

Supplementary information

Making metal surfaces strong, resistant, and multifunctional by nanoscale-sculpturing

M. Baytekin-Gerngross^a, M.D. Gerngross^a, J.Carstensen^a, and R. Adelung^a*Institute for Materials Science, Functional Nanomaterials, Kiel University, Kaiserstr. 2, 24143 Kiel, Germany.*

Materials and Methods:

In this work various commercially available Ti grades and alloys – Ti grade 2, Ti-3Al-2.5V (Ti-grade 9), metal injection molded (MIM) Ti-6Al-4V (Ti-grade 5) and Ti-6Al-4V ELI (Ti-grade 23), multiple commercially available Al alloys, AA1050 (Al99.5%), AA5754 (AlMg3), and AA6060 (AlMgSi0.5), and commercially available Zn 99.95% have been chemically structured.

In all cases the metal samples are degreased in acetone prior to the etching step. The Ti and Al alloy surface structuring is conducted in simple Teflon beakers, partially also with additional external electrolyte stirring. The Zn surface structuring is performed in an electrochemical cell in a four electrode arrangement.

Etch-sculpturing of metal surfaces

The etching electrolyte and procedure for chemical sculpturing the various Ti grades surfaces is adjusted to each Ti grade. The Ti grade 2 samples are etched in a two-step process. In step 1 the surface is homogenized by photochemical etching in concentrated H₂SO₄ under red illumination. A homogeneous illumination of the Ti grade 2 surface is obtained by a high-power LED array from Enfis, Uno Tag Array Red, operated at 300 mA. In the second step the Ti grade 2 sample is immersed into a 1:1 volume ratio mixture of concentrated HCl and concentrated H₂SO₄ for 3 h without prior water-rinsing. Both etching steps are performed without external stirring at room temperature. The etching of the Ti-3Al-2.5V substrates is performed in an electrolyte consisting of a 1:2 volume ratio mixture of concentrated HCl and concentrated H₂SO₄ with 1.67 g/l of alginate sodium salt for adjusting the viscosity without external stirring for 20 h at room temperature. The injection molded Ti-6Al-4V substrates are structured in a 1:1 volume ratio mixture of concentrated HCl and concentrated H₂SO₄ for 24 h at room temperature without external stirring. The Ti-6Al-4V ELI is etched in a two-step process. In the first step the surface is homogenized in concentrated H₂SO₄ for 20 h and chemically structured in the second step in a 1:1 volume ratio mixture of concentrated HCl and concentrated H₂SO₄ for 30 min. Both steps are performed at room temperature with external stirring.

The electrolyte for surface sculpturing of all Al alloys is an aqueous 7.25 wt% HCl electrolyte. The etching is performed at room temperature without external stirring.

For the Zn etching an aqueous 0.1 mol/l KCl electrolyte is used with 4.5 g/l PEG-3350 for adjusting the viscosity. The etching is

performed at 50°C. The electrolyte is constantly pumped through the etching cell at 50 rpm. A nucleation pulse of 0.5 V is applied for a homogeneous nucleation of the pores, followed by rectangular pulses with a pulse length of 5.4 s. The pulse length is divided into an anodic part with a typical potential of 0 V for 4.6 s and a cathodic part with –0.6 V for 0.8 s.

After surface structuring all samples are rinsed several times with deionized water and subsequently air-dried. All etched metal surfaces are optically investigated with a Zeiss Ultra Plus SEM. EDX elemental mapping is performed with an Oxford x-act detector at a beam acceleration voltage of 15 kV for AA5754 and at 20 kV for Ti-3Al-2.5V and Zn.

