Design of high strength polymer metal interfaces by laser microstructured surfaces

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Abstract. In the areas of automotive, aeronautics and civil structures, lightweight construction is a current and a future need. Thus, multi material design has rapidly grown in importance, especially hybrid materials based on fiber reinforced plastics and aluminum offer great potential. Therefore, mechanical interlocking is a convenient way of designing the interface. Laser structuring is already used to generate a variety of surface topographies leading to high bond strengths. This paper investigates different laser structures aiming on highest joint strengths for aluminum and glass fiber reinforced polyamide 6 interfaces. Self-organizing pin structures comprised by additional micro/nano features as well as drilled hole structures, both ranging on the micrometer range, are compared to corundum blasting as a standard method for surface conditioning. For the presented surface structures, thermal joining and ultrasonic assisted joining are regarded towards their potential for an optimum joint design.

1 Introduction

Lightweight construction is a supreme demand for a wide range of applications in order to save energy by weight reduction. High lightweight potential can be tapped through combining miscellaneous materials into hybrid composites. By an appropriate material selection, advantages such as low density, high bending resistance, high load-capacity and especially low weight can be achieved, for example through the use of sandwich structures [1]. In the automotive industry, especially polymer-metal hybrids (PMH) are used due to their beneficial strength-to-weight ratio and their easy processability.

Modern strategies such as adhesive bonding or micromechanical interlocking are promising due to their integrability into cost efficient series production. Adhesive bonding is based on generating mechanical and chemical bonds [2]. Mechanical interlocking is achieved by generating macroscopic, microscopic as well as nanoscopic surface structures at the metal adherend using mechanical, chemical, electrochemical or physical processes [3, 4]. In addition, the form fit can be combined with improved chemical interaction through adapted surface chemistry. For this, an increased formation of primary and secondary bonds with the polymer adherend is useful [5]. Thus, laser structuring may lead to adhesion promotion by multiple mechanisms, such as providing geometrical undercuts, increasing the surface area resulting in an increased number of chemical bonding sites and a suitable change in the surface chemistry.

Even there is no accepted scientific knowledge on the contribution of the elementary adhesion mechanisms to the increase in bond strength in aluminum-plastic joints, laser structuring is used in order to achieve interfaces for highest mechanical loading. Hence, it is necessary to identify appropriate structures and the corresponding manufacturing strategies to fulfill practical demands.
2 Laser surface modification

Laser structuring allows a high design flexibility in terms of structuring the surface. Different scientific working groups could provide valuable findings in the area of surface modification by laser ablation up to now. It was shown for example that microscopic pin structures can be realized on the surfaces of different metallic materials as for example steel, titanium, cooper as well as aluminum [6]. In this context a self-organized process that is characterized by local temperature differences and cooling speeds leads to the formation of micro pins with dimensions in the nanometer or micrometer range [6, 7].

Potential for the application of these microscopic structures was identified primarily for the modification of surface wettability and for the interface design of technical bonds [8]. By the help of periodic micro pins on titanium surfaces manufactured by a nanosecond laser system, a significant increase in adhesive bond strength compared to planar samples could be confirmed by Baburaj et al. [9]. The authors found that the excellent performance of the microstructured samples was caused by increased micromechanical interlocking, a significant surface area increases by an order of magnitude as well as the structure deformation under mechanical load and thermal expansion [9]. A modified surface chemistry with submicron-sized oxide particles was also identified as favorable for the increase of the bond strength [9, 10]. However, the comparison to conventional methods for surface preparation was not considered so far.

A further efficient strategy for surface preparation of bonds, the suitability of bore arrays by single pulse and percussion drilling was studied. By the help of this approach, only a slight increase of the strength of metal-ceramic bonds could be verified in comparison to abrasive blasting as surface preparation method [11, 12]. In the case of metal-metal adhesive joints [13] and metal-plastic joints [14] an increase of bond strength was documented for an increasing hole number per area. This can be traced to the increasing surface area that supports adhesion at the interface. By using laser drilled holes in the surfaces the sufficient filling of the structures was one of the main challenges. Compressed air in the microstructures can thereby weaken the connection between substrate and adhesive or counter body, respectively [14, 15].

