

THE CHARACTERIZATION OF Al ALLOY SURFACES AT EACH STAGE OF PREPARATION FOR ADHESIVE BONDING

KARAKTERIZACIJA Al ZLITIN – PRIPRAVA POVRŠINE ZA LEPLJENJE

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Many sets of AA 2024-T3 and 7075-T6 samples were fabricated and examined with X-ray Photoelectron Spectroscopy (XPS) for surface composition at different stages of preparation, for eventual adhesive bonding. With XPS, all elements except hydrogen and helium are detectable, with a detectability limit of about 0.1 to 1 atomic percent. The goal of this work was to build a database of the surface composition at each stage of substrate processing, namely, after (a) wiping with acetone, (b) hand-abrading with Scotch-Brite and Alconox, (c) grit blasting with alumina, (d) coating via a sol-gel process, and (e) priming. In some cases, steps (b) and (c) were replaced with abrasion using a Scotch-Brite Roloc disc driven by a high-speed grinder. Having such a database, allows one to examine and monitor surface composition changes with the various preparation steps, and ideally relate preparation methods to adhesive bond strength.

After acetone wiping, relatively high concentrations of Mg are present on the surface. The Mg is present as oxide and is due to the processing of the alloy by the supplier. Cu and Mg are the main alloying components in AA 2024-T3, and Zn, Mg and Cu are the main components in AA 7075-T6. No Cu was detected on the surfaces after acetone wiping, but Zn was found on all surfaces. After abrading, the Mg concentration was always less than that of Al. Grit blasting produced numerous changes in composition, but some new contaminants were found. These contaminants were found to be present on the alumina grit used. After sol-gel coating, Si and Zr from the sol-gel were detected. After priming, Zr from the sol-gel was still detected on all samples, indicating that the primer coating was thin or non-homogeneous in thickness. The Si/Zr ratio increased though, as Si is also present in the primer. Some measurements were also made using a commercial sol-gel kit, and they are compared to results using sol-gel prepared in our laboratory.

Key words: Al alloy, adhesive bonding, surface preparation, x-ray photoelectron spectroscopy, XPS, SEM, EDS, AA 2024-T3, AA 7075-T6

Izdelano je bilo več nizov vzorcev aluminijevih zlitin AA 2024-T3 in AA 7075-T6. Z rentgensko fotoelektronsko spektroskopijo (XPS) smo raziskali sestavo površine pri različnih fazah priprave za eventualno lepljenje. Z XPS lahko analiziramo vse elemente razen vodika in helija z mejo detekcije od 0,1 % do 1 %. Namen tega dela je zgraditi datoteko sestave površine za vsako fazo priprave podlage, namreč po (a) čiščenju z acetonom, (b) bročnem jedkanju s Scotch-Brite in Alconoxom, (c) peskanjem z glinico, (d) prekritju s sol-gel postopkom in (e) osnovnim premazom. V nekaterih primerih smo faze (b) in (c) nadomestili s strojim brušenjem in uporabo Scotch-Brite-Roloc. Tovrstna baza podatkov omogoča preiskave in kontrolo spremembe sestave površine v posameznih fazah in uporabo optimalne metodike lepljenja.

Po čiščenju z acetonom, je bila po pričakovanju na površini izmerjena relativno visoka koncentracija Mg, prisotna v obliki oksida. Cu in Mg sta glavna legirna elementa v zlitinah AA 2024-T3 in Zn, Mg ter Cu legirni elementi v zlitinah AA 7075-T6. Po čiščenju z acetonom nismo detektirali Cu, pač pa je bil povsod prisoten Zn. Po jedkanju je bila vsebnost Mg vedno nižja od vsebnosti Al. Peskanje z glinico je povzročilo številne spremembe v sestavi površine, najdene so bile nove nečistoče, ki so osnovna sestavina uporabljenih glinice. Po sol-gel nanosenemu premazu smo analizirali na površini Si in Zr. Po nanosu osnovnega premaza smo še vedno analizirali Zr, kar pomeni, da je bila plast osnovnega premaza pretanka ali pa neenakomerno nanosena. Razmerje Si/Zr je naraslo čeprav je Si vedno prisoten v osnovnem premazu. Naredili smo tudi nekaj meritev komercialne sol-gel opreme in primerjali rezultate s sol-geli narejenimi v našem laboratoriju.

Gljučne besede: Al zlitine (AA 2024-T3, AA 7075-T6), lepljenje, priprava površine, rentgenska fotoelektronska spektroskopija (XPS), vrstična elektronska mikroskopija (SEM), enrgijsko disperzijska spektroskopija (EDS)

1 INTRODUCTION

Aluminum alloys are used in aircraft structures, and most applications involve 2000 and 7000-series aluminum alloys. Aluminum oxidizes in air, and this surface oxide is removed as an initial surface preparation step prior to adhesive bonding. Additionally, corrosion protection methods are employed to ensure that the potential for oxidation after adhesive bonding does not degrade the bonded surface and limit the bond durability. Currently, the surface treatment and priming steps used

for adhesive bonding processes with aluminum alloys typically involve using volatile organic compounds (VOCs), chromates, and strong acids or bases. Specifically, surface preparation for adhesive bonding consists mainly of anodization or etching processes using strong acids or bases. Many of these contain hexavalent chromium, and the associated rinsing steps generate contaminated wastewater. This surface treatment is followed by the application of a corrosion-inhibiting adhesive primer that typically contains high VOC concentrations and hexavalent chromium. For example,

commonly used adhesive primers contain about 800 g/l VOC and the mass fraction 10 % of the solids as strontium chromate ¹.

In recent years, regulations in the United States of America have set strict limits in order to minimize or eliminate the use of hazardous materials and their associated waste. As a result of these regulations and the increased cost of hazardous waste disposal, it is necessary to develop low-VOC/nontoxic surface treatments and primers for structural adhesive bonding applications. Of course, any new processes cannot adversely affect performance, as this would cause safety issues. An additional problem that complicates the implementation of any new process is the fact that common requirements do not exist for aluminum surface preparation. Military specifications are nonexistent, and manufacturers use their own processes ¹.

It is obvious that aluminum surface preparation is important for the successful implementation of adhesive bonding technology. Both the initial bond strength and the subsequent bond durability are strongly dependent on the interaction between the adhesive (and/or primer) and the pre-treated adherend surface. Surface preparation therefore, involves both the removal of weak boundary layers or layers that are chemically incompatible with the adhesive, and the subsequent formation of stable, adherent layers that are mechanically and chemically compatible with the adhesive. Adhesion is also improved if the surface is roughened.

In our laboratory, sol-gel technology is being used to develop a new surface preparation for aluminum that will reduce the use of hazardous materials in adhesive bonding applications. Sol-gel is an abbreviation for solution-gelation and refers to a series of reactions where a soluble metal species (typically a metal alkoxide or metal salt) hydrolyzes to form a metal hydroxide ². The soluble metal species can also contain organic constituents that can be tailored for a specific application. The metal hydroxide functionalities condense to form an inorganic or organometallic polymer. The goal with the sol-gel process is to deposit thin organic-inorganic coatings on the surface in order to produce good adhesion between the aluminum and subsequently applied polymers (primer or adhesive). Therefore, it is paramount to optimize the aluminum surface preparation and be able to characterize the surface composition at each stage of the preparation process.

The goal of this work was to determine the surface composition of aluminum alloys 2024-T3 and 7075-T6 at each stage of preparation for adhesive bonding. This has produced a database for understanding the effects of each preparation step on the surface chemistry, and to characterize witness samples from each set of samples that was prepared for wedge, lap shear, or peel tests for determining initial bond strength and bond durability against moisture.

2 EXPERIMENT

Numerous sets of AA 2024-T3 and AA 7075-T6 samples were fabricated and examined with X-ray Photoelectron Spectroscopy (XPS) ³ for surface composition at each stage of preparation for adhesive bonding. The XPS equipment used was a Surface Science Instruments' M-Probe. This instrument has a monochromatic aluminum x-ray source and a hemispherical sector electron energy analyzer, and is used to measure the binding energies of electrons in the atoms that are in the several outermost atomic layers of the specimen surface. These measurements of electron binding energies are used to identify the elements present in this outermost (~10 nm) region of the specimen. All elements except hydrogen and helium are detectable, with a detectability limit of about $x = 0.1-1$ %, depending on the sensitivity factor for an element. The surface composition was determined at each stage of processing, namely, after (a) wiping with acetone, (b) hand-abrading with a Scotch-Brite™ ⁴ nylon pad and Alconox™ ⁵, (c) grit blasting with alumina, (d) coating using a sol-gel process, and (e) priming. In some cases, steps (b) and (c) were replaced by abrasion with a 7.5 cm diameter Scotch-Brite Roloc™ medium nylon pad using a 20,000 r/min nitrogen-driven rotary grinder. There are four components in the sol-gel formulation: g-glycidoxypropyl-trimethoxysilane (GTMS), zirconium n-propoxide (TPOZ), glacial acetic acid (GAA), and water.