Adhesion properties of etch-sculptured metal surfaces

The adhesion properties of the metal-polymer joint are investigated by standard lap shear tests based on the European norm DIN EN 1465. These metal-polymer adhesion is tested on metal-polymer-metal sandwich composites. These tests are performed on AA5754 stripes with the dimensions of 105 mm x 25 mm x 1.6 mm in length, width and thickness as representative for the Al alloy family and on Ti-3Al-2.5V stripes with the dimensions of 63.5 mm x 10 mm x 2 mm. In both cases the metal stripes are glued to each other with an overlap of 12 mm and a gap size of 0.5 mm in a self-made 3D-printed holder to maintain a precise overlap area and to avoid sample torsion during the polymer curing.

Three commercially available polymers are used for AA5754-based sandwich composites, a medical-grade silicon (PDMS), from Dow Corning (Sylgard 184), a polythiourethane (PTU), from Performance chemicals (24–205 V), and an epoxy resin from UHU (UHU Plus Endfest). The PDMS-sandwich composites are dried in an oven at 70 °C for 15.5 h and cured at 85 °C for 2 h without the sample holder, the epoxy-sandwich composites at 70 °C for 1 h, and the PTU-sandwich composites are dried at 70 °C for 24 hours and afterwards cured at 85 °C for 3 h without the sample holder. Grit-blasted AA5754 stripes are used as reference for the adhesion tests for all tested polymers. They are cleaned in acetone to remove residual grease and grit and subsequently dry-blown.

The influence of grease on the adhesion behavior is investigated for the grit-blasted and sculptured AA5754 surfaces. The surfaces are greased with a conventional gear oil in a sponge printing technique. Afterwards the sandwich composites are formed based on epoxy resins as described above. The influence of moisture on the adhesion is investigated by water-

sprinkling on the epoxy based sandwich composites in a weathering chamber at 80 °C for 72 h.

After cooling down to room temperature the sandwich composites are lap-shear-tested on a Zwick QuickTest 100 kN machine with a displacement rate of 1 mm/min. In addition photographs and SEM images of the failure surfaces of the sandwich structures are taken.

The Cu deposition is performed in an electrochemical cell in a three electrode arrangement under galvanostatic conditions at a current density of -1.3 mA/cm^2 for 210 min at room temperature. The electrolyte is an aqueous solution consisting of 18.5 g/l CuSO_4 , 1.1 g/l H_3BO_3 , and 1.1 g/l PEG 3350.

The Al particles are structured in an aqueous 7.25 wt% HCl electrolyte at 30°C under constant stirring. The electrolyte is seeded by previously dissolving 2.25 g/l Al powder. The particles are subsequently chemically sculptured in this electrolyte for 4.5 min. Afterwards, the particles are rinsed several times in deionized water and in acetone as last step prior to drying. The particle composites are formed by immersing the structured Al particles into PTU, EVA, and epoxy resin and filling up a Teflon casting mold (dog bone shape, 52 mm x 8 mm x 1 mm). The composite is then cured under ambient conditions for EVA, at 80°C for PTU for 3h, and epoxy resin at 70°C for 1h. For the polyoxymethylene (POM)-EVA joint the POM surface is softened by heating with a hot-air gun. The previously prepared sculptured Al micro-particles are distributed on and imprinted into the softened POM surface. Subsequently the softened EVA is pressed on it forming the joint. The POM-EVA joint with untreated Al particles is formed in the same manner, as well as the direct POM-EVA joint, but omitting here the application of Al particles.

Further properties of etch-sculptured metal surfaces

The corrosion experiments are performed in an electrochemical cell in a four electrode arrangement under galvanostatic conditions at a current density of 0 mA/cm^2 (quasi open circuit conditions) for 15 min, followed by an anodic current density of 6.4 mA/cm^2 for 5 min. The electrolyte is an aqueous solution inspired by sea water consisting of 0.5 mol/l NaCl and 0.056 mol/l Na_2SO_4 . The experiments are performed at 19°C.

