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Improving adhesion of copper/epoxy joints by pulsed laser ablation

Edwin Hernandez [a], Marco Alfano [b,*], Gilles Lubineau [a], Ulrich Buttner [c]

[a] King Abdullah University of Science and Technology, Physical Sciences and Engineering Division, COHMAS Laboratory, Thuwal 23955-6900, Saudi Arabia
[b] Department of Mechanical, Energy and Management Engineering, University of Calabria, Via P. Bucci 44C, 87036 Rende (CS), Italy
[c] King Abdullah University of Science and Technology, Computer, Electrical and Mathematical Sciences and Engineering Division, Electrical Engineering Department, Thuwal 23955-6900, Saudi Arabia

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ABSTRACT

The purpose of the present work is to analyze the effect of pulsed laser ablation on copper substrates (CuZn40) deployed for adhesive bonding. Surface pre-treatment was carried using an Yb-fiber laser beam. Treated surfaces were probed using Scanning Electron Microscopy (SEM) and X-Ray Photoelectron Spectroscopy (XPS). The mechanical performance of CuZn40/epoxy bonded joints was assessed using the T-peel test coupon. In order to resolve the mechanisms of failure and adhesive penetration within surface asperities induced by the laser treatment, fracture surfaces were surveyed using SEM. Finite element simulations, based on the use of the cohesive zone model of fracture, were carried out to evaluate the variation of bond toughness. Results indicated that the laser ablation process effectively modifies surface morphology and chemistry and enables enhanced mechanical interlocking and cohesive failure within the adhesive layer. Remarkable improvements of apparent peel energy and bond toughness were observed with respect to control samples with sanded substrates.

1. Introduction and motivation

Adhesive bonding is a suitable joining technique for the fabrication of lightweight structures, especially those requiring different materials (*e.g.* metals and composites) to be bonded together [1,2].

However, adhesive joints show a rich array of failure mechanisms which makes their optimization quite complex. For instance, interfacial fracture, which is usually the result of improper surface preparation, is a very widespread mechanism of failure in bonded structures. Indeed, fabrication of reliable adhesive bonds does not solely depend on joint design and adhesive type, but it strongly relies on the preparation of the mating surfaces [1,2]. As a matter of fact, yield and reliability of adhesive bonds are strongly affected by interfacial adhesion and appropriate surface preparation techniques are then needed.

Extensive studies have been performed in order to improve debonding resistance through the development of surface pretreatments which enable the formation of appropriate surface morphology and chemistry [1–3]. In general terms, surface pretreatments aim to promote intermolecular interactions at the adhesive/substrate interface as well as mechanical interlocking of the adhesive within surface asperities.

Current surface preparation techniques include mechanical abrasion by means of sanding or grit blasting [4]. However, limited repeatability and potential surface contamination may reduce the overall bond performance. There is a wide range of alternatives that can be undertaken, among the most sophisticated it is worth mentioning acid anodizing, which certainly plays a major role in the fabrication of bonded connections for the aerospace industry [5]. Yet, chemical treatments create a large volume of hazardous wastes and pose a greater risk to the environment and human health, as a result they have been progressively subjected to a stricter control regime by governmental organizations [6].

It follows that new surface preparation methods, which hold the promise of improved repeatability, cost reduction and waste minimization are becoming increasingly important. Alternative cleaner procedures include the use of solid state or fiber pulsed laser ablation (PLA) [7]. PLA relies on the use of highly focused laser beams which lead to material removal and redistribution on the target surface. PLA enables micro patterning of materials, cleaning of surfaces from contaminants layers and particulates and is employed in a wide range of applications in biotechnology and medicine [7]. On top of this, PLA improves bond repeatability, as well as waste and cost reduction, and is also prone to automation. Previous literature works have indicated that PLA promotes significant modifications of surface morphology [8,9] and chemistry [10,11], leading to improvement in surface wetting [12,13] and mechanical interlocking [12,14], with consequent increases in bond toughness [15,16] and long term joint stability [18]. It may

* Corresponding author. Tel.: +39 0984 494156.
E-mail address: marco.alfano@unical.it (M. Alfano).

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also outperform traditional joining techniques, such as riveting and fusion welding when dealing with dissimilar materials [19].

The objective of the present work is to survey the effect of Yb-fiber (1064 nm) PLA as surface pre-treatment of copper substrates for adhesive bonding. Nanosecond pulsed Yb lasers are provided with high vibrational stability and extended lifetime, and are often used to machine small to large scale metal surfaces in reliable fashion and at low cost. The model material system selected for the experiments is represented by copper substrates (CuZn40) bonded with an epoxy adhesive. The CuZn40 has good mechanical, thermal, corrosion and electrical properties. The good formability of the alloy has led to a vast number of applications in several industries, e.g. pipe fitting, domestic taps, radiator valves, gas appliances, window and door furniture, architectural panel sheets, large nuts and bolts, condenser plates and heat exchangers. However difficulties arise concerning joining, because traditional fusion welding is strongly affected by the presence of zinc, which evaporates during welding with a detrimental effect on the joint microstructure, which eventually features porous and weak layers of copper and copper oxide. It follows that the fabrication of high-quality and reliable joints demands alternative joining techniques.

