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Link to publication

Laser welding of polyamide-6.6 and titanium: a chemical bonding story

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Hybrid materials are more and more common in biomedical applications, such as implants. However, assembling the materials is still challenging. Mechanical fastening solutions present durability problems, and adhesive solutions rarely combine strong mechanical properties and biocompatibility. To address these difficulties laser welding is a promising solution. It is a fast process with great design freedom that requires no additional material at the interface. Since the process is quite recent, the involved fundamental mechanism are not well understood. Hence this work aims at exploring the existence of a chemical bond between two materials: titanium and polyamide-6.6. Samples composed of a block of polyamide-6.6 welded to a titanium sheet were broken and analysed using XPS and ToF-SIMS. Results show more polymer in the weld and the chemical bond seems to be a complexation of titanium with the amide function.

1 Introduction

Since early ages of humanity, assembling different kind of materials to combine their properties, for hunting for instance, is a great concern. Nowadays hybrid materials application are directed e.g. towards biomedical or automotive problems. Even if their use is successful, the main issue remains assembling the two materials. There are three ways to assemble materials: mechanical fastening, adhesive bonding, and welding. They all present several advantages and drawbacks, especially for biomedical purposes. For instance mechanical fastening presents low corrosion resistance and a lower durability, while adhesive bonding often involves harmful chemicals making it difficult to produce biocompatible adhesives. In this context, welding and especially laser welding appears as a promising solution. Indeed laser welding offers many advantages, as being a fast process, allowing complex geometries and no need for interstitial materials. Even if it is very promising, the fundamentals of adhesion are not well understood yet. Adhesion theory[1] proposes four effects: mechanical interlocking, chemical bonding, diffusion and electrostatic interactions. The work here concentrates on investigating chemical bonding between two commonly used materials in biomedical industry: titanium and polyamide-6.6. A combination of XPS and ToF-SIMS was used to achieve this goal. The interface was exposed after breaking the samples by applying a torsion force, allowing a comparison between the welded zone and outside of the weld.

2 Materials and method

2.1 Materials

0.5 mm thick Titanium (Ti-6Al-4V), purchased from E.Wagner, was cut into 30 mm x 60 mm coupons. 4 mm thick Polyamide-6.6 (PA-6.6) purchased by Dutec, was cut into 25mm x 70 mm coupons. Before welding, both materials were wiped with ethanol.

2.2 Laser welding

Laser beam welding was performed using fiber laser (TruFiber 400) from TRUMPF. Beam size was set to 31µm for a wavelength of 1070 nm and a power of 60 W. The beam followed a wobbling trajectory with a speed of 900 mm.s^{-1}.[2]

2.3 Breaking the samples

After welding, the samples were clamped from the metal side in a bench vice. Using pliers, torsional load was applied on the polymer part until the samples break. The breaking leaves residues of polymer at some places. Analysis were performed to compare two zones: out of the weld and in the weld. Failure in the weld zone is mixed (adhesive and cohesive). Practically, the measurements were performed in adhesive failure areas, where no residues are visible. In other areas where the failure is cohesive in the polymer, the residual polymer layer is too thick to make any interface analysis.

2.4 XPS measurements

Measurements were performed on a K-alpha apparatus from Thermo Fisher Scientific. Spot size was set to 300 µm. For each point a survey scan was acquired, with 200 eV pass energy and 3 scans, as well as high resolution spectra in the Ti 2p, C 1s, O 1s, N 1s, Al 2p and V 2p regions, with 20 eV pass energy and 20 scans. 9 points were taken on each zone. Each time the C-C/C-H bond was set to 284.80 eV.

2.5 ToF-SIMS measurements

Static SIMS spectra were measured with a TOF-SIMS IV (ION TOF) in both positive and negative mode, using a 25 keV Bi_3^+ analysis beam . The extraction voltage was set to 2 keV. The same calibration and peak list was used for all spectra. 9 points per zone were analysed. In the same conditions, large area images were obtained in both polarities.

3 Results and discussion

3.1 Amount of polyamide-6.6

Table 1: XPS average elemental composition out of the weld and in the weld

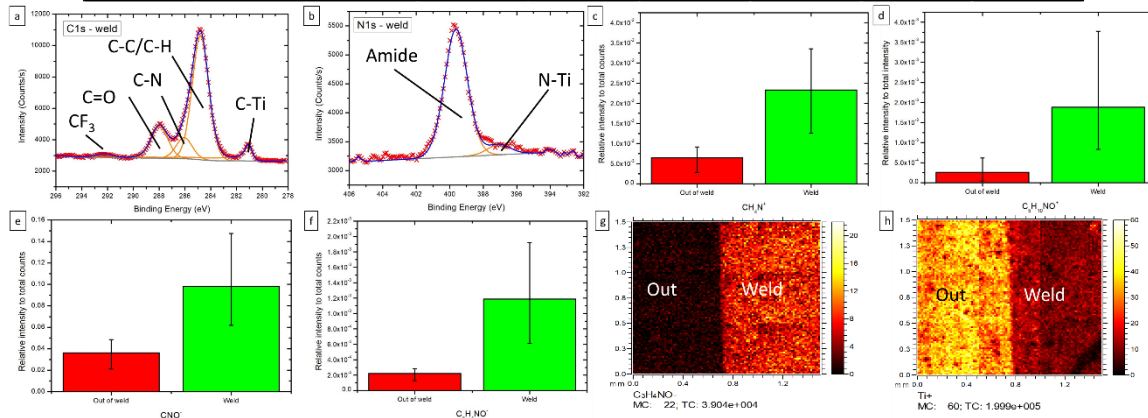| Points	% O	% Ti	% C	% N	% Al	% V	% Ca	%F
Out	33.43	14.88	45.01	1.29	0.91	0.36	2.86	1.26
Weld	32.67	15.47	42.32	4.67	0.88	0.34	2.52	1.14

