# Supporting Information

Title: Surface modification of ZnMgAl-coated steel by dielectric-barrier discharge plasma

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## 1. SEM and EDX characterisation of the untreated ZnMgAl surface

Figure S1 shows a SEM image of an untreated ZnMgAl surface. The dendrite structures of about 5-10 µm are characteristic for ZnMgAl-alloys.

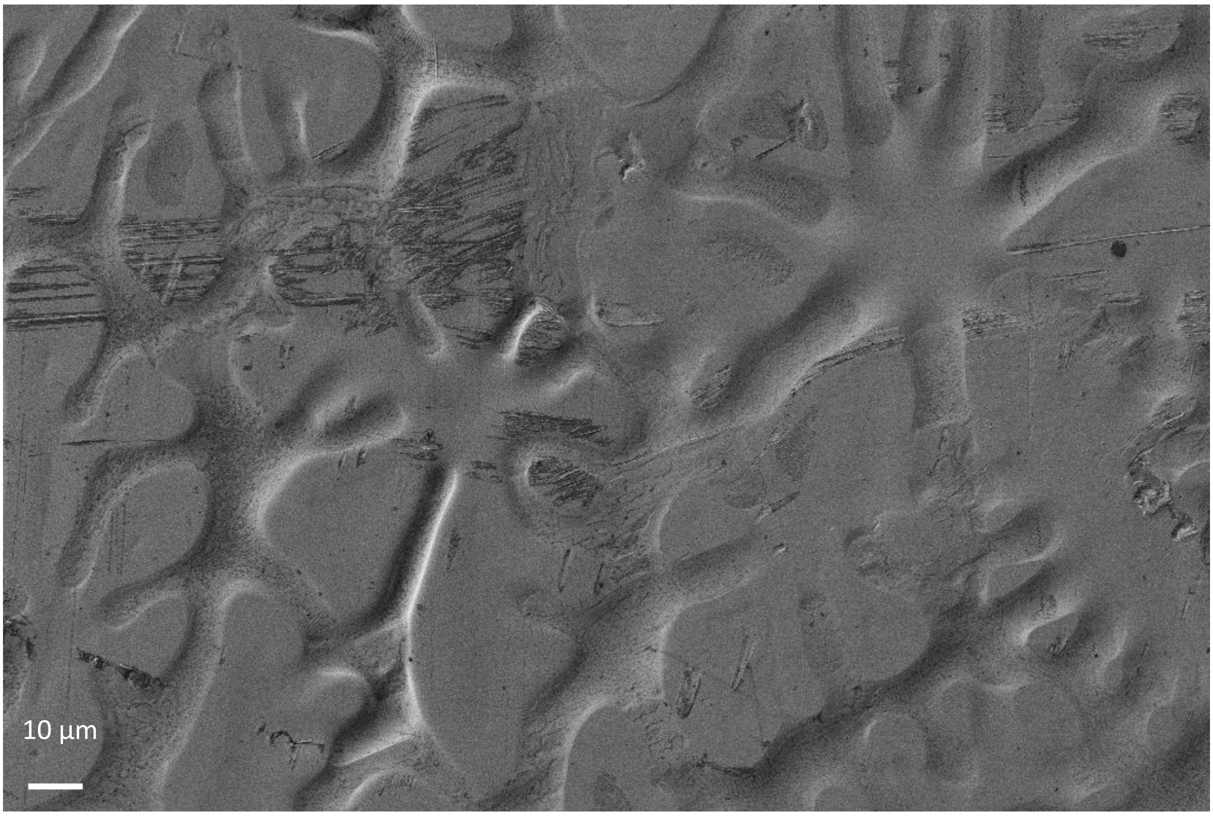

*Figure S1 SEM image of the native surface of a ZnMgAl alloy onto steel*

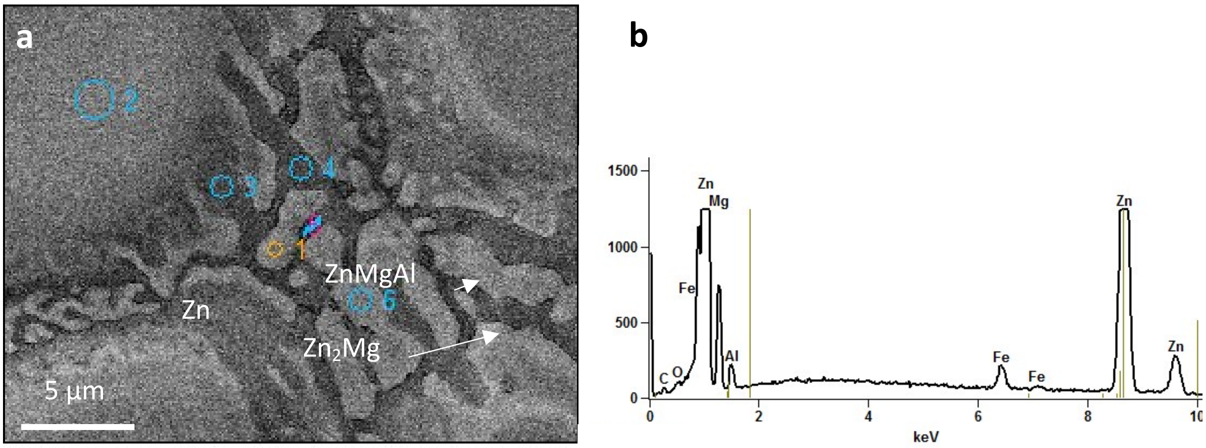

*Figure S2 a) SEM image of an untreated ZnMgAl sample. The circles (spots 1 to 6) mark the positions where EDX measurements where performed. (b) Typical EDX measurement showing Zn, Mg, Al, Fe, O and C on the surface.*

Figure S2a shows a SEM image of an untreated ZnMgAl showing the positions where EDX-measurements were performed. A characteristic EDX-spectrum is shown in Figure S3b. Iron, zinc, magnesium, aluminium, oxygen and carbon were present on the surface. The results of the quantifications are presented in Table S1.