3 Experimental design: generation of microstructures and joining processes

3.1 Materials

PMH joints were prepared from the aluminum alloy EN-AW-6082 T6 artificially aged (Gemmel Metalle) and the fiber reinforced plastic (FRP) Durethan BKV30 (Lanxess). The FRP is reinforced by glass short fibers using a fiber mass content of 30 %. The materials are presented in Table 1. Prior joining, the surfaces of the aluminum adherends were structured through different treatment methods (see 3.2) and cleaned ultrasonically assisted in ethanol.

Table 1: Material data

| Material          | Elastic modulus [GPa] | Yield Strength [MPa] | Ultimate Strength [MPa] | Elongation to failure [%] |
|-------------------|-----------------------|----------------------|-------------------------|--------------------------|
| Durethan BKV30    | 6.1                   | -                    | 105                     | 6                        |
| EN-AW-6082 T6     | 70                    | R_{P0.2} = 250       | R_{M} = 300             | 10                       |

3.2 Surface microstructuring

Laser ablation

For the experimental work the aluminum alloy EN-AW-6082 was used. The ablation of the material was carried out by a nanosecond laser system from Spectra Physics® with the following specifications:

- Laser medium: Nd:YVO4
- Wavelength: 532 nm
- Pulse duration: 10 ns
- Mean power: max. 13 W
- Focus diameter: ≈ 15 μm
During laser processing the material behavior depends significantly on the energy input into the surface. In order to characterize the ablation behavior depending on the intensity $I$, parameter experiments were carried out by the variation of the pulse frequency, the focus position, the pulse distance and the number of passes. In the preliminary parameter experiments the laser intensity $I$ was varied in the range from about 1.0 J/cm$^2$ to 100 J/cm$^2$, calculated on the basis of manufacturers data sheet. As scanning strategy, line scanning with a line distance equal to the pulse distance was performed.

![Figure 1: Selected examples showing ablated surfaces of EN-AW-6082 material, ablation with formation of micro pins, $I \approx 5.5$ J/cm$^2$ (A), ablation of micro holes, $d \approx 10 \mu$m, $h \approx 22 \mu$m (B)](image)

According to the wide range of tested energy densities, a diverse material behavior can be observed. Beside the tendency that higher intensity leads to higher surface roughness and stronger oxidation of the ablated surface, the formation of micro pins with high aspect ratio could be verified for different parameter combinations. It was found that the conditions for the generation of the structures prevail in the range of a defined laser intensity of $I \approx 3 \ldots 6$ J/cm$^2$.

For the comparison of the wetting behavior and filling conditions during the joining processes, hole drilling was used as a second approach for the surface modification of the metallic parts. In this context, the microstructures were generated on two different geometrical scales. Small scaled holes were produced by percussion drilling with 10 pulses each. This resulted in structure dimensions shown in Figure 1B. The large scale holes were magnified by factor 10 and manufactured by spiral drilling, resulting in $d \approx 100 \mu$m and $h \approx 120 \mu$m. magnified by factor 10 and manufactured by spiral drilling, resulting in $d \approx 100 \mu$m and $h \approx 120 \mu$m. In both cases, the structure density, that denotes the portion of the structured area in the total area, was set to $\approx 11 \%$. A visual comparison between the manufactured surfaces with formation of micro pin structures and surfaces with defined micro holes is presented in Figure 1.

Corundum blasting

To reference the joint strengths achieved by the different laser structures, aluminum specimens were corundum blasted, since it is a widely used pretreatment for PMH joints. The aluminum specimens were structured by the blasting abrasive EK 024 (Wiwox) for 10 s. A pressure of 0.2 MPa was used and the abrasive was shot onto the aluminum surface under an angle of 70° from a distance of 0.3 m.