Figure 1: XPS high resolution spectra in the weld of the (a) C 1s region and (b) N 1s region. ToF-SIMS relative intensity to total counts of (c) CH_4N^+, (d) $C_5H_{10}N^+$, (e) CNO^-, and (f) $C_3H_4NO^-$. ToF-SIMS large area images of the border between the out of weld and the weld of (g) $C_3H_4NO^-$ and (h) Ti^+.

Before looking at the chemical bonding, presence of polyamide must be proven. Table 1 presents the average elemental composition of the out of weld and the weld. The percentage of nitrogen increases nearly four times, which indicates the presence of polyamide in the weld. This is confirmed by looking at the C 1s and N 1s region in the weld in Figure 1 (a) and (b). Specific polyamide fragment ions in SIMS also show an increased intensity in Figure 1 (c) to (g). Looking at images (g) and (h), the separation between the two zones, out and weld, is sharp. Nonetheless, titanium related ions can still be detected in the weld, which means that the polymer layer thickness is very low (about 1-2 nm), so the polymer present must be chemically bonded to the surface. Looking at the reactivity of the polyamide, four kinds of bonds can

possibly be formed: the first involves a reaction with carbon atoms near the amide function, the second is a pure nitrogen bond with the metal, the third a pure oxygen bond, and the fourth a complexation reaction involving the oxygen and nitrogen of the amide function.
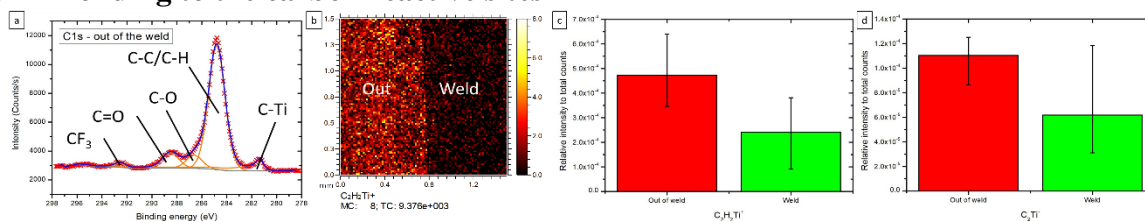
3.2 Bonding to the carbon reactive sites

Figure 2: (a) XPS high resolution spectrum out of the weld of the C 1s region. (b) ToF-SIMS large area image of the border between the out of weld and the weld of $C_2H_2Ti^+$. ToF-SIMS relative intensity normalised to total counts of (c) $C_2H_2Ti^+$ and (d) C_2Ti^-.

The presence at 281.3 eV of a C-Ti contribution is observed in Figure 1 (a).[3] However, this bond was already observed in the C 1s region out of the weld, shown in Figure 2 (a). Therefore, the Ti-C bond probably originates from contamination at the Ti surface prior to welding.

The image presented in Figure 2 (b), shows that the intensity of $C_2H_2Ti^+$ decreases coming into the weld. The decrease is less clear by looking at the intensities of the ions in (c) and (d), because of the high standard deviation. Only one ion related to C-Ti bonding has been detected in the negative polarity: C_2Ti^-. Both SIMS and XPS indicate that the C-Ti binding is not induced by laser welding but comes from contaminants that are not removed by the ethanol cleaning.

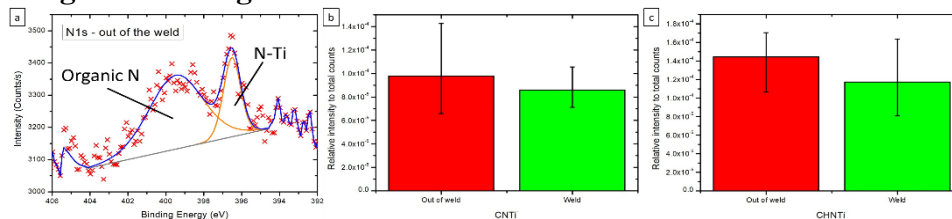## 3.3 Bonding to the nitrogen reactive site

Figure 3: (a) XPS high resolution spectra of the N 1s region out of the weld. ToF-SIMS relative intensity normalised to total counts of (b) $CNTi^-$ and (c) $CHNTi^-$.