*Table S1 Quantification of the EDX spectra measured at the spots shown in Figure S3*

| Atom-% | C-K | O-K | Mg-K | Al-K | Fe-K | Zn-K |
|---|---|---|---|---|---|---|
| Spot 1 | 5.72 | 3.11 | 3.58 | 2.55 | 2.57 | 82.47 |
| Spot 2 | 5.49 | 2.53 | 1.23 | 2.57 | 2.93 | 85.26 |
| Spot 3 | 3.66 | 1.99 | 18.07 | 2.90 | 2.26 | 71.11 |
| Spot 4 | 3.90 | 2.01 | 21.62 | 5.51 | 1.83 | 65.12 |
| Spot 5 | 3.15 | 2.94 | 1.98 | 19.38 | 2.15 | 70.40 |
| Spot 6 | 4.62 | 3.60 | 2.80 | 3.31 | 2.51 | 83.16 |

It is seen that Zn is dominant in all areas, while Mg and Al have high variations in their concentration dependent on the measured area. The presence of Fe in all positions is explained by the small thickness of the ZnMgAl-coating.

## 2. Ex-situ XPS analysis of surface chemical changes after plasma processing

Figure S3 shows the XPS surveys of ZnMgAl before and after the plasma treatments. All surveys only showed peaks of Zn, Mg, Al, C and O on the surface.