Witness samples were cut from the same panels used for mechanical testing, and two samples were processed at each stage for XPS analysis at the same time as the coupons were prepared for ultimate testing. The witness samples were smaller than the coupons so four could be mounted at a time on the sample holder for XPS analysis. The dimensions of the witness samples were 1 cm × 7.5 cm. After preparation, the two samples from each stage were placed in contact with each other so the surfaces would not be contaminated, wrapped in a Duralace™ ⁶ lint-free towel, and placed in a sealed plastic bag. Each measurement took a little over two hours to make, and quantification was performed using ESCAVB data reduction software from Surface Physics Inc. ⁷. Some analyses were run overnight, allowing an improvement in the signal-to-noise. Studies showed that storage of samples from minutes to several days did not affect results (see Section 3.9).

Approximately 130 witness samples were measured for this database, and the results are presented in **Table 1**. The results are in atomic percent and the calculation assumes that the surface is homogeneous within the outermost ~10 nm. Areas analyzed were 400 μm × 1000 μm. It should be noted that metal samples that have been exposed to air will always show carbon and oxygen on the surface. (Hydrogen is not detected in XPS). **Table 1** lists the results by preparation stage category.

Table 1: Compositions of AA 2024 T-3 and AA 7075 T-6 witness samples that were prepared for characterizing panels used for mechanical testing. The concentrations are in atomic percent, and the photoelectron transitions used are listed next to the chemical symbol for each element (Na was measured using the KLL Auger peak). An extra significant figure is given for each concentration for better comparison of data, but numbers should be rounded. The file names give the dates of analysis (year, month, day, sequence) with ac (acetone wipe), 2nd (second sample in the pair), 1t (long time analysis, overnight), SBal (Scotch-Brite with Alconox), w (water rinse), GB (grit blast), N (nitrogen blow dry), Roloc (medium nylon pad), SG (sol-gel), and Pr (primer).

Tabela 1: Sestava preiskovanih zlitin AA 2024 T-3 and AA 7075 T-6, ki so bile pripravljene za testiranje mehanskih lastnosti. Koncentracije so v atomskih procentih in fotoelektronski prehodi so navedeni poleg kemijskih simbolov elementov (Na je bil merjen z uporabo KLL Augerjevega vrha). Zelo pomembna številka je podana za vsako koncentracijo za lažjo primerjavo podatkov, številke morajo biti zaokrožene. Imena datoteke podajajo datum analize (leto, mesec, dan, niz) z ac (čiščenje z acetonom) 2nd (drugi vzorec v paru), 1t (dolgotrajne analize, preko noči) SBal (Scotch-Brite z Alconox-om), w (splakovanje z vodo), GB (peskanje), N (sušenje z dušikom), Roloc (srednja najlonska podloga), SG (sol-gel) in Pr (grundirna masa – osnovni premaz).

