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Use of high-energy laser radiation for surface preparation of magnesium for adhesive applications

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Abstract

This paper is intended to demonstrate how the parameters for the surface preparation of magnesium alloys for adhesive bonding can be optimized. The effects of different laser parameters are analyzed by using a combination of advanced sample preparation and ultra-high resolution scanning electron microscopy on a nanoscale level and a specific combination of mechanical tests on the macroscopic level. These data allow a discussion of the physical principles and the key parameters influencing the interaction of laser radiation with the magnesium surface.

Keywords: Micro processing, Surface functionalization

Background

Magnesium alloys are very versatile materials. Their high specific strength, combined with easy machining, suggest their application in any kind of lightweight structure [1]. For the use of magnesium in multi-material constructions, i.e. in combination with other materials, efficient joining technologies need to be developed.

Adhesive bonding is a process that is perfectly suited to connect different materials. Due to its position in the electrochemical series (standard potential E^0: −2.362 V), magnesium is a base metal [2]. This means that magnesium corrodes very easily, especially in contact with other metals. In this respect the surface pretreatment and corrosion protection are major challenges in order to ensure the durability of the adhesive bond. The functionalization of magnesium surfaces by high-energy laser radiation is a promising and cost saving alternative to mechanical (e.g. grinding) or chemical pretreatment methods like pickling or anodizing [3].

Experiments

For this work the magnesium alloy MgAl3Zn (AZ31) was used. This alloy is composed of at least 3.0 % aluminum (Al), 1.0 % zinc (Zn), 0.35 % manganese (Mn) and the rest magnesium (Mg) [4]. The thickness of the metal sheets was 0.5 mm.

For these experiments a Nd:YAG-Laser was used. It has a wavelength of 1064 nm, a maximum mean laser power of 100 W and the laser pulse frequency can be varied

between 1 Hz and 50 kHz. Because of the use of pulsed laser radiation with pulse duration of 70 ns, the thermal input is localized directly at the surface. The focusing of the short laser pulses to a footprint of approximately 200 µm in diameter results in very high energy densities, so that the magnesium surface is melted or sublimated within a few microseconds. At the same time, an explosively expanding plasma is generated, which needs the major part of the thermal energy provided by the individual laser pulses. Therefore, only very little heat is transferred into the bulk material [5]. Thus changes in microstructure can be avoided and makes it also possible to process very thin magnesium-substrates and pretreat them for adhesive bonding.

First of all, the surfaces treated by laser were investigated by a scanning electron microscope including energy-dispersive X-ray microanalysis for chemical analysis of the surface (SEM/EDX). The acceleration voltage was 5 kV, the magnification was 100 times, the working distance 25 mm and the scanning time 100 s. This acceleration voltage was selected due to the resulting low penetration depth in the material and to obtain sufficient information from the surface composition. With the above mentioned parameters the maximum penetration depth in accord with the formula of Castaing is 1,2 µm [6].

For a first assessment of different pretreatment methods like SACO blasting (DELO-SACO Plus) [7], pickling and some initial laser parameters, T-peel-tests according to DIN EN ISO 11339 [8] (corresponds to ASTM D1876) were performed. For this purpose two magnesium AZ31 stripes with identical pretreatment were glued together with 50 mm remaining free of adhesive. Then these edges were bent by 90° building a T-shape (see Fig. 1). The sample was then clamped in a tensile testing machine and pulled apart at a constant speed (here 100 mm per min). The length of the tested bonding must be at least 150 mm. One sample was prepared without special pretreatment, which means the surfaces were only rinsed with acetone and subsequently cleaned in an ultrasonic bath with isopropanol. The three conventional pretreatments were SACO-blasting and two pickling solutions based on concentrated nitric acid ([3], Table 12.1 No. 2) and chromic acid ([3], Table 12.1 No. 10).