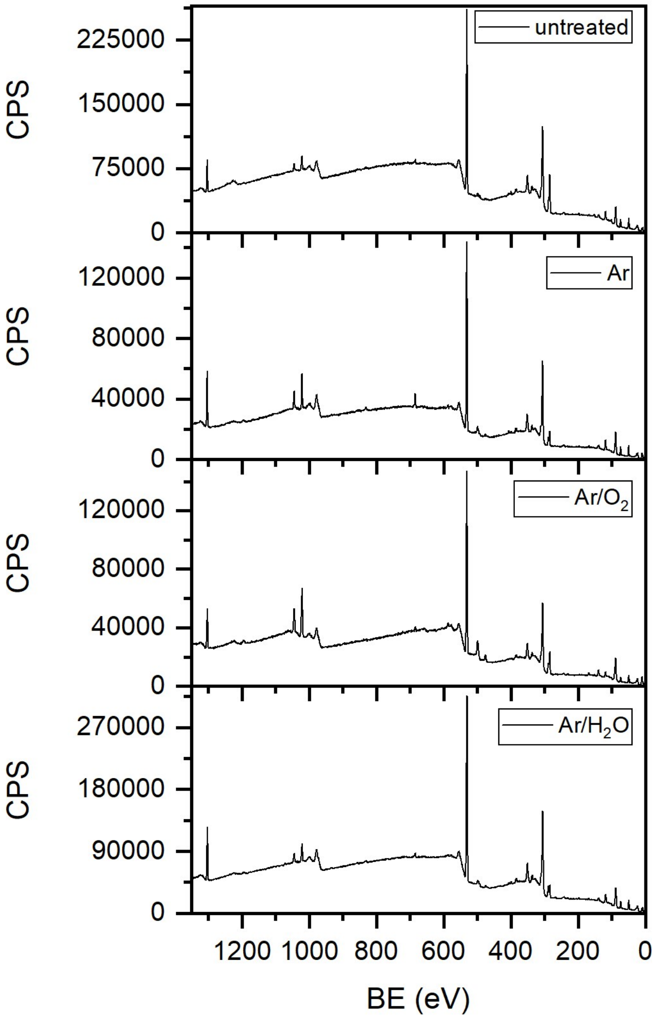

*Figure S3 XPS surveys of the ZnMgAl surface before, and after the plasma treatments.*

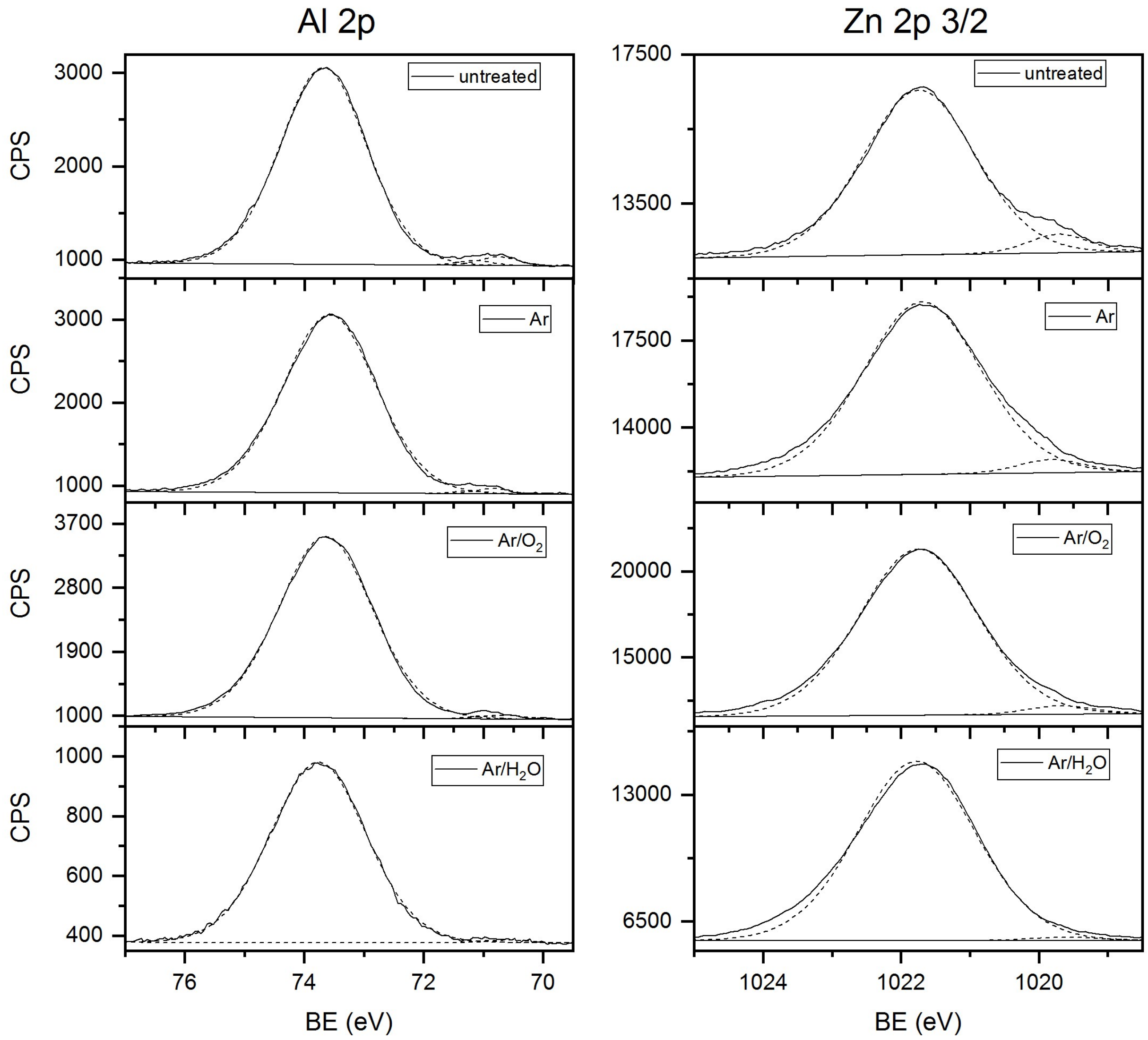

*Figure S4 Al 2p and Zn 2p 3/2 XPS core level peak of an untreated ZnMgAl sample and samples after the plasma treatments. The fits are displayed as dashed line.*