| File Name | Alloy | O 1s | C 1s | Al 2p | Mg 2p | Zn 2p1 | Cu 2p3 | Fe 2p3 | Zr 3d | Si 2s | Sr 3d | Cr 2p3 | Na a | N 1s | Ca 2s | S 2p | Cl 2p | P 2s | F 1s |
|--|---------|------|------|-------|-------|--------|--------|--------|-------|-------|-------|--------|------|------|-------|------|-------|------|------|
| <i>Acetone wiped</i> | | | | | | | | | | | | | | | | | | | |
| 03032601 ac | 2024-T3 | 38,8 | 41,1 | 3,0 | 11,6 | 0,36 | | | | 0,74 | | | 0,73 | 1,25 | 1,16 | 0,88 | 0,39 | | |
| 03032602 ac , 2nd | 2024-T3 | 37,6 | 37,0 | 3,8 | 19,1 | 0,38 | | | | | | | 0,48 | | 0,71 | 0,81 | | | |
| 03040101 ac | 2024-T3 | 37,0 | 41,2 | 2,8 | 14,7 | 0,44 | | | | 0,67 | | | 0,73 | | 1,33 | 0,89 | 0,30 | | |
| 03040102 ac , 2nd | 2024-T3 | 38,6 | 41,9 | 3,6 | 12,6 | 0,12 | | | | | | | 0,42 | | 1,10 | 1,27 | 0,36 | | |
| 03040301 ac | 2024-T3 | 39,1 | 39,7 | 2,7 | 13,7 | 0,34 | | | | | | | 0,81 | | 1,88 | 0,91 | 0,30 | | |
| 03040302 ac , 2nd | 2024-T3 | 35,3 | 38,8 | 3,9 | 18,4 | 0,46 | | | | 0,62 | | | 0,56 | | 0,88 | 0,74 | 0,33 | | |
| 03052202 ac | 2024-T3 | 35,9 | 41,7 | 3,4 | 16,3 | 0,26 | | | | | | | 0,80 | | 0,67 | 0,71 | 0,27 | | |
| 03052203 ac, 2nd | 2024-T3 | 35,5 | 43,2 | 2,5 | 14,3 | 0,47 | | | | | | | 0,85 | | 1,26 | 1,55 | 0,34 | | |
| 03052705 ac | 2024-T3 | 35,6 | 39,6 | 3,4 | 15,9 | 0,32 | | | | 0,66 | | | 1,07 | | 1,81 | 1,42 | 0,19 | | |
| 03052705 ac, 1t | 2024-T3 | 36,3 | 37,8 | 3,9 | 17,3 | 0,41 | | | | 0,83 | | | 0,76 | | 1,04 | 1,28 | 0,37 | | |
| 03052801 ac, 2nd | 2024-T3 | 37,0 | 38,6 | 3,9 | 15,1 | 0,50 | | | | 0,82 | | | 0,88 | | 1,34 | 1,51 | 0,31 | | |
| 03052905 ac | 2024-T3 | 35,9 | 45,5 | 3,1 | 12,4 | 0,39 | | 0,38 | | 0,64 | | | 0,45 | | 0,33 | 0,59 | 0,37 | | |
| 03052906 ac, 2nd | 2024-T3 | 34,2 | 44,6 | 2,9 | 16,7 | 0,17 | | 0,10 | | 0,64 | | | | | | 0,58 | 0,12 | | |
| 03061203 ac | 2024-T3 | 38,0 | 44,0 | 2,6 | 12,6 | 0,09 | | 0,37 | | | | | 0,49 | | | 0,68 | 0,39 | | 0,81 |
| 03040701 ac | 7075-T6 | 41,2 | 42,3 | 5,1 | 7,0 | 0,42 | | | | | | | 0,78 | | 0,56 | 2,09 | 0,56 | | |
| 03040702 ac, 2nd | 7075-T6 | 45,1 | 37,0 | 7,9 | 6,7 | 0,30 | | | | | | | 0,89 | | | 1,88 | 0,16 | | |
| 03040902 ac | 7075-T6 | 38,7 | 44,6 | 5,2 | 7,0 | 0,21 | | | | | | | 0,85 | 0,69 | 0,29 | 1,90 | 0,45 | | |
| 03040902 ac, 2nd | 7075-T6 | 42,7 | 39,6 | 6,9 | 7,5 | 0,20 | | | | | | | 0,58 | 0,24 | 0,27 | 2,00 | | | |
| 03041401 ac | 7075-T6 | 39,7 | 45,5 | 4,8 | 5,9 | 0,60 | | | | | | | 0,83 | | 0,45 | 1,98 | 0,33 | | |
| 03041402 ac, 2nd | 7075-T6 | 41,2 | 42,2 | 6,0 | 6,4 | 0,41 | | | | | | | 0,73 | 0,40 | | 2,70 | | | |
| 03041701 ac | 7075-T6 | 42,1 | 40,4 | 7,2 | 6,5 | 0,50 | | | | | | | 0,96 | | | 2,28 | | | |
| 03041702 ac, 2nd | 7075-T6 | 39,2 | 43,2 | 4,7 | 7,8 | 0,42 | | | | | | | 1,20 | | 0,58 | 2,22 | 0,62 | | |
| 03042102 ac | 7075-T6 | 40,5 | 42,4 | 6,4 | 5,7 | 0,36 | | | | | | | 1,20 | | 0,53 | 2,54 | 0,33 | | |
| 03042103 ac, 2nd | 7075-T6 | 39,9 | 42,2 | 4,9 | 7,7 | 0,50 | | | | | | | 1,31 | 0,67 | | 2,30 | 0,51 | | |
| 03042402 ac | 7075-T6 | 39,3 | 42,7 | 7,1 | 7,1 | 0,55 | | | | | | | 0,93 | | | 2,21 | 0,12 | | |
| 03042402 ac, 1t | 7075-T6 | 40,5 | 40,1 | 8,1 | 6,3 | 0,56 | | | | | | | 0,83 | 0,62 | 0,47 | 2,37 | 0,13 | | |
| 03042403 ac, 2nd | 7075-T6 | 40,6 | 41,3 | 6,7 | 6,4 | 0,56 | | | | | | | 0,92 | 0,50 | 0,62 | 2,29 | 0,11 | | |
| 03043003 ac | 7075-T6 | 35,7 | 48,6 | 5,1 | 6,3 | 0,32 | | | | | | | 0,80 | | 1,19 | 1,42 | 0,52 | | |
| 03043004 ac, 2nd | 7075-T6 | 37,8 | 46,7 | 4,9 | 5,8 | 0,56 | | | | | | | 1,23 | 0,50 | 0,63 | 1,57 | 0,40 | | |
| 03043004 ac, 2nd, 1t | 7075-T6 | 37,5 | 45,0 | 5,4 | 6,6 | 0,66 | | | | | | | 1,28 | 0,66 | 0,61 | 1,84 | 0,46 | | |
| 03051301 ac | 7075-T6 | 36,0 | 46,6 | 5,4 | 7,5 | 0,32 | | | | | | | 1,12 | 0,69 | | 1,94 | 0,31 | | |
| 03051302 ac, 2nd | 7075-T6 | 38,7 | 42,8 | 6,9 | 7,2 | 0,47 | | | | | | | 0,73 | 0,54 | | 2,55 | 0,08 | | |
| 03060901 ac | 7075-T6 | 39,4 | 47,6 | 3,5 | 5,8 | 0,22 | | | | | | | 0,81 | 1,23 | | 1,14 | 0,35 | | |
| 03060902 ac, 2nd | 7075-T6 | 36,3 | 49,3 | 8,0 | 4,4 | 0,33 | | | | | | | 0,37 | | | 1,32 | | | |
| 03061002 ac, dark blotch | 7075-T6 | 42,0 | 42,3 | 7,6 | 5,5 | 0,39 | | | | | | | 0,43 | | | 1,46 | 0,24 | | |
| <i>Acetone wiped, then Scotch-Brite abraded with Alconox</i> | | | | | | | | | | | | | | | | | | | |
| 03040303 ac, SBal, w, ac | 2024-T3 | 46,8 | 33,6 | 14,9 | 0,8 | | | | | | | | 0,72 | | 1,16 | 0,67 | 0,34 | 0,89 | |
| 03040304 ac, SBal, w, ac, 2nd | 2024-T3 | 45,8 | 34,7 | 15,5 | 0,9 | | | | | | | | 0,23 | | 1,20 | 0,67 | 0,45 | 0,68 | |
| 03040703 ac, SBal, w, ac | 7075-T6 | 45,0 | 36,3 | 9,0 | 3,4 | | | | 0,99 | | | | 0,61 | | 2,26 | 1,36 | 1,10 | | |
| 03040703 ac, SBal, w, ac, 2nd | 7075-T6 | 42,5 | 40,7 | 7,3 | 5,5 | | | | 0,47 | | | | 0,32 | | 1,49 | 1,02 | 0,65 | | |
| 03040703 ac, SBal, w, ac, 2nd , 1t | 7075-T6 | 42,0 | 41,2 | 7,5 | 4,8 | 0,06 | | | 0,39 | | | | 0,26 | | 1,66 | 1,03 | 0,66 | 0,46 | |
| 03041403 ac, SBal, w, ac | 7075-T6 | 40,1 | 39,7 | 9,6 | 5,3 | 0,34 | | | | | | | 0,47 | | 2,22 | 1,48 | 0,66 | | |
| 03041404 ac, SBal, w, ac, 2nd | 7075-T6 | 43,3 | 36,4 | 10,1 | 5,4 | 0,17 | | | | | | | 0,62 | | 2,00 | 1,35 | 0,59 | | |
| 03041404 ac, SBal, w, ac, 2nd, 1t | 7075-T6 | 42,6 | 35,8 | 10,7 | 5,9 | 0,10 | | | | | | | 0,49 | 0,11 | 2,30 | 1,32 | 0,65 | | |
| 03042104 ac, SBal, w, ac | 7075-T6 | 44,4 | 35,2 | 11,9 | 4,5 | 0,34 | | | | | | | 0,56 | | 1,58 | 1,18 | 0,30 | | |
| 03042104 ac, SBal, w, ac, 1t | 7075-T6 | 44,4 | 33,5 | 13,0 | 4,7 | 0,32 | | | | | | | 0,72 | | 1,79 | 1,24 | 0,34 | | |
| 03042301 ac, SBal, w, ac, 2nd | 7075-T6 | 44,6 | 33,1 | 11,5 | 4,5 | 0,47 | | | | | | | 2,12 | | 1,76 | 1,63 | 0,23 | | |
| 03042601 ac, SBal, w, ac | 7075-T6 | 45,1 | 33,2 | 12,0 | 5,2 | 0,09 | | | | | | | 0,50 | | 2,12 | 1,41 | 0,43 | | |
| 03042601 ac, SBal, w, ac, 1t | 7075-T6 | 46,3 | 29,6 | 13,6 | 5,5 | 0,20 | | | | | | | 0,72 | | 2,23 | 1,41 | 0,49 | | |
| 03042901 ac, SBal, w, ac, 2nd | 7075-T6 | 43,6 | 35,1 | 10,6 | 5,9 | | | | | | | | 0,52 | | 2,09 | 1,67 | 0,55 | | |
| 03051303 ac, SBal, w, ac | 7075-T6 | 38,6 | 40,7 | 9,3 | 6,4 | 0,14 | | | | | | | 0,57 | | 2,09 | 1,67 | 0,50 | | |
| 03051303 ac, SBal, w, ac, 1t | 7075-T6 | 39,0 | 38,8 | 10,2 | 7,0 | 0,11 | | | | | | | 0,44 | | 2,24 | 1,72 | 0,49 | | |
| <i>Acetone wiped, Scotch-Brite abraded with Alconox, then grit blast</i> | | | | | | | | | | | | | | | | | | | |
| 03040402 ac, SBal, w, ac, GB, N | 2024-T3 | 56,5 | 15,1 | 18,0 | 0,6 | | | | | | | | 9,59 | | | | | | 0,21 |
| 03040403 ac, SBal, w, ac, GB, N, 2nd | 2024-T3 | 54,9 | 15,1 | 18,6 | 1,6 | | | | | | | | 9,41 | | | | | | 0,40 |
| 03040901 ac, SBal, w, ac, GB, N | 7075-T6 | 54,7 | 16,3 | 18,2 | 0,8 | | | | | | | | 9,53 | | | | | | 0,55 |
| 03040901 ac, SBal, w, ac, GB, N, 2nd | 7075-T6 | 53,5 | 16,1 | 19,3 | 1,1 | | | | | | | | 9,53 | | | | | | 0,46 |

