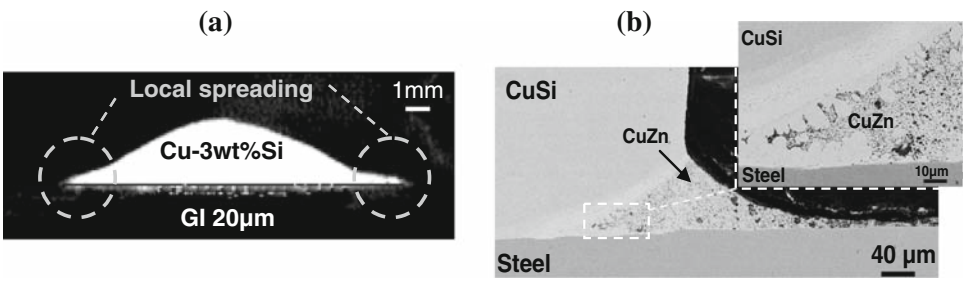

Fig. 8 Brazing alloy droplet profile at the end of spreading on GI 20 μm material (**a**), SEM micrograph of a cross-section near the triple line for brazing alloy deposited at 1400 °C on GI 20 μm material (**b**)

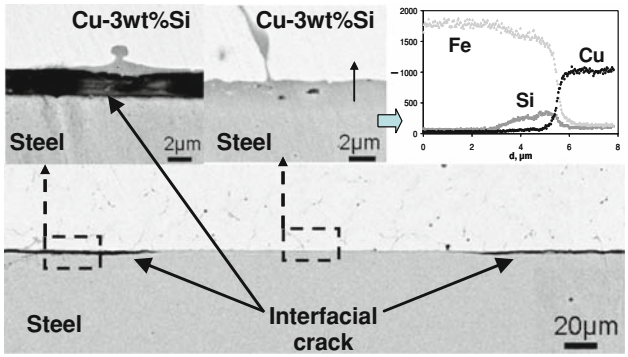

Fig. 9 SEM micrograph of a cross-section at the centre of the brazing alloy/bare steel interface in the case of braze drop deposited at 1400 °C

the iron silicide reaction layer will decrease the contact angle to the values close to θ on GI 8 μm or EG 8 μm substrates (same type of reaction product at the interface). The SEM characterisations of brazing alloy/bare steel system illustrate the formation in some areas of the interface of iron silicide layer similar to that obtained on GI or EG materials. However, in the areas where deoxidation was not completed the interfacial cracks are developed, indicating that the formed interface is mechanically weak (Fig. 9).

Therefore, the better wetting behaviour on the EG and GI coatings than on bare steel allowing the formation of mechanically strong interfaces is attributed to the "clean" surface (no iron oxide) under the zinc layer exposed once the GI or EG coating is removed during brazing.

Influence of the brazing alloy drop temperature on wetting

The initial temperature of liquid braze drop has an important influence on its cooling rate (Fig. 3) and, thus, on its spreading kinetics. The decrease of the initial braze drop temperature (T_i) from 1400 to 1300 °C slows the drop spreading, as well as leads to the higher final contact angle on GI 8 μm material (Fig. 10). On the GI 20 μm substrate the final contact angle has almost the same value at both drop-deposition temperatures due to the formation of local spreading areas at the TL. The drop temperature effect exists also for EG material, but it is less significant.

Regarding interfacial reactivity on GI and EG products, the decrease of drop deposition temperature from 1400 to 1300 °C has no influence on morphology of reaction layer, but it reduces slightly its thickness: the iron silicide layer thickness is of 2–3 μm for drop deposited at 1400 °C and of 1–2 μm for drop deposited at 1300 °C.

Laser brazing

There are three main brazing process parameters responsible of the laser brazed joints' quality: P—the laser power on parts (in W), BS–the brazing speed (in m/min) and FWS–the filler wire speed (in m/min).