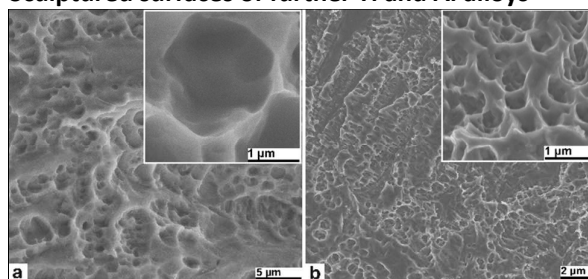
The characteristic sculptured Al surface structure can also be obtained in a "green" electrochemical way. The etching of the AA5754 stripe is performed in an electrochemical cell in a three electrode arrangement under galvanostatic conditions at a current density of 50 mA/cm^2 at room temperature. The electrolyte is an aqueous solution inspired by sea water and consists of 0.5 mol/l NaCl and 0.056 mol/l Na_2SO_4 .

The contact angle measurements are performed on a self-made standard test setup sculptured AA5754 and Ti-3Al-2.5V surfaces and grit-blasted surfaces AA5754 and Ti-3Al-2.5V as reference. The volume of the droplets is 5 μl in all cases. The images are recorded with a conventional camera.

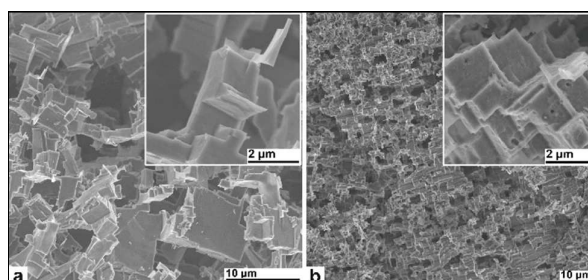
The reflection experiments are performed on sculptured AA5754 and Ti-3Al-2.5V surfaces and grit-blasted surfaces AA5754 and Ti-3Al-2.5V as reference. The samples are mounted into the self-made setup under an angle of 52° with respect to the ground and a laser beam incident angle of 35° with

respect to the sample surface. The used laser has a wavelength of 650 nm and an output power of less than 5mW. The images are recorded with a conventional camera.

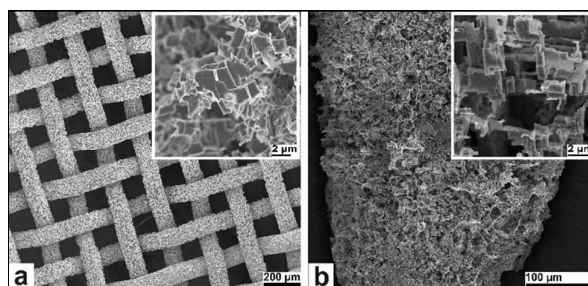
Sculptured surfaces of further Ti and Al alloys



S.1 SEM images of the sculptured surface of a) injection molded Ti-6Al-4V, inset: in high magnification, b) casted Ti-6Al-4V ELI, inset: in high magnification.

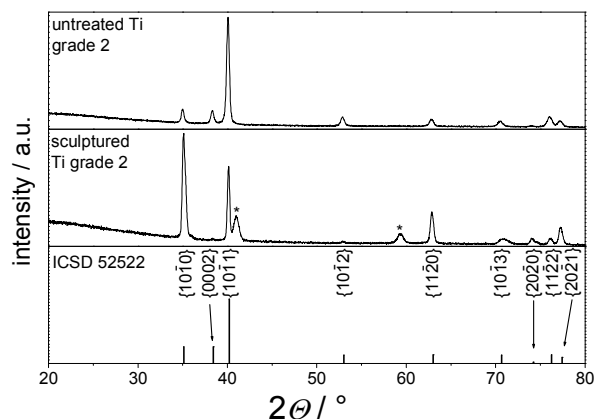


S.2 SEM images of the sculptured surface of a) AA1050, inset: in high magnification, b) AA6060, inset: in high magnification.



S.3 SEM images of the structured surface of a) AA5019 micro-mesh sheets, inset: in high magnification, b) Al micro-particle, inset: in high magnification.