continued

| File Name | Alloy | O 1s | C 1s | Al 2p | Mg 2p | Zn 2p1 | Cu 2p3 | Fe 2p3 | Zr 3d | Si 2s | Sr 3d | Cr 2p3 | Na a | N 1s | Ca 2s | S 2p | Cl 2p | P 2s | F 1s |
|---|---------|---------|---------|----------|----------|-----------|-----------|-----------|----------|----------|----------|-----------|---------|---------|----------|---------|----------|---------|---------|
| 03041601 ac, SBal, w, ac, GB, N | 7075-T6 | 53,5 | 15,6 | 19,2 | 1,4 | | | | | | | | 9,76 | | | | | | 0,55 |
| 03041602 ac, SBal, w, ac, GB, N, 2nd | 7075-T6 | 53,4 | 16,1 | 19,1 | 1,2 | | | | | | | | 9,62 | | | | | | 0,63 |
| 03042302 ac, SBal, w, ac, GB, N | 7075-T6 | 53,2 | 17,9 | 17,4 | 1,7 | | | | | | | | 9,29 | | | | | | 0,57 |
| 03042302 ac, SBal, w, ac, GB, N, 2nd | 7075-T6 | 53,6 | 16,4 | 17,9 | 1,6 | | | | | | | | 9,86 | | | | | | 0,58 |
| 03042501 ac, SBal, w, ac, GB, N | 7075-T6 | 55,8 | 14,3 | 18,3 | 0,8 | | | | | | | | 10,18 | | | | | | 0,68 |
| 03042502 ac, SBal, w, ac, GB, N, 2nd | 7075-T6 | 54,3 | 14,8 | 19,6 | 0,9 | | | | | | | | 10,12 | | | | | | 0,39 |
| 03042502 ac, SBal, w, ac, GB, N, 2nd, lt | 7075-T6 | 53,9 | 13,1 | 21,5 | 0,8 | | | | | | | | 9,98 | | | 0,05 | | | 0,72 |
| 03051401 ac, SBal, w, ac, GB, N | 7075-T6 | 52,2 | 17,1 | 18,8 | 1,9 | | | | | | | | 9,61 | | | | | | 0,40 |
| 03051402 ac, SBal, w, ac, GB, N, 2nd | 7075-T6 | 51,6 | 17,3 | 19,4 | 1,6 | | | | | | | | 9,57 | | | | | | 0,48 |
| Acetone wiped, and then abraded with a Roloc pad | | | | | | | | | | | | | | | | | | | |
| 03032603 ac, Roloc, N | 2024-T3 | 31,5 | 44,0 | 21,8 | 1,6 | | 0,10 | | | | | | | 1,01 | | | | | |
| 03032604 ac, Roloc, N, 2nd | 2024-T3 | 22,6 | 58,9 | 16,6 | 0,5 | | 0,05 | | | | | | | 1,40 | | | | | |
| 03032604 ac, Roloc, N, 2nd, lt | 2024-T3 | 20,6 | 60,7 | 16,2 | 1,1 | | 0,09 | | | | | | | 1,25 | | | | | |
| 03032701 ac, Roloc, N | 2024-T3 | 35,6 | 38,8 | 22,9 | 1,2 | | 0,13 | | | | | | | 1,45 | | | | | |
| 03032702 ac, Roloc, N, 2nd | 2024-T3 | 33,4 | 39,4 | 23,7 | 2,2 | | 0,16 | | | | | | | 1,12 | | | | | |
| 03040103 ac, Roloc, N | 2024-T3 | 37,7 | 36,4 | 23,5 | 1,0 | | 0,10 | | | | | | | 1,37 | | | | | |
| 03040104 ac, Roloc, N, 2nd | 2024-T3 | 26,8 | 51,8 | 18,9 | 1,6 | | 0,07 | | | | | | | 0,75 | | | | | |
| 03052702 ac, Roloc, N | 2024-T3 | 32,2 | 46,0 | 19,2 | 0,9 | | | | | | | | | 1,67 | | | | | |
| 03052703 ac, Roloc, N, 2nd | 2024-T3 | 33,5 | 44,6 | 19,9 | 0,7 | | 0,11 | | | | | | | 1,27 | | | | | |
| 03052802 ac, Roloc, N | 2024-T3 | 10,3 | 81,3 | 8,4 | | | | | | | | | | | | | | | |
| 03052803 ac, Roloc, N, 2nd | 2024-T3 | 22,3 | 60,7 | 15,7 | 0,7 | | | | | | | | | 0,61 | | | | | |
| 03052907 ac, Roloc, N | 2024-T3 | 19,4 | 65,6 | 14,1 | 0,5 | | | | | | | | | 0,37 | | | | | |
| 03052908 ac, Roloc, N, 2nd | 2024-T3 | 16,9 | 69,7 | 12,4 | 0,7 | | | | | | | | | 0,33 | | | | | |
| 03052908 ac, Roloc, N, 2nd, lt | 2024-T3 | 14,7 | 72,3 | 12,1 | 0,6 | | | | | | | | | 0,26 | | | | | |
| 03061204 ac, Roloc, N | 2024-T3 | 22,3 | 61,5 | 15,2 | 0,7 | | | | | | | | | 0,33 | | | | | |
| 03061204 ac, Roloc, N, lt | 2024-T3 | 20,2 | 64,3 | 14,7 | 0,4 | | | | | | | | | 0,41 | | | | | |
| 03061301 ac, Roloc, N, 2nd | 2024-T3 | 23,2 | 59,1 | 16,4 | 0,8 | | | | | | | | | 0,54 | | | | | |
| 03040903 ac, Roloc, N | 7075-T6 | 25,9 | 56,0 | 15,9 | 2,2 | | | | | | | | | | | | | | |
| 03040903 ac, Roloc, N, lt | 7075-T6 | 18,2 | 65,8 | 14,2 | 1,4 | | | | | | | | 0,16 | 0,24 | | | | | |
| 03041001 ac, Roloc, N, 2nd | 7075-T6 | 27,3 | 51,8 | 18,3 | 1,8 | | | | | | | | 0,35 | 0,45 | | | | | |
| 03041703 ac, Roloc, N | 7075-T6 | 20,6 | 62,9 | 13,8 | 1,8 | | | | | | | | 0,24 | 0,56 | | | | | |
| 03041704 ac, Roloc, N, 2nd | 7075-T6 | 22,8 | 60,3 | 14,6 | 1,2 | | | | | | | | 0,29 | 0,86 | | | | | |
| 03050101 ac, Roloc, N | 7075-T6 | 20,1 | 64,6 | 13,8 | 1,3 | | | | | | | | | 0,18 | | | | | |
| 03050101 ac, Roloc, N, 2nd | 7075-T6 | 30,8 | 46,7 | 19,0 | 2,1 | | | | | | | | 0,32 | 1,00 | | | | | |
| 03050101 ac, Roloc, N, 2nd, lt | 7075-T6 | 28,2 | 50,0 | 18,6 | 1,9 | | | | | | | | 0,25 | 1,15 | | | | | |
| 03060903 ac, Roloc, N | 7075-T6 | 20,1 | 65,2 | 12,3 | 1,7 | | | | | | | | | 0,69 | | | | | |
| 03060903 ac, Roloc, N, lt | 7075-T6 | 17,0 | 69,4 | 11,4 | 1,6 | | | | | | | | 0,19 | 0,37 | | | | | |
| 03061001 ac, Roloc, N, 2nd | 7075-T6 | 24,0 | 59,4 | 14,1 | 1,7 | | | | | | | | 0,53 | 0,33 | | | | | |
| Sol-gel coated, grit blast samples | | | | | | | | | | | | | | | | | | | |
| 03040305 ac, SBal, w, ac, GB, N, SG | 2024-T3 | 48,7 | 29,7 | 15,1 | | | | 1,13 | 4,06 | | | | 1,02 | | | | | | 0,26 |
| 03040305 ac, SBal, w, ac, GB, N, SG, lt | 2024-T3 | 47,6 | 29,0 | 16,6 | | | | 1,18 | 4,24 | | | | 0,98 | | | | | | 0,29 |
| 03040401 ac, SBal, w, ac, GB, N, SG, 2nd | 2024-T3 | 47,2 | 30,6 | 15,7 | | | | 1,14 | 4,31 | | | | 0,92 | | | | | | 0,12 |
| 03040801 ac, SBal, w, ac, GB, N, SG | 7075-T6 | 44,1 | 35,2 | 12,6 | | | | 1,76 | 5,12 | | | | 0,98 | | | | | | 0,26 |
| 03040802 ac, SBal, w, ac, GB, N, SG, 2nd | 7075-T6 | 42,8 | 38,9 | 9,8 | | | | 1,89 | 5,77 | | | | 0,86 | | | | | | |
| 03041603 ac, SBal, w, ac, GB, N, SG | 7075-T6 | 42,3 | 39,4 | 10,3 | | | | 1,49 | 5,60 | | | | 0,90 | | | | | | |
| 03041603 ac, SBal, w, ac, GB, N, SG, 2nd | 7075-T6 | 44,0 | 34,2 | 14,2 | | | | 1,42 | 4,65 | | | | 1,18 | | | | | | 0,36 |
| 03041603 ac, SBal, w, ac, GB, N, SG, 2nd, lt | 7075-T6 | 43,5 | 33,0 | 15,6 | | | | 1,46 | 4,75 | | | | 1,39 | | | | | | 0,33 |
| 03042401 ac, SBal, w, ac, GB, N, SG | 7075-T6 | 45,9 | 33,5 | 13,0 | | | | 1,35 | 4,91 | | | | 1,08 | | | | | | 0,30 |
| 03042401 ac, SBal, w, ac, GB, N, SG, 2nd | 7075-T6 | 44,5 | 37,2 | 10,5 | | | | 1,59 | 5,37 | | | | 0,87 | | | | | | |
| 03051403 ac, SBal, w, ac, GB, N, SG | 7075-T6 | 41,3 | 39,5 | 11,3 | | | | 1,67 | 5,57 | | | | 0,62 | | | | | | |
| 03051404 ac, SBal, w, ac, GB, N, SG, 2nd | 7075-T6 | 39,0 | 44,0 | 8,8 | | | | 1,84 | 5,99 | | | | 0,40 | | | | | | |
| 03051404 ac, SBal, w, ac, GB, N, SG, 2nd, lt | 7075-T6 | 39,7 | 41,9 | 9,7 | | | | 1,90 | 6,37 | | | | 0,35 | | | | | | 0,08 |
| Sol-gel coated, Roloc abraded samples | | | | | | | | | | | | | | | | | | | |
| 03032703 ac, Roloc, N, SG | 2024-T3 | 21,9 | 70,2 | 2,6 | | | | 1,36 | 3,58 | | | | | 0,39 | | | | | |
| 03032704 ac, Roloc, N, SG, 2nd | 2024-T3 | 23,6 | 66,5 | 3,6 | | | | 1,37 | 4,94 | | | | | | | | | | |
| 03040105 ac, Roloc, N, SG | 2024-T3 | 17,1 | 76,1 | 1,4 | | | | 0,86 | 4,50 | | | | | | | | | | |
| 03040106 ac, Roloc, N, SG, 2nd | 2024-T3 | 27,0 | 62,4 | 2,5 | | | | 1,43 | 6,62 | | | | | | | | | | |
| 03040106 ac, Roloc, N, SG, 2nd, lt | 2024-T3 | 25,3 | 64,3 | 2,5 | | | | 1,47 | 6,12 | | | | | 0,31 | | | | | |
| 03052701 ac, Roloc, N, SG | 2024-T3 | 29,5 | 59,3 | 2,3 | | | | 1,43 | 7,45 | | | | | | | | | | |
| 03052704 ac, Roloc, N, SG, 2nd | 2024-T3 | 17,6 | 75,7 | 1,9 | | | | 1,05 | 3,71 | | | | | | | | | | |
| 03052804 ac, Roloc, N, SG | 2024-T3 | 21,8 | 71,7 | 1,0 | | | | 1,48 | 4,00 | | | | | | | | | | |
| 03052804 ac, Roloc, N, SG, lt | 2024-T3 | 17,2 | 75,9 | 1,3 | | | | 1,36 | 3,99 | | | | | 0,19 | | | | | |
| 03052904 ac, Roloc, N, SG, 2nd | 2024-T3 | 20,5 | 72,7 | 2,2 | | | | 1,21 | 3,39 | | | | | | | | | | |
| 03053001 ac, Roloc, N, SG | 2024-T3 | 27,5 | 60,9 | 5,1 | | | | 1,49 | 4,77 | | | | 0,21 | | | | | | |
| 03053002 ac, Roloc, N, SG, 2nd | 2024-T3 | 25,3 | 64,2 | 4,1 | | | | 1,40 | 4,38 | | | | | 0,63 | | | | | |
| 03061302 ac, Roloc, N, SG | 2024-T3 | 21,9 | 70,4 | 1,4 | | | | 1,35 | 4,91 | | | | | | | | | | |
| 03061303 ac, Roloc, N, SG, 2nd | 2024-T3 | 20,1 | 73,0 | 1,1 | | | | 1,25 | 4,54 | | | | | | | | | | |
| 03041002 ac, Roloc, N, SG | 7075-T6 | 17,4 | 76,0 | 1,7 | | | | 1,17 | 3,78 | | | | | | | | | | |
| 03041003 ac, Roloc, N, SG, 2nd | 7075-T6 | 26,3 | 63,3 | 2,7 | | | | 1,75 | 5,52 | | | | | 0,37 | | | | | |
| 03041801 ac, Roloc, N, SG | 7075-T6 | 28,5 | 60,3 | 4,4 | | | | 1,63 | 5,12 | | | | | | | | | | |
| 03041802 ac, Roloc, N, SG, 2nd | 7075-T6 | 26,0 | 64,2 | 3,1 | | | | 1,56 | 4,26 | | | | | 0,87 | | | | | |
| 03050901 ac, Roloc, N, SG | 7075-T6 | 11,6 | 83,3 | 1,4 | | | | 0,85 | 2,88 | | | | | | | | | | |
| 03051101 ac, Roloc, N, SG, 2nd | 7075-T6 | 22,3 | 66,8 | 4,2 | | | | 1,91 | 4,87 | | | | | | | | | | |