The robustness of the laser brazing process can be evaluated by defining a processing range (so-called brazability range) [19, 20] as presented on Fig. 11. It takes into account the range of heat input of the process (linear brazing energy E_l) and of the amount of filler wire needed to fill the joints (feeding rate r) to obtain good quality joints. E_l and r are defined by the following formulas:

$$\text{Linear brazing energy (in J/cm): } E_l = \frac{60}{100} \times \frac{P_{\text{laser}}}{\text{BS}} \quad (1)$$

$$\text{Feeding rate: } r = \frac{\text{FWS}}{\text{BS}} \quad (2)$$

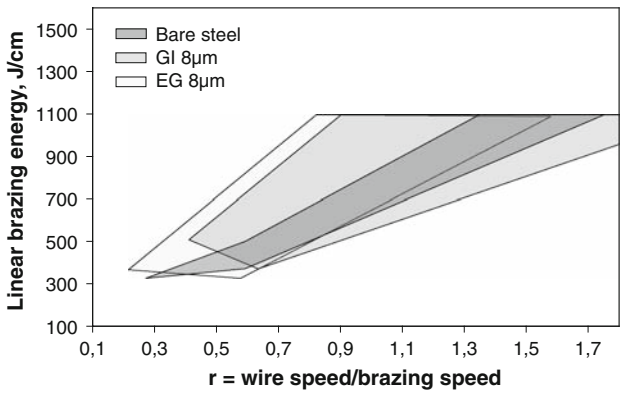

Fig. 11 Brazing range of the bare steel, EG 8 μm and GI 8 μm materials using filler wire preheating by Jules effect at current value of 110 A

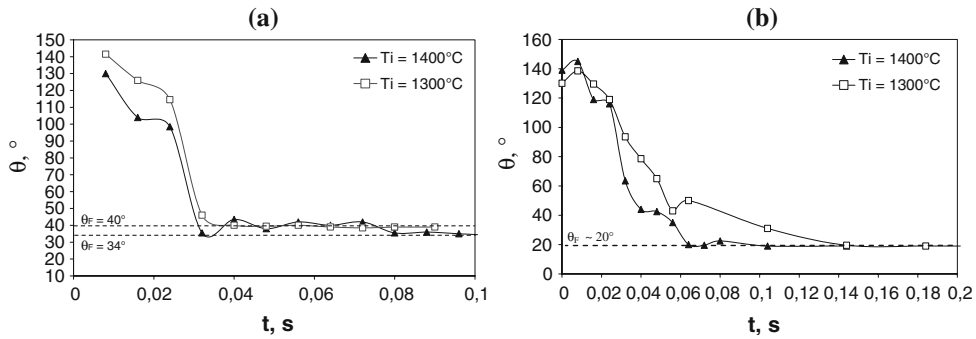

Fig. 10 Spreading curves of 0.9 ± 0.1 g brazing alloy droplets deposited on GI 8 μm (**a**) and GI 20 μm (**b**) materials at 1400 and 1300 °C. $t = 0$ is taken to be the first contact of the liquid droplet with the substrate surface