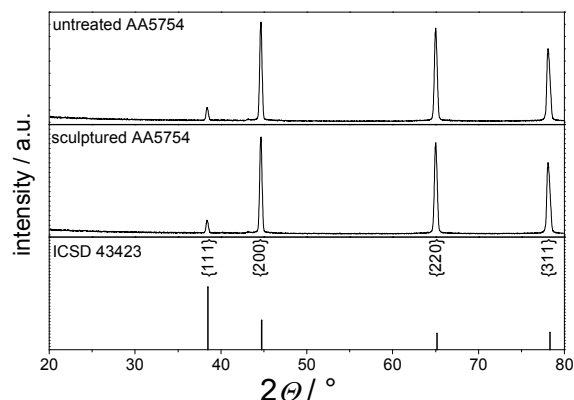
XRD diffractograms



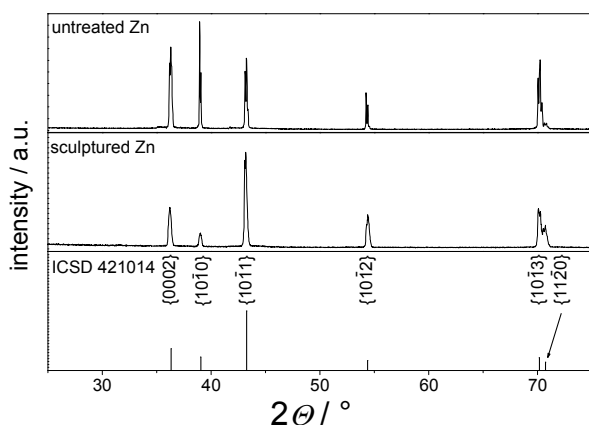
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S.4 XRD diffractogram of untreated Ti grade 2, sculptured Ti grade, and ICSD 52522 as reference. The two peaks marked with an asterisk, could not be identified, but they are not associated with any kind of Ti oxides.

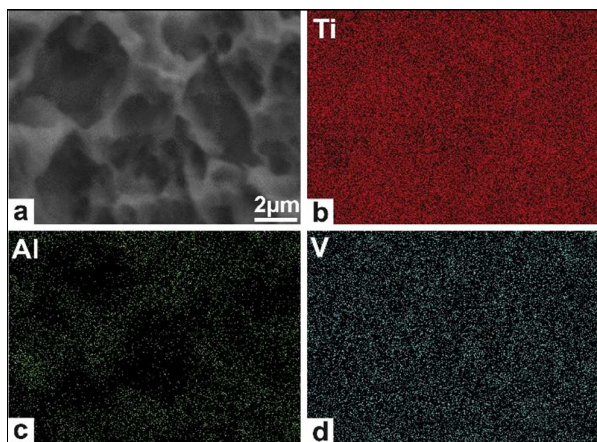


S.5 XRD diffractogram of untreated AA5754, sculptured AA5754, and ICSD 43423 as reference for Al.



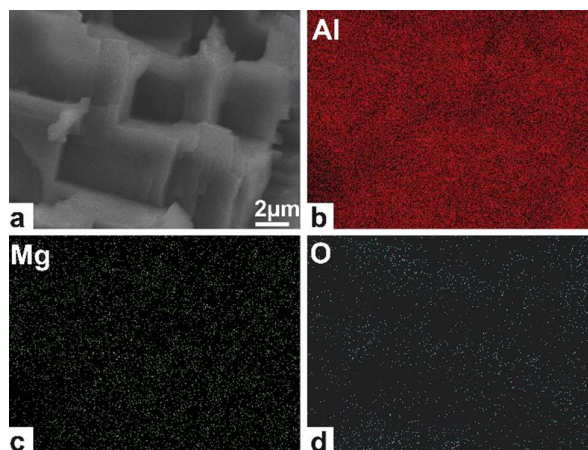
S.6 XRD diffractogram of untreated Zn, sculptured Zn, and ICSD 421014 as reference.