The fitting of the Al 2p and Zn 2p 3/2 core level peaks is presented in Figure S4 before and after the plasma treatments. For each peak, two components were fitted, representing the oxidized and reduced species respectively ($Zn^{2+}$ (2021.8 eV) and $Zn^0$ (1019.6 eV) or $Al^{3+}$ (73.6 eV) and $Al^0$ (70.6 eV)). The fitted peaks are displayed as dashed lines. Based on the fitting results, the oxide layer was calculated following Strohmeier [1]:

$$d = \lambda_o \sin(\theta) \ln\left[\frac{N_m \lambda_m I_o}{N_o \lambda_o I_m} + 1\right]$$

where $d$ is the oxide layer thickness, $\lambda_m$ and $\lambda_o$ are the inelastic mean free paths of the emitted photoelectrons within the metal and oxide layers, $\theta$ is the take-off angle with respect to the surface, $N_m$ and $N_o$ are the volume densities of the metal and oxide phases (see table S2) and $I_m$ and $I_o$ are the fitted intensities of the respective metal and oxide photoelectron peaks. The mean free paths were calculated using the Software Quases[2], which based on the calculations of Tanuma.[3]

*Table S2 Constant values for calculating the oxide layer thickness*

| | $\lambda_m$ [Å] | $\lambda_0$ [Å] | $\theta$ [°] | $N_m$ $[g\ cm^{-3}]$ | $N_0$ $[g\ cm^{-3}]$ |
|---|---|---|---|---|---|
| Aluminium | 30.85 | 32.56 | 30 | 2.7 | 3.99 |
| Zinc | 9.81 | 11.38 | 30 | 7.14 | 5.47 |

## 3. TOF-SIMS imaging and depth profiling

To compare the results of XPS and TOF-SIMS, the sputter depth was estimated from the sputter times for the TOF-SIMS sputter profiles.

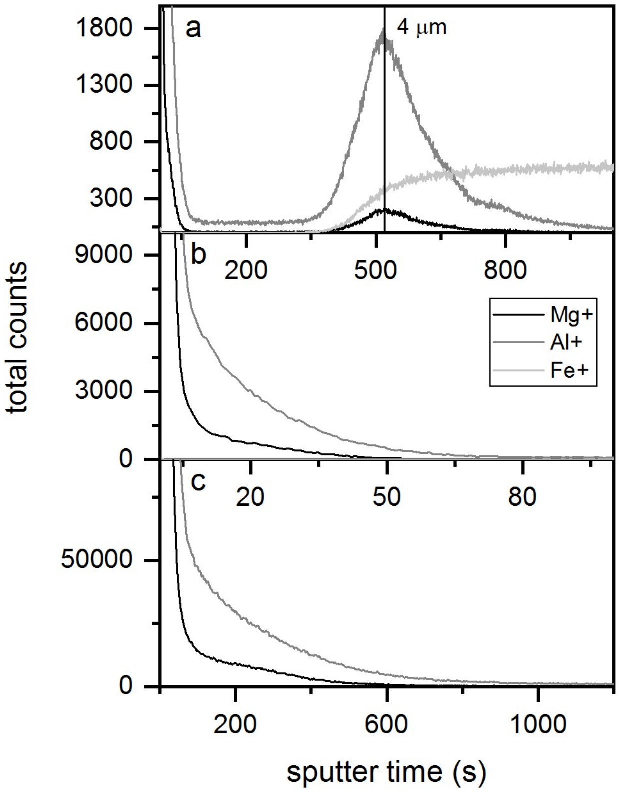

*Figure S5 Sputter depth profile calibration of the ToF-SIMS experiment. The depth profile through the complete material (fast small area depth profiling) is compared to the alloy layer thickness taken from SEM cross-section (a). The initial intensity curves obtained during fast small area depth profiling (b) are then compared intensity curves obtained during large area depth profiling (c).*

Therefore, the average thickness of the ZnMgAl-film was determined by SEM (around 4 µm) and compared to a sputter profile going through the complete ZnMgAl-film, indicated by the appearance of the $Fe^+$-signal. But in the ToF-SIMS depth profile shown in Figure S5a, no sharp transition of Mg, Al and Fe is seen at the interface between steel and ZnMgAl. Thus, the sputter time at the maximum of Al and Mg at the interface were taken as end of the oxide layer and correlated to the SEM result. To finally estimate the sputter ratio for the large area sputtering, the small area (Figure S5b) was compared to that of the large area sputtering (Figure S5c). It is seen, that 100 s of the small field sputtering are equivalent to 1200 s of the large area sputtering.