continued

| File Name | Alloy | O 1s | C 1s | Al 2p | Mg 2p | Zn 2p _{1/2} | Cu 2p _{3/2} | Fe 2p _{3/2} | Zr 3d | Si 2s | Sr 3d | Cr 2p _{3/2} | Na a | N 1s | Ca 2s | S 2p | Cl 2p | P 2s | F 1s |
|--|---------|------|------|-------|-------|----------------------|----------------------|----------------------|-------|-------|-------|----------------------|------|------|-------|------|-------|------|------|
| 03051101 ac, Roloc, N, SG, 2nd, lt | 7075-T6 | 21,9 | 66,2 | 4,1 | | | | | 1,87 | 5,40 | | | | 0,48 | | | | | |
| 03061003 ac, Roloc, N, SG | 7075-T6 | 21,7 | 71,3 | 1,0 | | | | | 1,34 | 4,63 | | | | | | | | | |
| 03061003 ac, Roloc, N, SG, lt | 7075-T6 | 16,2 | 77,4 | 1,5 | | | | | 1,16 | 3,80 | | | | | | | | | |
| 03061101 ac, Roloc, N, SG, 2nd | 7075-T6 | 21,8 | 70,2 | 2,3 | | | | | 1,26 | 4,44 | | | | | | | | | |
| Primed samples that had been grit blast | | | | | | | | | | | | | | | | | | | |
| 03040201 ac, SBal, w, ac, GB, N, SG, Pr, 2nd | 2024-T3 | 23,0 | 68,5 | 1,4 | | | | | 0,30 | 2,30 | 0,18 | | | 4,32 | | | | | |
| 03040201 ac, SBal, w, ac, GB, N, SG, Pr, 2nd, lt | 2024-T3 | 22,1 | 70,0 | 1,4 | | | | | 0,28 | 2,21 | 0,14 | | 0,21 | 3,60 | | | | | |
| 03040201 ac, SBal, w, ac, GB, N, SG, Pr | 2024-T3 | 23,7 | 67,6 | 1,4 | | | | | 0,29 | 2,51 | 0,17 | | | 4,34 | | | | | |
| 03040803 ac, SBal, w, ac, GB, N, SG, Pr | 7075-T6 | 18,1 | 79,4 | 0,4 | | | | | 0,12 | 0,89 | | | | 1,16 | | | | | |
| 03040804 ac, SBal, w, ac, GB, N, SG, Pr, 2 | 7075-T6 | 17,8 | 79,6 | 0,2 | | | | | 0,07 | 0,76 | | | | 1,54 | | | | | |
| 03040804 ac, SBal, w, ac, GB, N, SG, Pr, 2, lt | 7075-T6 | 17,1 | 80,4 | 0,3 | | | | | 0,08 | 0,59 | | | | 1,49 | | | | | |
| 03041102 ac, SBal, w, ac, GB, N, SG, Pr | 7075-T6 | 15,8 | 81,7 | | | | | | 0,07 | 0,88 | 0,05 | | | 1,45 | | | | | |
| 03041103 ac, SBal, w, ac, GB, N, SG, Pr, 2nd | 7075-T6 | 16,5 | 81,0 | | | | | | 0,07 | 0,57 | 0,02 | | | 1,83 | | | | | |
| 03042303 ac, SBal, w, ac, GB, N, SG, Pr | 7075-T6 | 21,9 | 71,1 | 0,9 | | | | | 0,22 | 2,18 | 0,09 | | | 3,60 | | | | | |
| 03042304 ac, SBal, w, ac, GB, N, SG, Pr, 2nd | 7075-T6 | 23,2 | 69,5 | 1,2 | | | | | 0,24 | 2,32 | 0,05 | | | 3,51 | | | | | |
| 03042304 ac, SBal, w, ac, GB, N, SG, Pr, 2nd, lt | 7075-T6 | 21,6 | 71,1 | 1,3 | | | | | 0,22 | 2,18 | 0,06 | | 0,42 | 3,13 | | | | | |
| 03052101 ac, SBal, w, ac, GB, N, SG, Pr | 7075-T6 | 22,0 | 69,5 | 1,4 | | | | | 0,34 | 2,67 | 0,06 | | | 4,07 | | | | | |
| 03052101 ac, SBal, w, ac, GB, N, SG, Pr, lt | 7075-T6 | 21,6 | 70,4 | 1,3 | | | | | 0,35 | 2,63 | 0,06 | | 0,22 | 3,49 | | | | | |
| 03052201 ac, SBal, w, ac, GB, N, SG, Pr, 2nd | 7075-T6 | 21,6 | 70,4 | 1,2 | | | | | 0,27 | 2,61 | 0,06 | | | 3,89 | | | | | |
| Primed samples that had been abraded with a Roloc pad | | | | | | | | | | | | | | | | | | | |
| 03032802 ac, Roloc, N, SG, Pr, 2nd | 2024-T3 | 11,4 | 83,9 | 0,7 | | | | | 0,20 | 1,63 | 0,17 | | | 2,04 | | | | | |
| 03053003 ac, Roloc, N, SG, Pr | 2024-T3 | 10,9 | 84,9 | | | | | | 0,12 | 1,34 | 0,04 | | | 2,71 | | | | | |
| 03053003 ac, Roloc, N, SG, Pr, lt | 2024-T3 | 9,4 | 86,8 | | | | | | 0,09 | 1,37 | 0,03 | | | 2,34 | | | | | |
| 03060101 ac, Roloc, N, SG, Pr, 2nd | 2024-T3 | 11,6 | 84,6 | | | | | | 0,11 | 1,30 | 0,05 | | | 2,40 | | | | | |
| 03060101 ac, Roloc, N, SG, Pr, 2nd, lt | 2024-T3 | 10,7 | 85,2 | | | | | | 0,05 | 1,33 | 0,03 | | | 2,67 | | | | | |
| 03041004 ac, Roloc, N, SG, Pr | 7075-T6 | 12,9 | 81,9 | | | | | | 0,18 | 1,78 | 0,05 | | | 3,26 | | | | | |
| 03041004 ac, Roloc, N, SG, Pr, lt | 7075-T6 | 11,7 | 83,7 | 0,2 | | | | | 0,16 | 1,75 | 0,05 | | 0,06 | 2,42 | | | | | |
| 03041101 ac, Roloc, N, SG, Pr, 2nd | 7075-T6 | 10,8 | 84,8 | 0,3 | | | | | 0,18 | 1,72 | 0,08 | | | 2,13 | | | | | |
| 03041803 ac, Roloc, N, SG, Pr | 7075-T6 | 4,5 | 95,0 | | | | | | 0,02 | 0,40 | | | | | | | | | |
| 03041803 ac, Roloc, N, SG, Pr, lt | 7075-T6 | 5,6 | 92,8 | | | | | | 0,03 | 0,96 | 0,01 | | | 0,54 | | | | | |
| 03042101 ac, Roloc, N, SG, Pr, 2nd | 7075-T6 | 10,0 | 87,1 | 0,7 | | | | | 0,18 | 0,90 | 0,07 | | | 1,13 | | | | | |
| 03051201 ac, Roloc, N, SG, Pr | 7075-T6 | 14,1 | 81,7 | 0,4 | | | | | 0,36 | 1,71 | 0,03 | | | 1,60 | | | | | |
| 03051202 ac, Roloc, N, SG, Pr, 2nd | 7075-T6 | 7,4 | 90,3 | 0,3 | | | | | 0,20 | 1,19 | 0,04 | 0,18 | | 0,36 | | | | | |
| 03061102 ac, Roloc, N, SG, Pr | 7075-T6 | 6,4 | 92,4 | | | | | | 0,07 | 0,69 | | | | 0,45 | | | | | |
| 03061103 ac, Roloc, N, SG, Pr, 2nd | 7075-T6 | 11,5 | 85,4 | 0,9 | | | | | 0,16 | 0,78 | 0,07 | | | 1,21 | | | | | |
| 03061103 ac, Roloc, N, SG, Pr, 2nd, lt | 7075-T6 | 11,1 | 86,0 | 0,4 | | | | | 0,17 | 0,89 | 0,05 | | | 1,37 | | | | | |
| 03061201 ac, Roloc, N, SG, Pr, Green | 7075-T6 | 6,8 | 91,0 | | | | | | 0,12 | 1,17 | | | | 0,96 | | | | | |