EDX-surface analysis

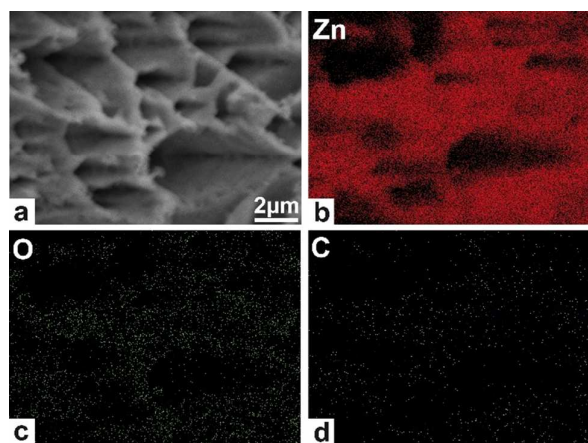


S.7 EDX analysis of the sculptured Ti-3Al-2.5V surface at 20 keV, a) SEM image of the investigated surface, b) Ti map, c) Al map, d) V map. In case of Ti alloys EDX analysis indicates a preferential dissolution of Al-rich surface regions. This is a

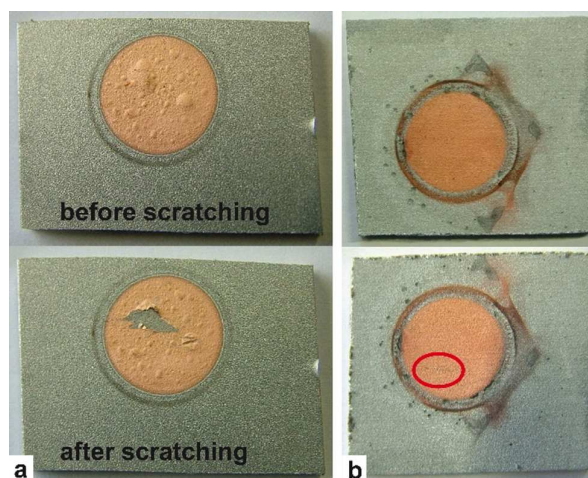
clear hint for the preferential dissolution of higher corrosive α -phase parts within the host-matrix.



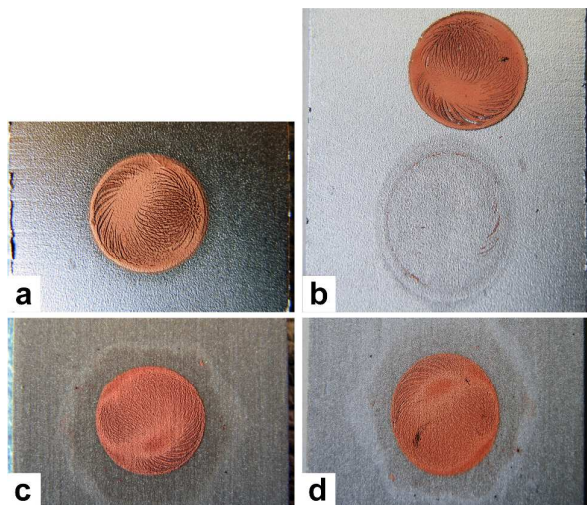
S.8 EDX analysis of the sculptured AA5754 surface at 15 keV, a) SEM image of the investigated surface, b) Al map, c) Mg map, and d) O map. The EDX analysis of AA5754 indicates a surface coverage only with a native oxide layer, but no preferential removal of alloying elements.



S.9 EDX analysis of the sculptured Zn surface at 20 keV, a) SEM image of the investigated surface, b) Zn map, c) O map, and d) C map. The EDX analysis of the sculptured Zn surface shows that the pore walls are pure Zn and only covered with a native oxide layer. The C signal most likely originates from carbon deposition from the chamber atmosphere due frequent scanning over the surface.