The optimization of the laser parameters was done by means of roller peel tests according to DIN EN 1464 [9] (corresponds to ASTM D3167). Therefore a thin flexible adherent (here Mg) is peeled from a sufficient stiff adherent (here Al). With this test, the

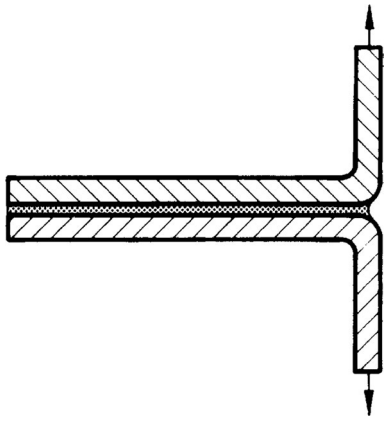

Fig. 1 Schematic illustration of a T-Peel-Test ([3], p. 786)

peel strength of an adhesive bonding can be determined more precisely than with the T-Peel-test because of the use of a different peel angle and fixed radii (see Fig. 2).

The experiments were performed with a film adhesive FM® 73 (hot-curing), a fracture tough adhesive often used in bonded repairs [10]. Its performance is well known from a lot of other experiments in the past, so that the influence of the surface preparation could be clearly determined. Some of the samples were cured in an autoclave process, the others were cured by means of a Hot Bonder (mobile curing system especially for repair applications). The parameters of the standard cure cycle according to manufacturer's instructions were as follows [10]:

1. Apply pressure at 40 ± 5 psi (0.28 ± 0.03 MPa)
2. Heat up to 120 °C in 30 min
3. Hold at (120 ± 3) °C for 60 min

During the process, a vacuum of 500 mbar must be applied.

For the optical inspection of the surfaces a field emission scanning electron microscope (FE-SEM) was used. The cross section samples were prepared with a cross section polisher (CSP) by means of a defocussed argon ion beam.

Results and discussion

The laser induced a melting and evaporation of the top layer of the magnesium. The evaporated material recondensed which enlarged the surface significantly (see Fig. 3a–d).

In order to get an impression of the influence of the laser parameter on the chemical composition of the surface, the laser treated surfaces were examined with SEM/EDX. The laser parameter with the biggest influence was the laser pulse frequency, which determined the laser fluence of the Nd:YAG-Laser in this experiment. In Fig. 4 (a), the measured weight- % of magnesium (acceleration voltage $V_{acc} = 5$ kV) is plotted via the laser pulse frequency. At low laser pulse frequencies the measured weight- % of magnesium decreased compared with the initial value of the untreated AZ31. Raising the laser pulse frequency up to 11 kHz led to higher measured values. Up to 21 kHz the measured

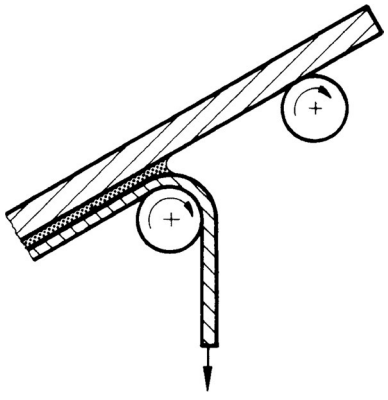

Fig. 2 Schematic illustration of a Roller-Peel-Test ([3], p. 788)