Thus, the sputter rate for the large area sputtering is $\frac{4\,\mu m}{525\,s} = 0.0076\frac{\mu m}{s} = 7.6\frac{nm}{s}$. When the sputter ratio is adjusted to the small area sputter conditions, a sputter ratio of $\frac{100\,s}{1200\,s} \cdot 7.6\frac{nm}{s} = 0.63\frac{nm}{s}$ is estimated for the small area sputtering.

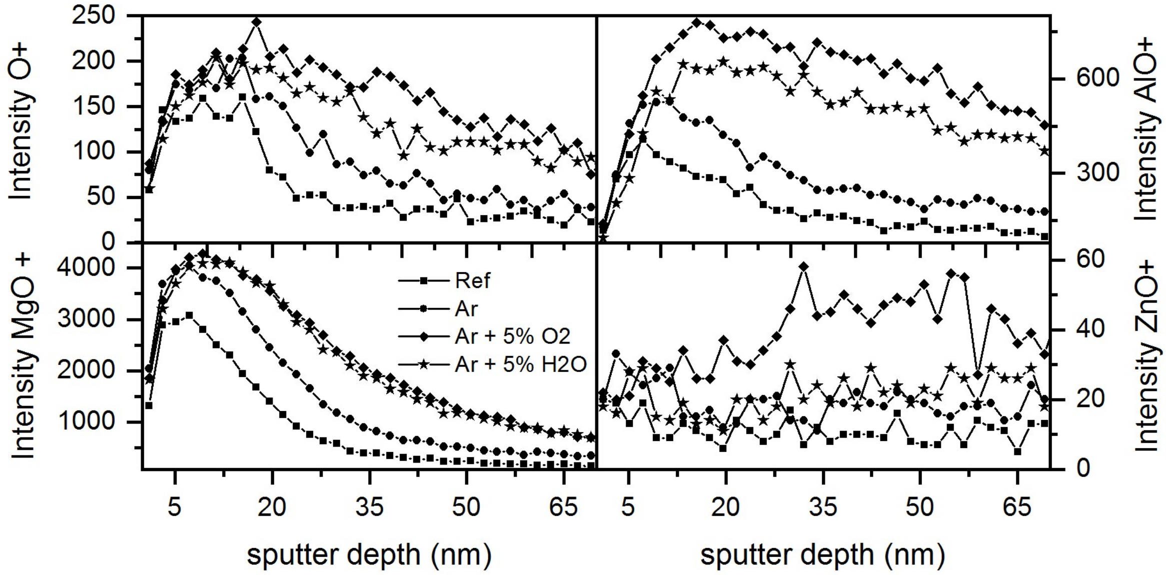

*Figure S6 ToF-SIMS depth profiles of the fragments $O^+$, $AlO^+$, $MgO^+$ and $ZnO^+$ for the surface-near region before and after plasma treatments with different gas mixtures.*

Figure S6 shows the ToF-SIMS depth profiles of the fragments $O^+$ and the single positive charged metal oxides. The depth profiles show an accumulation of $MgO^+$ and $AlO^+$ on the surface, which is associated to the oxide layer. The $O^+$ signal seems thereby to be dominated by the $AlO^+$ spectrum, why only the spectra of the metals where evaluated.

The lateral distribution of the single positive charged metals is shown in Figure S7.