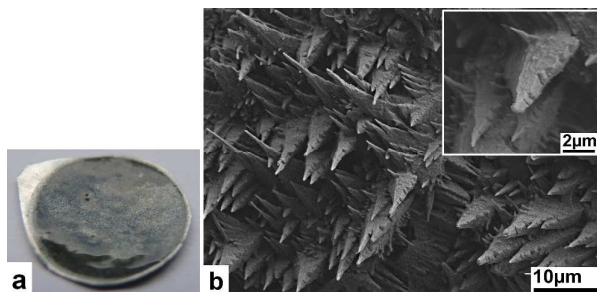


S.10 Scratch-test on Cu layer deposited on top of a) grit-blasted AA5754 surface b) etched AA5754 surface.



S.11 AA5754/ Cu composites a) grit-blasted AA5754/ Cu composite before and b) after tensile testing till fracture of the AA5754 stripe, c) sculptured AA5754 composite before and d) after tensile testing till fracture of the AA5754 stripe.

In Fig. S.11 the grit-blasted, respectively the sculptured AA5754/ Cu composites are depicted before and after tensile testing. For both AA5754 surfaces the Cu film is electrochemically grown directly on the surface of an AA5754 stripe with the same film thickness. Subsequently, the Cu coated AA5754 stripes are pulled apart till complete fracture of the stripes. Figure S.11b shows that the Cu film completely delaminated from the grit-blasted AA5754 substrate under mechanical load. Detachment occurs at a stress of about 8.7 MPa (with respect to the AA5754 cross-sectional area) and a corresponding strain of about 2.3 %, complete delamination at a stress of about 9.3 MPa and a corresponding strain of about 4.1 %. No detachment of the Cu film could be observed for the sculptured AA5754, see Fig. S.11d. One only observes that the Cu film seems to have elongated in the same manner as the underlying sculptured AA5754 stripe. This is a clear indicator for the extremely good adhesion between the sculptured AA5754 surface and the Cu film, since this interface allows for direct transfer of the stress from the AA5754 into the Cu film.



S.12 a) sculptured Zn/ ethyl-2-cyanoacrylate composite, b) SEM top view on the ethyl-2-cyanoacrylate pore cast after dissolution of the sculptured Zn component, inset: high magnification on the pore cast.

In Fig. S.12a the sculptured Zn/ ethyl-2-cyanoacrylate composite is shown. The dark part is the porous Zn, the ethyl-2-cyanoacrylate is transparent only detectable via light reflection. To obtain a view directly at the joint interface of sculptured Zn and ethyl-2-cyanoacrylate the sculptured Zn component of the composite is chemically dissolved leaving just the ethyl-2-cyanoacrylate as a cast of the pores. Figure S.12b shows this ethyl-2-cyanoacrylate pore cast. One observes that the pores have grown under various angles in Zn forming a three dimensional hook network which is further enhanced by branching of side pores out of the root pores as shown in the inset of S.12b.

It is obvious from the image S.12b that the joint can only fail cohesively under mechanical load either in the Zn or the polymer component. Adhesive failure at the interface is impossible due to the three-dimensionally arranged pore network with branched side pores. Thus, the joint strength between sculptured Zn and any polymer is only limited by the mechanical properties of Zn and the polymer itself.

S.13 Video Single-lap shear test of sandwich composites composed of grit-blasted AA5754/ medical PDMS and sculptured AA5754/ medical PDMS.

S.14 Video Adhesive-free joining of grit-blasted and sculptured AA5754 with thermoplastic acrylonitrile-butadiene styrene (ABS).

S.15 Video Joints of polyoxymethylene (POM) and ethylene-vinyl acetate (EVA) directly formed, via untreated Al micro-particles, and via sculptured Al micro-particles.

S.16 Video Water jet reflection on polished and sculptured AA6060.