Yb-fiber PLA is herein carried out in order to impart significant modifications in surface topography and chemistry. An assessment of surface characteristics, both in terms of topography and chemistry, is firstly made for a variety of laser speed. Based on the results of surface analyses, a proper combination of processing parameters is selected and adhesive bonded T-peel joints are prepared and tested. The T-peel test configuration is very advantageous when testing flexible adherents because samples can be easily fabricated and closely resembles actual bonded structures, e.g. automotive components [3,20–22]. Moreover it is very convenient to compare adhesives or surface treatments and delivers useful insights about the ability of the joint to resist debonding. The global load–displacement response of laser treated samples is herein compared with those obtained from baseline joints made-up with sanded substrates. Meaningful metrics (e.g. peak load, total dissipated energy) are extracted from the global response in order to make quantitative assessments among the various sets of results. Post failure SEM analyses of fractured surfaces are then performed to resolve the mechanisms of failure and analyze the extent of mechanical interlocking at the adhesive/substrate interface. Finally, finite element simulations, based on the use of the cohesive zone model of fracture [16,23,24], are carried out to infer the enhancement of bond toughness that follows to PLA.

2. Experimental details

2.1. Materials and surface treatments

The adhesive selected for joint fabrication is a bi-component (resin+hardener) room temperature curing epoxy (Araldite 420 A/B, Huntsman, Salt Lake City, UT, USA). It is a structural adhesive with very high shear and peel strengths which bonds materials such as metals, composites and thermoplastics. The basic mechanical properties of the adhesive provided by the manufacturer through tensile tests are as follows: Young's modulus, $E=1.5$ GPa; elongation at break $\epsilon_f=4.6\%$; tensile strength, $\sigma_f=29$ MPa. The substrates consisted of thin copper foils (CuZn40) with nominal thickness equal to $t=0.5$ mm. CuZn40 copper alloy usually contains 59–63% in weight of Cu, Pb < 0.3%, Fe < 0.3% and Zn (balance). It is this high quantity of zinc in brass which leads to a dual phase (duplex) structure, *i.e.* alpha–beta brasses. Notice that alpha–beta brasses have higher hardness, strength, and in general better mechanical properties. Also brasses of higher zinc contents have a lower cost and thus influence the total life-time costs. The mechanical properties of the alloy were determined through dedicated tensile tests and are given as follows: Young's modulus $E=90$ GPa; elongation at break $\epsilon_f=12.5\%$; yielding stress $\sigma_y=85$ MPa.

Copper substrates have been surface treated using a 1.06 μm ytterbium fiber laser (PLS6MW Multi-wavelength Laser Platform by Universal Laser Systems, NY, USA) with a 30 W maximum output average power. In PLA a strongly localized area of the target is heated by the laser pulses, while the surrounding is basically unaffected. The spatial and temporal localizations of laser-material interaction give raise to very large heating/cooling rates and small material volumes are subjected to the thermal induced defects [7]. Surface modifications are generally imparted by controlling adjustable laser process parameters, such as laser average power, laser scanning speed (*i.e.* speed of the beam relative to the substrate) and spacing (*i.e.* laser pitch). Moreover, actual depth and quantity of affected material mainly depend on the energy density, or pulse fluence (F_p), which is transmitted to the target surface:

$$F_p = I_p \cdot t_p = \frac{W_{ave}}{f \cdot A_s}. \tag{1}$$

where I_p represents the laser irradiance, t_p is the laser pulse duration, W_{ave} is the average output power, f the pulse frequency and A_s is the spot size. Preliminary analyses have shown that laser power significantly affects the resulting morphological modifications. Indeed, for a given pulse frequency, an average power below 30 W could not induce any significant variation in surface morphology. In addition, it was observed that a laser spacing equal to 30 μm allowed the whole target surface to receive laser processing and to be fully treated. For these reasons the subsequent processing was executed at 30 W and 30 kHz and pattern density was held constant by holding the pitch fixed to 30 μm. Therefore surface processing was always carried out at the maximum pulse fluence allowed by the available in-lab hardware ($F_p=200$ J/cm^2), while the laser scanning speed was varied in the range (50–500) mm/s. Notice, finally, that compressed air was injected onto the work surface to suppress potential combustion flame and blow away smoke and prevent debris accumulation during the process. The use of compressed air in the working area can provide superior processing results and prevent melt-back on the lens. A set of substrates was processed replacing compressed air with nitrogen and the associated potential implications in terms of oxidation and joint performance were also surveyed. A summary of the processing parameters considered for the experimental campaign is given in Table 1.

2.2. Surface morphology and composition

A Scanning Electron Microscope (FEI Quanta 200) was used to analyze surface morphological modifications. In addition, back-scattered electron analysis was also carried out to probe the fractured surfaces and highlight mechanical keying of the adhesive

Table 1
Laser processing parameters.

Process parameter	Value
Laser wavelength (nm)	1064
Focal distance (mm)	46
Spot size (μm)	25
Pulse repetition rate (kHz)	30
Pulse duration (FWHM) (ns)	> 10
Pulse energy (max) (mJ)	2.0
Max average power (W)	30
Laser speed (V) (mm/s)	50/250/500
Processing gas (–)	Air/nitrogen

FWHM: full width at half maximum.