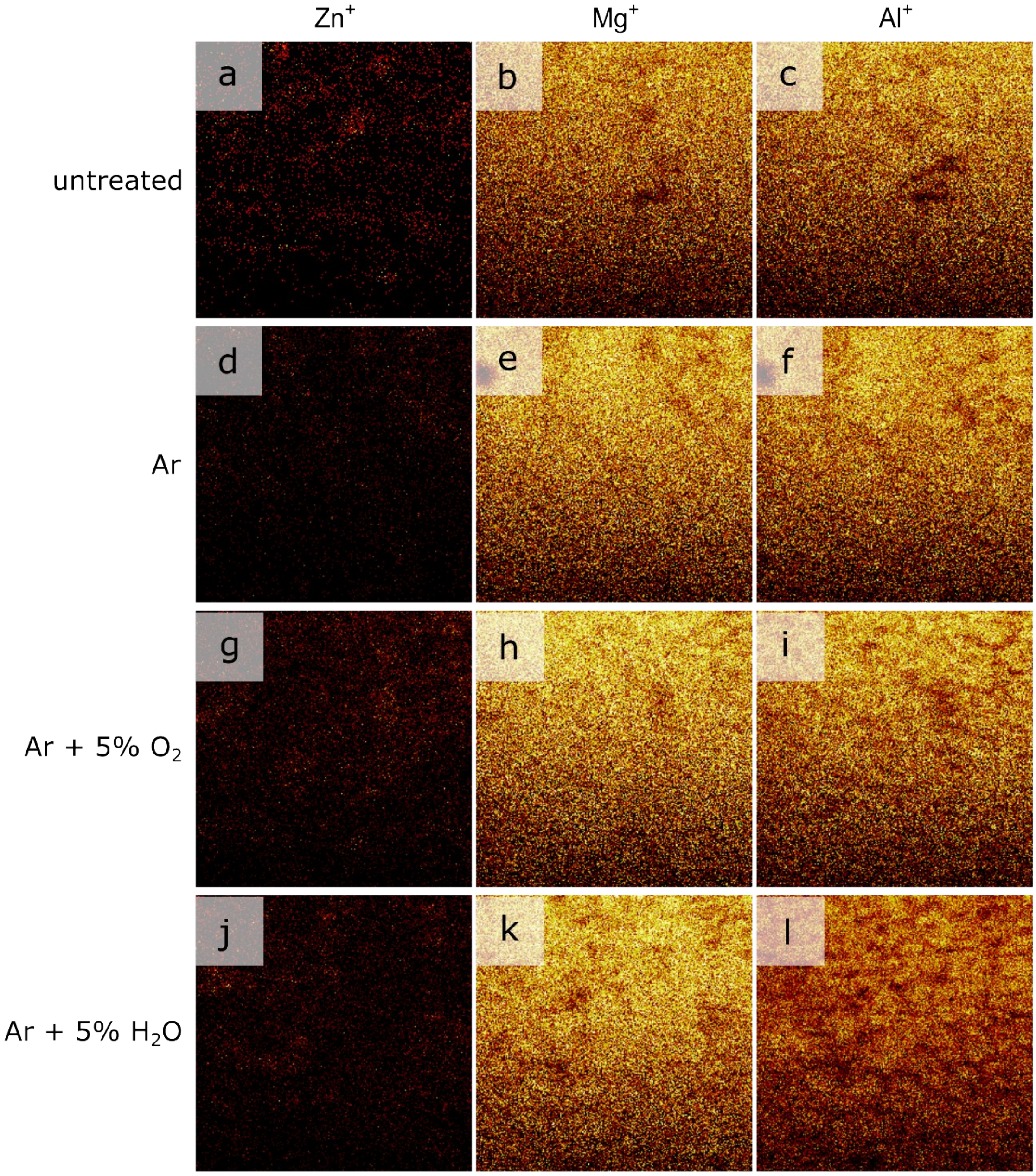

*Figure S7 400x400 µm² TOF-SIMS mappings of Zn⁺, Mg⁺ and Al⁺(from left to right) integrated over 10 nm, before and after the plasma treatments*

The oxide layer is dominated by Aluminium and Magnesium as already seen in the sputter depth profiles. The lateral composition is quite homogeneous in the micrometre range and does not change after the plasma treatments.

## Notes and references

1 B. R. Strohmeier, An ESCA method for determining the oxide thickness on aluminum alloys, *Surf. Interface Anal.*, 1990, **15**, 51–56. DOI: 10.1002/sia.740150109.

2 Sven Tougaard, *Quases. IMFP calculation by TPP2M formula*, Quases-Tougaard Inc., 2000-2016.

3 S. Tanuma, C. J. Powell and D. R. Penn, Calculations of electron inelastic mean free paths (IMFPS). IV. Evaluation of calculated IMFPs and of the predictive IMFP formula TPP-2 for electron energies between 50 and 2000 eV, *Surf. Interface Anal.*, 1993, **20**, 77–89. DOI: 10.1002/sia.740200112.