3 RESULTS AND DISCUSSION

The XPS results are given and discussed separately for each stage of sample preparation.

3.1 Acetone wiped

The most striking result for these witness samples is the presence of relatively high concentrations of Mg on the surface. The Mg is present as oxide and is due to the processing of the alloy by the supplier. Cu and Mg are the main alloying components in AA 2024-T3, and Zn, Mg and Cu are the main alloying components in AA 7075-T6. No Cu was detected on the surfaces after acetone wiping, but Zn was found on all surfaces. The Mg concentrations fall into two classes of $x \approx 6.5\%$ and $\approx 15\%$, and correlate with the alloy type, AA 7075-T6 and AA 2024-T3 respectively. The correlation is rather surprising since the Mg concentration in the bulk AA 7075-T3 is about twice that in AA 2024-T3, whereas the opposite is found for Mg at the surface.

An XPS spectrum from the surface of an AA 2024-T3 sample after wiping with acetone is shown in **Figure 1**. The peaks used for the quantitative analysis are marked in the figure. Normally, the most intense peaks from each element are used for quantitative

analysis but where peaks from different elements overlap, other peaks should be used when possible. (Of course, spectrum subtraction and other numerical methods could be used also). For example, in determining the Zn concentration, the Zn 2p_{1/2} peak area was used rather than the more intense Zn 2p_{3/2} peak (the peak immediately to the right of the Zn 2p_{1/2} peak) as the Zn 2p_{3/2} peak overlaps the smallest of the three O KLL Auger peaks. Similarly, the Mg 2p peak was used for determining the concentration of Mg rather than the much more intense Mg KLL Auger peak immediately to the left of the C 1s photoelectron peak.

The presence of similar concentrations of Zn on all surfaces was also surprising, since the Zn concentration in the bulk AA 2024-T3 is about 1/20th that in AA 7075-T6. To examine the Zn distribution below the surface, samples were sputtered with argon to remove surface layers. In both cases, the Zn decreased with distance from the surface, although somewhat more slowly in the AA 7075-T6. In the case of AA 7075-T6, the Zn increased together with Cu after much more sputtering into the alloy. Of course, for the AA 2024-T3, the Cu increased (without Zn). Eventually, the Mg oxide was also removed from the surface by further sputtering.

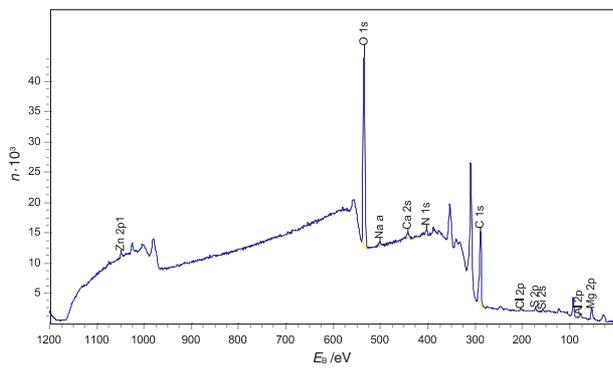


Figure 1: XPS survey spectrum from AA 2024-T3 after wiping with acetone

Slika 1: XPS spekter AA 2024-T3 po čiščenju z acetonom

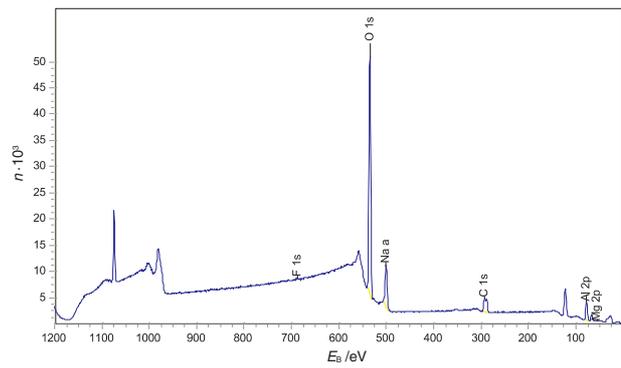


Figure 3: XPS survey spectrum after grit blasting with alumina

Slika 3: XPS spekter po peskanju z glinico

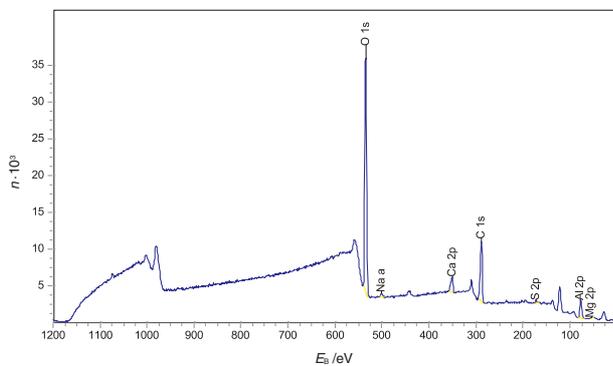


Figure 2: XPS survey spectrum from AA 2024-T3 after wiping with acetone, hand abrading with a Scotch-Brite pad and Alconox, rinsing with water, and finally rinsing with acetone

Slika 2: XPS spekter AA 2024-T3 po čiščenju z acetonom, ročnem brušenju s Scotch-Brite pad in Alconoxom, splakovanju z vodo in končnem splakovanju z acetonom

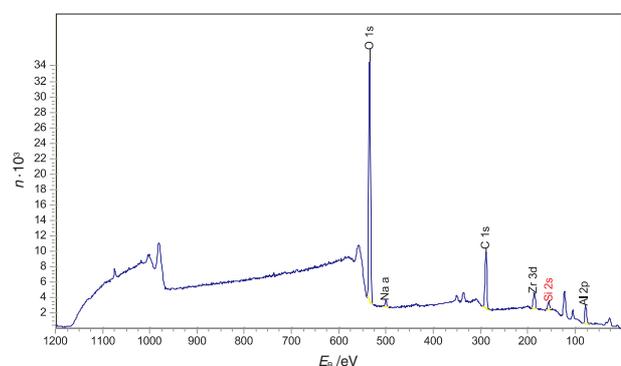


Figure 4: XPS survey spectrum after coating a sample using the sol-gel process, which had been previously grit blast with alumina

Slika 4: XPS spekter po nanosu prekritja s sol-gel postopkom, predhodno očiščenega s peskanjem z glinico

Si was also found on some samples, and it might not be from the alloy, but from surface contamination. Other contaminants were also observed, including Na, S and Cl (see **Table 1**).

3.2 Acetone wiped, then Scotch-Brite abraded with Alconox

After acetone wiping, some samples were Scotch-Brite abraded with Alconox, then rinsed in water and later with acetone. An XPS spectrum from an AA 2024-T3 sample after this treatment is shown in **Figure 2**. The Mg concentration was now always less than that of Al (note that the two AA 2024-T3 samples showed considerably less Mg than the AA 7075-T6 samples at this stage). Most of the AA 7075-T6 samples still showed a low Zn concentration. Na, S and Cl contaminants were also found at this stage. All samples showed Ca on the surface as well, and this is most likely from the tap-water rinse that was used.