3.3 Joining procedures

Hot pressing

The FRP and the aluminum were joined by a hot pressing process using a constant pressure of 0.4 MPa during the whole joining process, which was found to ensure satisfying penetration of the polymer melt into the laser generated microstructures of the aluminum adherend. Conductive heat transfer from a copper heating into the aluminum adherend and therefrom to the FRP was utilized. The temperature progress inside the aluminum bulk material next to the joining zone was measured by a thermocouple. A temperature ramp was applied until a maximum temperature of 205 °C was reached. Then, the heating was turned off, the temperature increased to a peak value of 230 °C and the specimens cooled down to 100 °C via air cooling. The specimens were subsequently conditioned to a normal climate according to DIN EN ISO 1110 [16] in order to adjust the moisture absorbed by the polyamide 6 based matrix prior mechanical testing.
Ultrasonic joining

An alternative method for the production of a joint between FRP and metallic materials such as aluminum is the ultrasonic assisted (US) joining with a vibration direction acting parallel to the surface of the workpiece. The normal force acts perpendicular superimposed on the vibration direction. An anvil fixes the lower joining part while the upper joining part is set in motion by the oscillating tool, the sonotrode (Figure 2). Due to the interaction of the oscillations of the tool system in the ultrasonic range and the acting normal force, the boundary friction between the joining partners leads to a localized heat input into the joining area and a melting of the thermoplastic polymer or the matrix occurs. The process times for generating a joint produced by means of ultrasonic assisted joining are highly dependent on the material combination used and the state of the surface structure of the metallic joining partner [17]. For the sample geometry used, the joining time is about 1.6 seconds. The following settings were used as machine parameters, the energy was 300 Ws, the amplitude of the oscillating system was 30 μm and the air pressure for the pneumatic press was 0.25 MPa, which corresponds to an acting joining pressure of 2.6 MPa at the joining area.

Figure 2: Principle of ultrasonic joining with vibration direction parallel to the workpiece surface and perpendicular acting joining force with arrangement of specimen [18]

3.4 Static single leg tensile shear test

To evaluate the PMH joint strengths achieved through the different surface structures and joining procedures, single leg lap shear tests according to DIN EN 1465 [19] were performed at a test speed of 1 mm/min. In contrast to the standardized geometry, the overlap length was reduced to 5 mm in order to enable testing of higher shear strengths, while still achieving interfacial failure due to an adapted stress distribution among the specimen [20]. The specimen geometry is depicted in Figure 3.

Figure 3: Geometry lap shear specimen
The maximum shear strength value is calculated following equation (1).

$$\sigma_{max} = \frac{F_{max}}{A} = \frac{F_{max}}{b \cdot l} \quad (1)$$

4 Results and discussion

4.1 Results with thermal joining

Cross-sectional images were taken at the joining zones of the PMH specimens in order to evaluate the potential of each structure and the thermal joining process for generating a mechanically performant joint (Figure 4). The micro pin structures and corundum blasted surfaces were completely penetrated and surrounded by polymer. Above, no air cells are located at the interfacial zone. Thus, the quality of the joints for both structures is concluded to be high, even though an improvement is possible by positioning the reinforcing fibers closer to the geometrical structure to support interfacial load transfer. In contrast, the joint quality is lower for both hole structures. For the major (100 µm) holes, all of the holes were penetrated by polymer melt, but not completely filled. Thus, a gap exists between aluminum and the polymer, which is likely a consequence of locked in air and unequal thermal shrinkage of the adherends. No fibers penetrating the major holes were observed at the cross-sectional images. The joint quality of the minor (10 µm) hole structure is the least, since only a low percentage of the holes is penetrated by plastic melt. Overall, none of the three ablated structures was penetrated by glass fibers or an agglomeration of fibers next to geometrical features of the structures took place.

![Cross-sectional images of thermally joined aluminum-FRP hybrids: micro pin (A), hole 10 µm (B), hole 100 µm (C) and corundum blasted structures (D).](image)

Figure 4: Cross-sectional images of thermally joined aluminum-FRP hybrids: micro pin (A), hole 10 µm (B), hole 100 µm (C) and corundum blasted structures (D).

The presented structures were designed in order to achieve high strength PMH interfaces. The micro pin structure fulfills this demand, since shear stresses above 30 MPa were sustained (Figure 5). Thus, a strong improvement compared to widely used corundum blasting (12 MPa) is achieved. An investigation of the fractured surfaces showed, that in general the micro pins remain undamaged, while cohesive failure inside the FRP took place at the joining zone (Figure 6A). Two microscopic fracture modes are stochastically distributed at the fractured surface, forming small microscopic zones each. No clear arrangement of the zones was observed. On one side, there are nearly flat areas of polymer residing between the micro pins. The flat areas end around the top height of the micro pins and no indication of remaining reinforcing fibers was observed. Thus, these areas likely developed through shear away of
small volumes of locally unreinforced polymer. On the other side, crater-shaped polymer residues protrude out of the micro pin structure. It is assumed, that the local presence of glass fibers next to the micro pins led to increased local load transfer causing cohesive failure as well as polymer-fiber delamination.