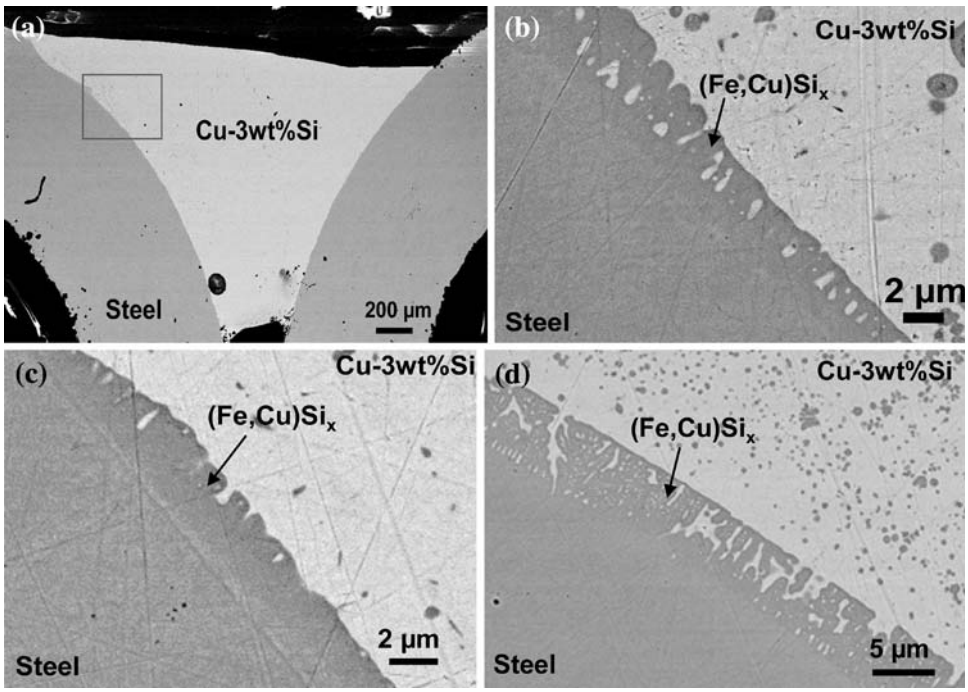

Fig. 12 SEM micrograph of a cross-section of the laser brazed joint (**a**). Zoom of the braze/steel interface in the square area for EG 8 µm (**b**), GI 8 µm (**c**) and GI 20 µm (**d**) brazed materials

The comparison of the laser brazability of bare steel, GI 8 µm and EG 8 µm substrates is accomplished by focusing on the size and shape of the processing window (Fig. 11).

The results and conclusion obtained by comparing the brazability range of different products can be interpreted based on the results of the wettability test:

- The very sensitive behaviour of bare steel during laser brazing operation (narrow process window) is related to the worse wetting of its surface by Cu-3 wt% Si alloy due to the presence of thin passive oxide layer. This layer can be only partially removed by liquid braze at the short contact time during laser brazing operation.
- A wider brazability range is observed for GI coating (compared to EG), despite of the fact that the final contact angles on GI 8 µm and EG 8 µm coatings are close ($\sim$35°). Particularly, it is observed that good quality joints can be obtained at higher speed on GI than on EG : this may be related to the more rapid spreading of brazing alloy on the first product than on the second one (Figs. 6, 11).
- Also, a better wettability is observed at higher droplet temperature: this can be correlated to the wider processing window observed at higher heat input, i.e. with a higher filler wire deposition temperature (Fig. 11).

In brazing configuration, as in the wetting one (see "Wetting" section), at the contact of the GI or EG steel surfaces with the liquid braze, the Zn coating is removed from the steel surface (partly dissolved in the brazing alloy and partly rejected to the periphery areas of the joint) and a micrometric layer of iron silicide is formed at the brazing alloy/steel interface. The Fig. 12 represents the SEM micrographs of the braze/substrate interface for GI and EG systems brazed at 1400 °C. From the Figs. 5b, 7a, 12 comparison it can be concluded that the interfacial reactivity observed in wetting configuration is almost the same that for industrially brazed samples. Therefore, the configuration that has been chosen for wetting approach in this study allows to describe the braze/substrate interaction phenomena taking place during industrial brazing operation.

Conclusion

A specific methodology has been defined to reproduce the conditions of laser brazing and understand the wetting kinetics of CuSi drop on different coated steel sheets.

At the first contact the Cu-3 wt% Si brazing alloy does not wet bare steel and Zn-coated steel products. The presence of iron oxides on the bare steel surface inhibits wetting process. On the EG and GI coatings after short stage of non-reactive wetting the contact angle decreases to the values of 20–40° depending on the type of Zn coating. This improvement is attributed to suppression of the nanometric zinc and aluminium (for GI coating) oxide layers, as well as to the removal of zinc coating and formation at the interface of a micrometric layer of iron silicide (reactive wetting). The reactive spreading rate on EG is lower than on GI material. The brazing alloy initial temperature has an effect on spreading kinetics and interfacial reactivity: reducing of the liquid braze initial temperature leads to the decrease of the reactive spreading rate.

The laser brazing trials confirm the trends noticed during wetting experiments: (i) superior brazing ability of the GI and EG products (wider process window) relatively to this of bare steel, correlated to the final wetting angle; (ii) more robust brazing ability at high processing speed of the GI 8 μm product relatively to the EG one, correlated to the higher spreading rate on GI; (iii) influence of the brazing energy (braze temperature) on the process window width.

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