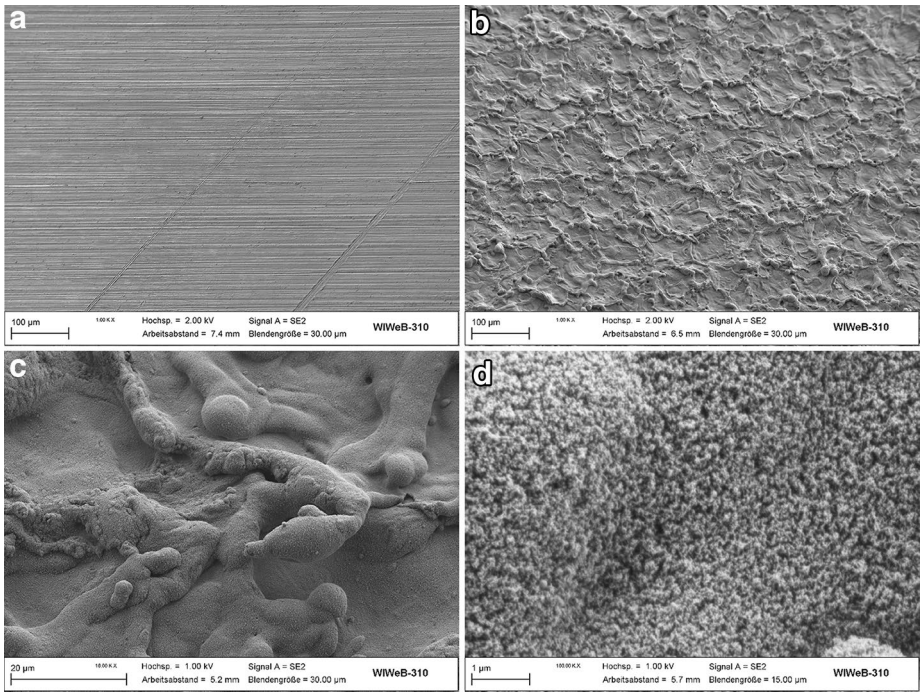

Fig. 3 **a**–**d** FE-SEM pictures of the surface of a AZ31-alloy before (**a**) and after (**b**–**d**) treatment with a Nd:YAG-Laser [magnification 1.000x (**a**) and (**b**), 10.000x (**c**) and 100.000x (**d**)]

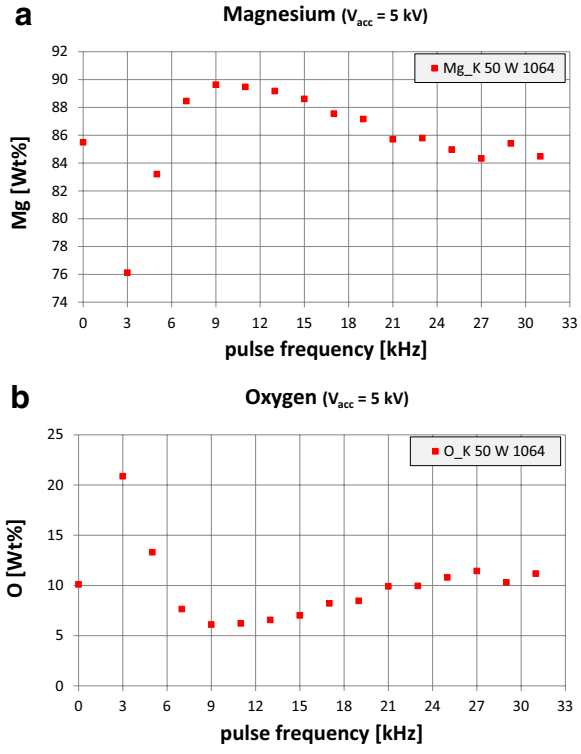

Fig. 4 **a** Measured weight- % of magnesium via the laser pulse frequency (acceleration voltage 5 kV); **b** measured weight- % of oxygen via the laser pulse frequency (acceleration voltage 5 kV)

weight- % decreased to the initial value of the untreated AZ31. That matches the visual appearance, because above 21 kHz laser pulse frequency there was no longer any visible change detectable.

The measured values for the weight- % of oxygen behaved quite opposite (see Fig. 4b). That means, that at lower laser pulse frequencies the values were higher than the initial value, then they decreased to a minimum at 11 kHz before they increased to the initial value of the untreated AZ31.

The observed effects can be explained as follows. As the surface of the magnesium is covered with a thin layer of natural magnesium oxide, a specific amount of oxygen is measured even on the surface of untreated AZ31. During laser treatment we assume that three different types of reaction occur depending on the incoming energy:

1. Melting, sublimation and oxidation

   Low laser pulse frequency is equivalent to high laser fluence and therefor a high ablation rate, which means significant changes in the surface topography. The natural magnesium oxide is removed and magnesium is sublimated and recondenses on the rough surface. Here it reacts with the ambient oxygen building different types of magnesium oxides (see Fig. 3b–d). The best results to get a nearly homogenous oxide layer on the surface were achieved with a laser pulse frequency of 7 kHz.
2. Removal of the oxide layer
   With increasing laser pulse frequency (decreasing laser fluence) only the natural magnesium oxide layer is removed but no more magnesium is sublimated. That is the reason for the maximum value of magnesium by coinstantaneous measuring the minimum value of oxygen.
3. Removal of contaminates

   By furthermore increasing laser pulse frequencies the available energy is not sufficient anymore for any changes at the metallic surface except the ablation of contaminates. Consequently the initial value of the weight- % of magnesium and of oxygen is measured again.