Figure 3 (a) shows the N 1s region out of the weld, showing the presence of Ti-N bonds[4] at 396.9 eV before welding . Such bond is also observed after welding, as shown in Figure 1 (b). Just as Ti-C, Ti-N bonding likely comes from unremoved contamination present at the surface prior to welding.

In SIMS, $C_xH_yNTi_z$ type ions are only detected in the negative mode, presented in Figure 3 (b) and (c). As the ions' intensities are rather constant from out of the weld to the weld, we can conclude that the Ti-N bond are not induced by the welding.
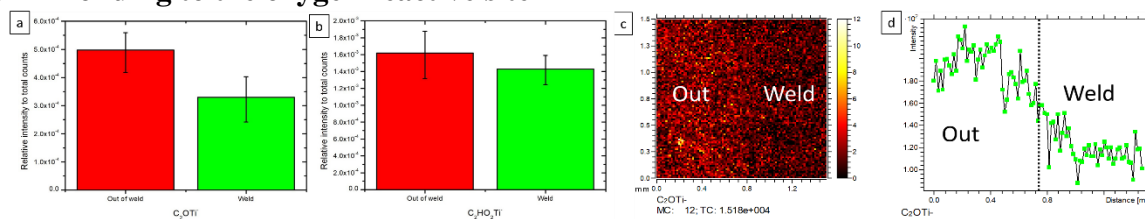
3.4 Bonding to the oxygen reactive site

Figure 4: ToF-SIMS relative intensity normalised to total counts of (a) C_2OTi^-, and (b) $C_2H_2OTi^-$. (c) ToF-SIMS large area image of the border between the out of weld and the weld of C_2OTi^- and (c) its area integration in the y direction.

The XPS measurement in the O 1s and the Ti 2p region, not shown here, just demonstrate the presence of titanium oxide, but were not instructive towards potential chemical bonding at the interface. Once again, SIMS data, shown in Figure 4, indicate higher ion

intensities for the $C_xH_yO_zTi^-$ ions prior to welding. Indeed, only negative ions could be identified, exhibiting constant or decreasing intensities in the weld. This effect is emphasised in the image (c) and its area integration (d). So those ions must come mostly from surface contaminants, possibly carbonates bound to the Ti surface.

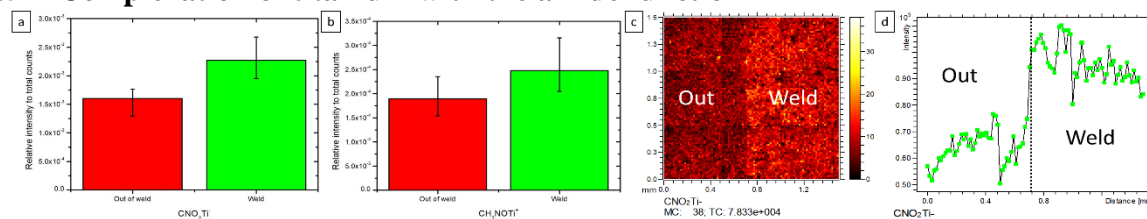### 3.5 Complexation of titanium with the amide function

Figure 5: ToF-SIMS relative intensity normalised to total counts of (a) CNO_2Ti^-, and (b) CH_3NOTi^+. (c) ToF-SIMS large area image of the border between the out of weld and the weld of CNO_2Ti^- and (d) its area integration in the y direction.

Here also the XPS data could not be of any support to discuss a complexation bonding at the interface as presented in Figure 6. The SIMS results, summed up in Figure 5, show the presence of $C_xH_yNO_zTi_z^{+/-}$ ions in both positive and negative mode, which intensities tend to increase in the weld, especially in (c) and its area integration (d). These hybrid ions containing nitrogen and oxygen increase in intensity, whereas hybrid ions' intensity containing only nitrogen or only oxygen decrease (see 3.3 and 3.4). This leads to the conclusion that the polymer complexes the surface titanium to bridge chemically both materials.
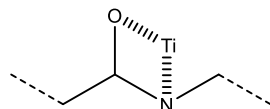

Figure 6: Complexation of the Titanium by the amide function of the polyamide-6.6.

4   Conclusion

It was evidenced that the polymer could be identified in the weld zone and not outside. This polymer layer is covering the metal, but it is very thin, since the metal can still be detected even with ToF-SIMS. This certainly demonstrates the occurrence of a chemical bonding between both materials. By looking at the reactivity of the polymer, several possibilities of bonding were studied: a carbon bonding, a pure nitrogen bonding, a pure oxygen bonding and a complexation involving the oxygen and the nitrogen of the amide. The presence of Ti-N, Ti-C and Ti-O bonds was already evidenced on the Ti surfaces prior to welding and the intensities of the SIMS fragments related to these bonds did not increase after welding, but rather decreased. The only ions exhibiting a clear increase in SIMS where those containing Ti, O, C and N simultaneously, hinting at a complexation of the titanium by the amide function, i.e. the oxygen and nitrogen atoms in the polyamide chain (Figure 6).

5   Acknowledgements

6   References

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