3.3 Acetone wiped, Scotch-Brite abraded with Alconox, then grit blast

After grit blasting with alumina, quite a number of changes in surface composition occurred for all samples, and an XPS survey spectrum from such a surface is shown in **Figure 3**. The most notable effect with grit blasting was the large reduction in C on the surface, to a level about one-half of that before grit blasting. Other important changes included the increased Al concentration, and the decreased Mg concentration. Further, no Zn was detected on any grit blast sample, and S, Cl and Ca contaminants were generally absent.

However, new contaminants of Na and F were detected on the surface. These contaminants are from the alumina grit used in grit blasting, as was determined by XPS studies of the grit itself. All these surfaces, including the two AA 2024-T3 samples are quite similar in terms of surface composition.

3.4 Acetone wiped, and then abraded with a Roloc pad

Several samples were also abraded with a Scotch-Brite Roloc medium nylon pad, instead of the

Scotch-Brite hand abrasion with Alconox that was followed by grit blasting. After Roloc abrasion, the surfaces were similar in composition to those prepared by Scotch-Brite abrasion and grit blasting regarding Al and Mg, but the surface carbon was much higher, the oxygen concentration was significantly reduced, and the F contamination (from grit blasting) was absent.

The Na contamination was removed in most cases, except for some of the AA 7075-T6 samples. The high Na concentration from the grit blast material was not present. However, contamination with N was observed. This would most likely be from the nylon pad although it could be from reaction with air, as the samples would have been hot locally during abrasion. Several of the AA 2024-T3 samples also showed low concentrations of Cu.

3.5 Sol-gel coated, grit blast samples

The Si and Zr from the sol-gel process were detected, and the Si/Zr ratio was fairly constant at ~ 3.5 for all samples. An XPS spectrum from a coated sample is shown in **Figure 4**. Al was still detected from the substrate but no alloying elements were observed. This means that the coating was quite thin or not uniform in thickness. This is confirmed by the presence of a lower concentration of Na after coating. Recall that the Na contamination after the grit blast process was relatively high.

3.6 Sol-gel coated, Roloc abraded samples

Again, Si and Zr from the sol-gel process were detected, and the Si/Zr ratio was fairly constant at ~ 3.5 for all these samples as well. The Al concentration is much lower than with the sol-gel process on the grit blast samples, indicating a thicker or more uniform coating. Some samples showed N, perhaps from the Roloc-abraded substrate.

The lower initial oxygen content on the Roloc-abraded samples is still evident after the sol-gel coating process, as is the lower carbon content on the grit blast samples.

3.7 Primed samples

Sol-gel treated samples of both alloys that had been prepared by grit blasting or by Roloc abrasion were primed. No significant differences were found between the alloys, but the lower initial oxygen content on the Roloc-abraded samples is still evident after priming, as is the lower carbon content on the substrates that were grit blast. An XPS survey spectrum after priming a sample prepared with a Roloc pad before coating it with the sol-gel process, is shown in **Figure 5**.

Zr from the sol-gel process was still detected on all samples, indicating that the primer coating is also thin. The Si/Zr ratio increased though, as Si is also present in the primer. Generally, Sr and N were detected from the

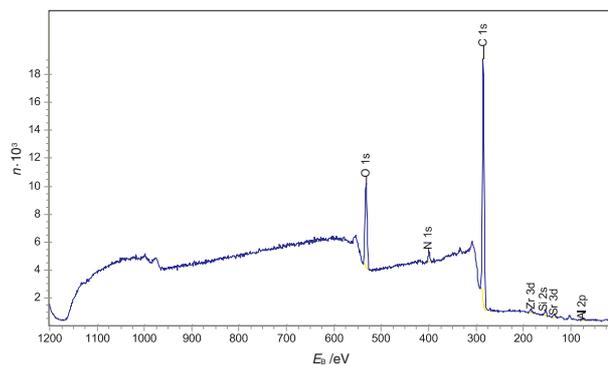


Figure 5: XPS survey spectrum after priming a Roloc-prepared sample that had been coated using the sol-gel process

Slika 5: XPS spekter po grundiranju vzorca, ki je bil prekrit s sol-gel postopkom

primer, but surprisingly Cr was detected on only a few samples. The detection of Cr is hindered as the main Cr peaks occur on the background signal of oxygen.

3.8 SEM and EDS studies of grit blast and coated samples

Electron micrographs of both grit blast and coated samples were taken in an SEM and are shown in **Figures 6 and 7**, respectively. There are no obvious differences in these micrographs between samples that had been coated using the sol-gel process and those that were uncoated. Micrographs were obtained at lower magnifications, and from acetone rinsed, and Scotch-Brite abraded surfaces as well.

Energy dispersive spectroscopy (EDS) measurements were also performed on the grit blast sample that had been coated using the sol-gel process. Three regions were examined as marked in the micrograph in **Figure 8**, which is at a lower magnification than the micrographs

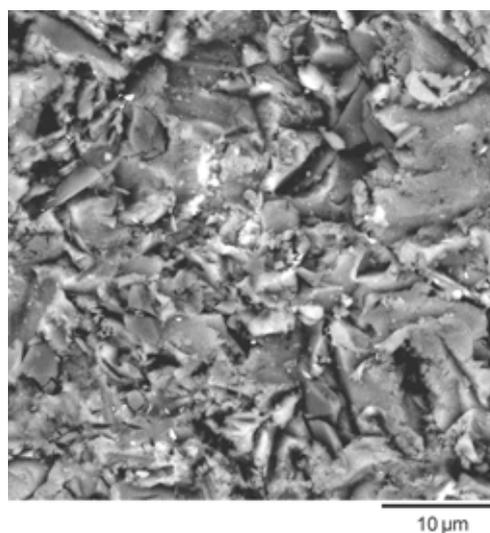


Figure 6: Scanning electron micrograph of grit blast AA 2024-T3
Slika 6: SEM posnetek AA 2024-T3 zlitine po peskanju

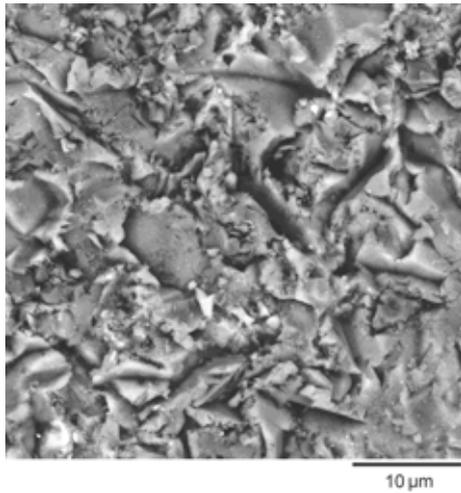


Figure 7: Scanning electron micrograph of grit blast AA 2024-T3 after coating using the sol-gel process

Slika 7: SEM posnetek peskane AA 2024-T3 po prekritju s sol-gel postopkom

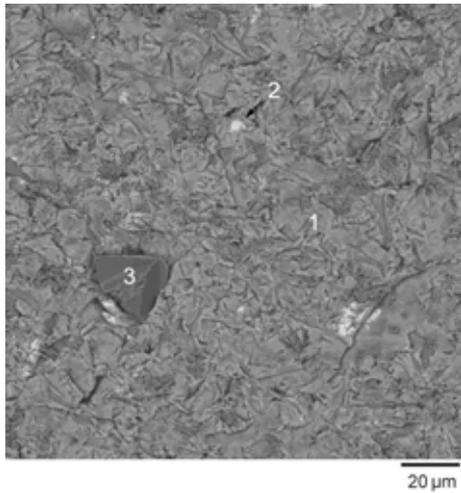


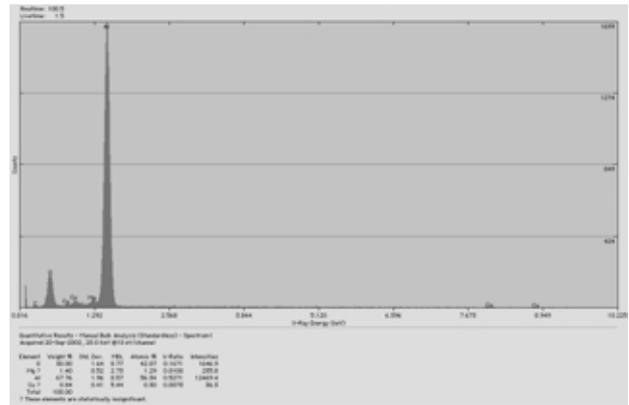
Figure 8: Scanning electron micrograph of grit blast AA 2024-T3 that had been coated using the sol-gel process. The three regions examined with EDS are marked as 1, 2 (the white region indicated by the arrow), and 3 on the micrograph

Slika 8: SEM posnetek peskane AA 2024-T3, po prekritju s sol-gel postopkom. Tri področja (1, 2, 3) smo analizirali z EDS

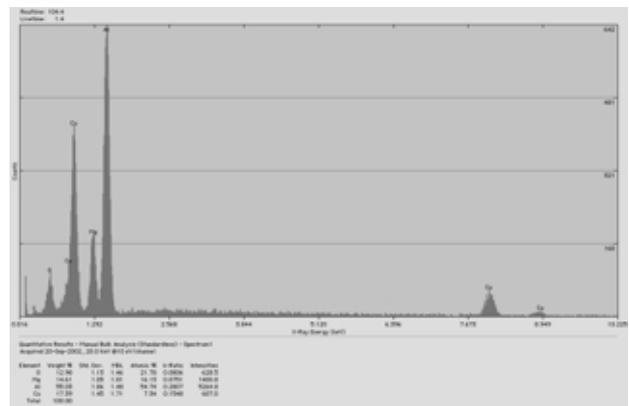
in **Figures 6 and 7**. The EDS results from the three regions marked in **Figure 8** are shown in **Figure 9**. Region 1 is the alloy matrix and shows about 1 wt. % each for Cu and Mg; region 2 has a much higher concentration of Cu and Mg (the mass fraction about 15 % each) than the surrounding alloy matrix and is probably a precipitate; and region 3 is Al_2O_3 and is probably an embedded grit particle from the grit blast.