So it is clearly evident, that the laser treatment with a Nd:YAG-Laser generates an oxide layer on the surface which is essential for the strength of the bonding. This oxide layer has a maximum thickness of approx. 350 nm. It is not possible to create thicker oxide layers with this method, because with every laser treatment the oxide layer is removed and then build again.

To get a first impression of the performance of the laser surface preparation compared to conventional pretreatments like SACO-blasting or pickling, T-Peel-tests according to DIN EN ISO 11339 [8] were performed. For this purpose the mean laser power was set to 50 W and three different laser pulse frequencies (3, 9 and 21 kHz) were chosen which represent the three earlier described reactions. The used forward speed and line spacing resulted in an overlap of 50 % per pulse in each direction to get a homogeneous processing of the surface. The samples were prepared using a hot bonder. The results of these tests are shown in Fig. 5.

The excellent suitability of the laser pretreatment was already visible in these simple tests. However, it is noticeable that there were some significant variations in the average peel strength at one and the same laser parameters. This was a first indication that the curing process by Hot Bonder must be done very carefully in order to prevent a falsification of the measurement results. The results with samples cured in an autoclave were quite similar (not shown here), so that the advantages of the laser treatment become clearly evident.

To optimize these first laser parameters, roller peel tests according to DIN EN 1464 [9] were performed. Although the peel strengths were very high, there were still some small areas with adhesive fracture patterns. To investigate this phenomenon, some cross sections of these specimens were examined with the high resolution FE-SEM (see Fig. 6a, b). The adhesive, the Mg bulk and also the laser induced oxide layer with a thickness of about 200 nm were displayed. However the oxide layer seemed to be not very homogenous. The crack started in a region of adhesive failure directly on the surface in the middle of a depression created by a single laser pulse. At the edge of the depression, the crack moved into the adhesive and caused cohesive failure in the adhesive. Consequently the correlation of the adhesion to the distribution of the oxide was of particular interest. The oxide was located mostly on the edges of the depressions created by single laser pulses whereas inside the depressions there was little or no oxide detectable. This is a result of the explosively expanding plasma created by the ablation process. This induces the transport of the ablated material to the edges of the depressions where it condenses and reacts with oxygen. Furthermore there is an oxygen reduced zone on the surface during the plasma expansion. To illustrate this phenomenon a spatial resolved chemical analysis of the surface was made by EDX. The SEM-picture and the distribution of the elements oxygen and magnesium are displayed in Fig. 7a, b.