By means of corundum blasting, rough geometrical features suitably orientated towards shear loads were generated. No polymer residues were observed at the fractured surface, since the polymer was drawn-off due to local plastic deformation. The joint strength achieved by the hole structures were comparatively low, which is a consequence of incomplete polymer penetration into holes and the low structure density. Thereby, the load transfer from aluminum into the FRP causes stress concentrations at the few undercut sides. Thus, cohesive failure takes place and led to sheared away polymer at the topside of the holes at relatively low stress levels (Figure 6B). In order to achieve higher joint strengths, the structural density has to be increased and fibers have to penetrate the holes to support the load transfer.

Figure 5: Maximum shear strengths for diverse surface geometries of aluminum-FRP hybrids.

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Figure 6: Scanning electron microscope images taken at the fractured surface of aluminum indicating plastic residues: micro pin (A) and major hole (100 µm) structure (B)

4.2 Results with ultrasonic joining
Using the ultrasonic assisted joining method leads to a local melting of the polymer matrix and an adhesive bond between polymer melt and metal surface. In combination with the pressure acting at the same time on the joining area, the polymer melt penetrates into the cavities of the microstructures.
Depending on the microstructure of the surface, the adhesive part of the bond strength can be increased, resulting in an increase in the tensile shear strength.

To achieve an increase in the load transfer through the joining zone, an involvement of the reinforcing fibers into the structures is required. Thus, a weakened interlayer only consisting of unreinforced polymer can be minimized or avoided and an increased joint strength can be achieved [17]. Figure 7 shows cross-sectional images of ultrasonically joined aluminum-FRP hybrids. It can be seen that the microstructures are filled with polymer matrix as well as for the thermal joining process. However, the adhesive bonding of the polymer to the metallic joining partner is not uniform. Furthermore, in the case of the selected joining parameters, a shearing of the micro pins occurred (Figure 7A). The generated fragments are placed in the cavities of the microstructure and partially close them. A similar effect can also be observed with the corundum blasted samples (Figure 7B). In contrast to the micro-pin structure, a smoothing of the surface roughness was observed. This also negatively affected the achievable bond strength and resulted in a significant reduction in tensile shear strength compared to thermally bonded samples with the same microstructure. In addition, an involvement of the fiber component with the microstructures can be excluded. Further investigations are necessary to counteract the mentioned effects and to enable an incorporation of the reinforcing fibers into the joint.

Figure 7: Cross-sectional image of ultrasonically joined aluminum-FRP hybrids: micro pins (A), corundum blasted (B).

5 Conclusions

Based on the experimental results the following conclusions were drawn:

- Formation of pin microstructures can be realized by laser processing of aluminum using a well-defined energy input
- Shear stresses above 30 MPa were achieved with outwardly oriented micro pin structures and thermal joining what seems reasoned by appropriate polymer penetration and higher thermal shrinkage of the polymer compared with the metal adherend
- Joint strength achieved by hole structures were comparatively low, which is a consequence of incomplete polymer penetration and interlinking into the holes and the comparatively low structure density
- None of the tested microstructures can be penetrated by load-supporting glass fibers using the regarded joining technologies
- Ultrasonic joining with the used parameters was found to be unappropriated for the joining of polyamide 6 based FRP materials with aluminum alloy EN-AW-6082
- Thermal joining was found to be more appropriate for the considered material combination, however full penetration of the hole structures by polymer melt was not yet achieved

More study will be necessary to understand and to influence the complex mechanisms of pin structure formation during laser processing. Adapted geometrical properties and arrangements of these structures might improve the strength of metal-plastic joints further. In addition to that, future work must be
focused on the contribution of the diverse adhesion mechanisms to the measured strength and the fracture behavior.

6 References

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