3.9 Comparison with coatings using a commercial sol-gel kit

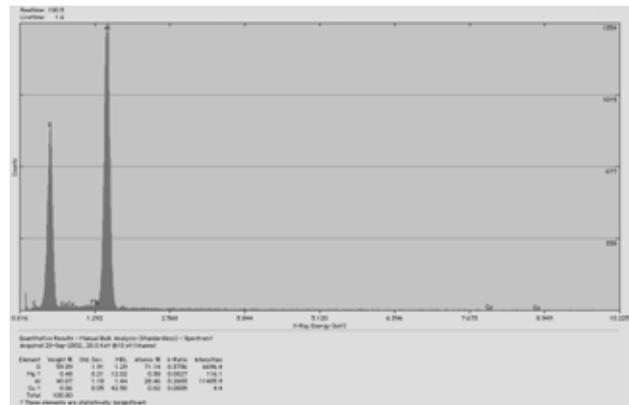
Several AA 2024-T3 samples were made and prepared in the usual way (including grit blast) and then



Region 1



Region 2



Region 3

Figure 9: EDS spectra from the regions 1, 2, and 3 that are marked in **Figure 8**

Slika 9: EDS spektri s področij 1, 2 in 3 označenih na **sliki 8**

coated using either a commercial sol-gel kit or a freshly made in-house sol-gel mix. Samples were processed at the same time. Most of the samples had some darker "water lines" on them after coating. During coating, the sol-gel using the commercial kit seemed to dry very quickly, so the samples were brushed a few times with the solution. Four samples (two from each sol-gel

Table 2: Surface composition (x/%) of coatings made from a commercial sol-gel kit and from a mix in our laboratory (lab)**Tabela 2:** Sestava površine (x/%) prevlek narejenih s komercialnimi sol-gel pripomočki in mešanic narejenih v našem laboratoriju

| | O 1s | C 1s | Zr 3d | Si 2s | Al 2p | Na a |
|---|------|------|-------|-------|-------|------|
| After preparation: | | | | | | |
| Commercial kit, sample 3 | 36 | 53 | 2.3 | 7.1 | 1.4 | 0.5 |
| Commercial kit, sample 7 | 36 | 52 | 2.2 | 6.7 | 3.1 | |
| 25 hours after preparation: | | | | | | |
| Commercial kit, sample 1, spot 1 | 37 | 52 | 2.3 | 6.6 | 2.4 | |
| Commercial kit, sample 1, spot 2, dark line | 36 | 55 | 2.0 | 7.7 | | |
| Commercial kit, sample 5 | 35 | 54 | 2.3 | 7.1 | 1.8 | |
| 8 days after preparation: | | | | | | |
| Commercial kit, sample 2, spot 1, darker side | 36 | 54 | 2.2 | 7.0 | 1.0 | |
| Commercial kit, sample 2, spot 2, dark line | 33 | 58 | 2.0 | 7.1 | | |
| Commercial kit, sample 2, spot 3, darker side | 35 | 53 | 2.3 | 7.5 | 1.9 | |
| Commercial kit, sample 8, spot 1 | 36 | 53 | 1.9 | 6.2 | 2.9 | 0.5 |
| Commercial kit, sample 8, spot 2, dark line | 34 | 56 | 2.0 | 7.3 | | |
| After preparation: | | | | | | |
| Lab mix, sample 3 | 39 | 45 | 1.6 | 6.4 | 7.8 | |
| Lab mix, sample 3, dark line | 37 | 51 | 2.3 | 8.2 | 1.2 | |
| Lab mix, sample 3, other side of dark line | 39 | 43 | 1.8 | 4.6 | 11.1 | |
| Lab mix, sample 7, spot 1 | 41 | 43 | 1.7 | 6.0 | 8.4 | 0.3 |
| Lab mix, sample 7, spot 2, dark line | 38 | 52 | 2.0 | 8.1 | | |
| 25 hours after preparation: | | | | | | |
| Lab mix, sample 4, spot 1 | 39 | 46 | 1.6 | 5.6 | 7.7 | |
| Lab mix, sample 4, spot 2, dark line | 36 | 52 | 2.1 | 6.9 | 2.7 | |
| Lab mix, sample 4, spot 3 | 38 | 49 | 1.5 | 6.3 | 4.8 | |
| Lab mix, sample 4, spot 4, dark line | 37 | 51 | 1.8 | 7.6 | 2.9 | |
| Lab mix, sample 8, spot 1 | 41 | 41 | 1.6 | 5.7 | 10.8 | |
| Lab mix, sample 8, spot 2, dark line | 38 | 50 | 2.1 | 7.8 | 1.8 | |
| 8 days after preparation: | | | | | | |
| Lab mix, sample 1, spot 1 | 39 | 47 | 1.8 | 6.4 | 5.8 | 0.6 |
| Lab mix, sample 1, spot 2, dark line | 37 | 53 | 1.8 | 7.9 | 0.7 | |
| Lab mix, sample 2, spot 1 | 40 | 43 | 1.5 | 5.6 | 9.3 | |
| Lab mix, sample 2, spot 2, dark line | 37 | 51 | 2.1 | 7.9 | 1.4 | |

source) were mounted 30 min, 25 h and 8 d after coating, to see if there were any time effects on composition.

The results of the XPS analysis are shown in **Table 2**. There are several important conclusions that can be drawn from **Table 2**. First, the surface compositions using the two sol-gel sources are very similar, as can be seen from the Zr and Si concentrations. Second, the coatings are thicker at the "water lines" compared to the other regions. This can be seen in **Table 2**, where the "water lines" are referred to as "dark lines", and the lower Al concentration indicates a thicker coating. The Al concentration is always lower (or not measurable) on the dark lines. Third, the coatings made from the commercial kit were thicker in all cases (away from the dark lines) than the coatings made from our laboratory mix, but this might be due to the re-brushing with the solution prepared using the commercial kit. Fourth, no significant differences in composition were found following 25 h or 8 d of room-air exposure after preparation.

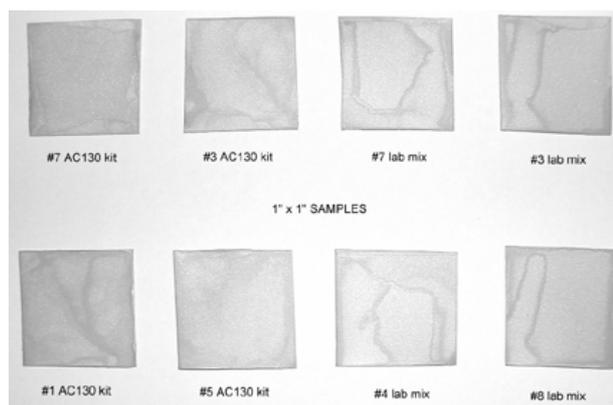


Figure 10: Photographs of eight AA 2024-T3 samples that had been coated using the sol-gel process. The sample dimensions are 2.5 cm × 2.5 cm. The four samples on the left were coated using a commercial mix, whereas the four on the right were coated using a fresh mix in our laboratory. Note the "water lines" formed on drying

Slika 10: Fotografije osmih vzorcev zlitine AA 2024-T3, ki so bile prekrite s sol-gel postopkom. Dimanzija vzorcev je 2,5 cm × 2,5 cm. Štirje vzorci na levi strani so bili prekrite s komercialnimi sol-gel mešanicami, medtem ko preostali štirje vzorci s svežimi mešanicami, pripravljenimi v našem laboratoriju.

4 CONCLUSIONS

XPS has been shown to be a very useful method to characterize the surface composition of AA 2024-T3 and AA 7075-T6 at each stage of sample preparation for adhesive bonding. This has led to the development of a database that can be used to track sample chemistry at each stage of preparation and help in the interpretation of data from mechanical testing of subsequent adhesive bonds. Significant differences in surface composition were found after using different abrasion methods, grit blasting, coating via a sol-gel process, and priming.

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