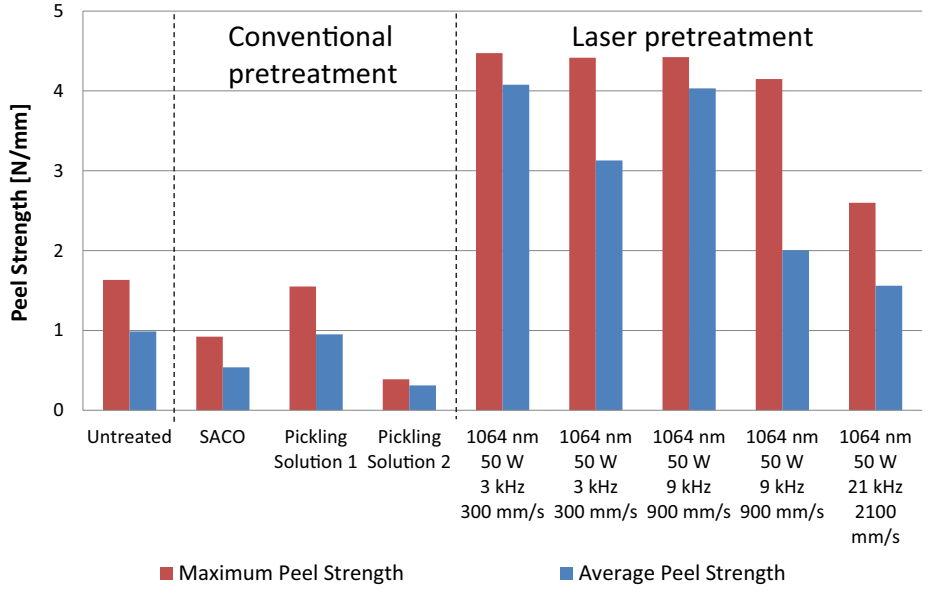

Fig. 5 Peel strength (T-Peel-Test) of bonded AZ 31 magnesium-sheets with conventional pretreatment or laser pretreatment

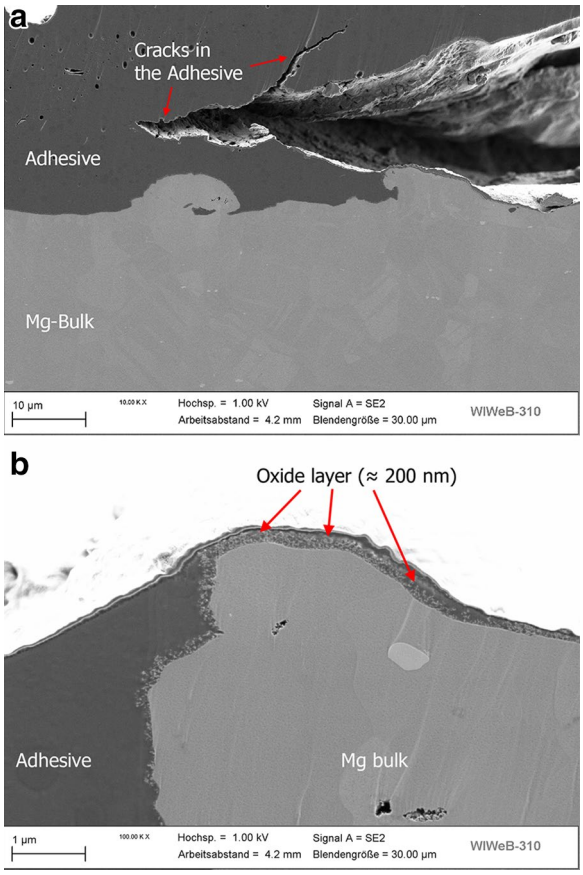

Fig. 6 **a**, **b** High resolution FE-SEM images of cross sections of destructive tested bonded AZ31specimen

To achieve a more homogenous oxide layer, the forward speed of the laser beam was halved to realize a bigger overlap of the single laser pulses. So the overlap of the single laser pulses was raised from approximately 50 % which corresponds to the forward speed of 700 mm/s up to 75 % overlap which corresponds to the forward speed of 300 mm/s. The results of peel tests of this improvement are displayed in Fig. 8. The use of an additional primer BR 127 CF [11] did not further enhance the adhesion in the unaged specimens. The influence of the curing process either with a hot bonder or an autoclave was relatively small, only the average peel strength for the specimens cured in the autoclave showed slightly higher values.

Conclusion

It was shown that pulsed high energy laser radiation in combination with a film adhesive is a very promising alternative for the pretreatment of thin magnesium sheets compared to conventional methods like SACO-blasting or pickling. The laser pretreatment generates a thin oxide layer on the surface of the magnesium, which results in a very good improved molecular interaction of the adhesive with the surface. All parameter have to be optimized regarding the building of a homogenous oxide layer. The most important

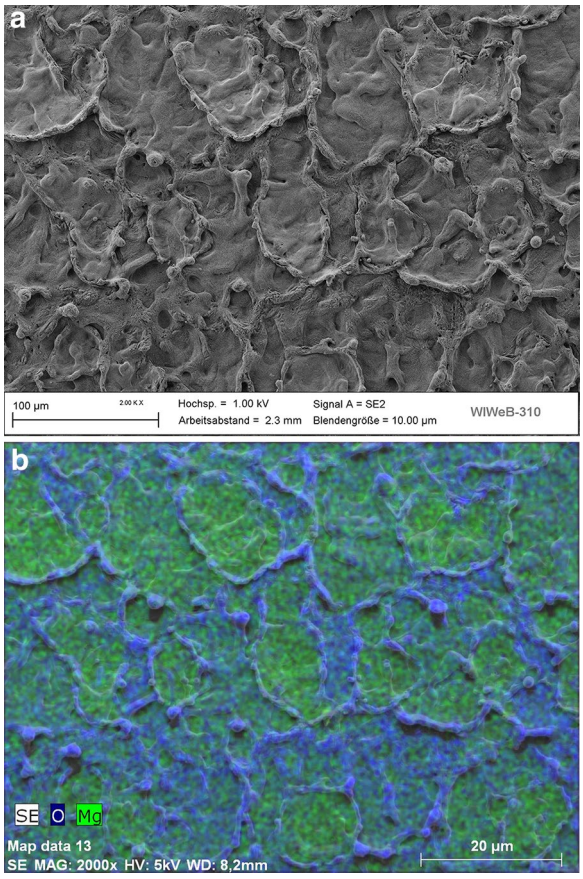

Fig. 7 **a** SEM picture of the surface of a AZ31-alloy after treatment with a Nd:YAG-Laser; **b** EDX mapping of a laser treated magnesium surface with the distribution of the elements oxygen (*blue*) and magnesium (*green*)

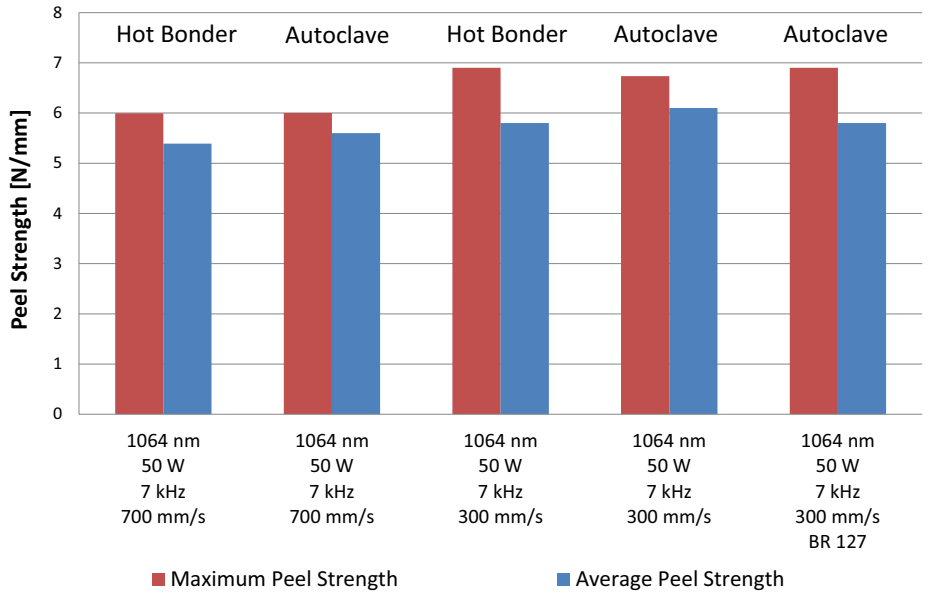

Fig. 8 Improvement of the peel strength through variation of the overlap of the single laser pulses

parameter is the forward speed of the guided laser beam. The halving of the forward speed increases the peel strength significantly.

By combining destructive tests, innovative preparation methods and FE scanning microscopy (especially fracture analysis of cross sections), the surface pretreatment could be optimized. As a result, high strength of adhesive bonding of magnesium-alloys could be achieved. This fast physical process fulfils all legal requirements concerning environmental protection and occupational safety and also has low operating costs.

Authors' contributions

NS designed the study, supervised the experimental work and evaluation and wrote the manuscript. CW performed the experimental work and evaluation. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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