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Electroplating on Al6082 Aluminium: A New Green and Sustainable Approach

Andrea Comparini [1,2,*], Ivan Del Pace [2], Walter Giurlani [1,3], Roberta Emanuele [1,2], Margherita Verrucchi [1], Marco Bonechi [1,*] and Massimo Innocenti [1,3,4,5]

1. Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019 Sesto Fiorentino, Italy
2. Valmet Plating Srl, Via Erbosa 5, 50041 Calenzano, Italy
3. National Interuniversity Consortium of Materials Science and Technology (INSTM), Via G. Giusti 9, 50121 Firenze, Italy
4. CNR-ICCOM, Insititute of Chemistry of Organometallic Compounds, National Research Council (CNR), via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy
5. CSGI, Center for Colloid and Surface Science, via della Lastruccia 3, 50019 Sesto Fiorentino, Italy
* Correspondence: a.comparini@unifi.it (A.C.); marco.bonechi@unifi.it (M.B.); Tel.: +39-055-457-3097 (A.C. & M.B.)

Abstract: Aluminium and its alloys are interesting for many applications because they are very light, cheap, and unlimitedly recyclable. Despite being a promising base material for the fashion-jewellery sector, their tendency to form a passivating film makes them difficult to be galvanized, even more when recycled aluminium contains impurities of refractory elements. Indeed, the most common processes for galvanising aluminium are often expensive and not environmentally sustainable because they involve the use of cyanides. In this work we focussed on the pre-treatments and electroplating on Al6082 aluminium which is largely used for fashion-jewellery applications. The objective of the present study was to assess whether Al6082 series aluminium is suitable a as base material for the fashion market; therefore, we investigated the effectiveness of plating pre-treatments and the success of electroless zinc deposition using an innovative alkaline cyanide-free zincate solution. After the electroplating, adhesion between the deposited layers was evaluated both with cross-sectional scanning electron microscope (SEM) analysis as well as with an adhesion evaluation test (ISO2819:2018): no detachments confirmed the positive test outcomes and thereby highlighted that Al6082 can be exploited as base material in the fashion-jewellery market.

Keywords: aluminium; Al6082; electroplating; film characterization; sustainability; metal coatings; fashion; decorative

1. Introduction

Differently from a few years ago, "sustainability", "green" and "environmentally safe" are becoming keywords for business opportunities. Industrial leaders of different market sectors are indeed nowadays paying more and more attention to the consumers' needs of feeling like an active part within a transition towards a better world. Making use of recyclable materials is therefore paramount, especially in those sectors wherein a vast number of precious resources are being depleted day by day. Among those resources, metals depletion is one of the most concerning, hence scientists are called upon to find renewable alternatives as fast as possible [1–6]. The fashion-jewellery industry makes extensive use of scarcely available metals, which in most cases come from ore extraction. Nevertheless, alternatives do exist, despite the fact that, from a technological point of view, a lot of work has yet to be done to ensure at least the same performance of the materials nowadays being used [7–9]. Since fashion-jewellery market players are constantly seeking new, viable ways to render their whole value chain more sustainable, they are constantly looking at making use of green and eco-compatible base materials, yet ensuring economically feasible

processes [10–12]. Concerning fashion items and accessories like chains, rings, earrings, bracelets and so on, among a wide variety of suitable base materials, aluminium is one of the most interesting because is unlimitedly recyclable and is spread throughout the world, hence is largely available and cheap [13–15]. However, aluminium galvanization is challenging, especially when it comes down to the so-called "secondary aluminium" which is aluminium that comes from the recycling process. Indeed, besides quickly and spontaneously forming a layer of oxide when exposed to the air [16,17]—also primary aluminium undergoes this natural process—secondary aluminium might contain a broad range of metallic, semi-metallic or non-metallic impurities that hinder the electroplating process, leading to weak adhesions between galvanic layers being deposited [18–21]. Since most of the available aluminium on the market is recycled, it has been catalogued by type of impurities in order to properly set up chemical and mechanical treatments depending on the chemical composition [22–24]. Methods for cleaning, properly activating its surface and for plating ensuring adhesion have been developed through the years and have turned out to be different depending on the aluminium series considered [25–27]. For the aforementioned reason, each aluminium series has to be separately studied from the others. In particular, 6082 series aluminium alloys are nowadays getting more and more interest from the fashion market due to its workability as well as for the large availability and therefore the low market price. However, belonging to the "anticorodal" series, Al6082 contains silicon traces, and its electroplating becomes thereby challenging [28,29]. Accordingly, a proper customized sample preparation before galvanization is paramount [30]. Scientific work focusing on the electroplating of a single type of aluminium have to date already been done but a holistic study making use of a sustainable approach focusing on the electroplating of aluminium 6082 series for fashion-jewellery industries is missing [31]. By means of the present work focusing on fashion-jewellery applications we propose an innovative process that, following appropriate treatments, leads to a well-adhered zinc layer deposited from an electroless cyanide-free galvanic process. The electroless deposition of a layer of zinc on aluminium also allows the electrodeposition of other galvanic layers commonly used in the fashion-jewellery industry such as nickel, bronze and palladium. What is more, the final products obtained meet the common quality standards required by the fashion-jewellery industry. To be plated, aluminium typically undergoes a pre-treatment involving activation with acidic and alkaline fluorides-containing solutions followed by a double-zincating step [32]. In this work a commercial cyanide-free zincate process was used in order to assess the effectiveness of this solution towards Al6082 and to show that a green approach can be pursued not only from a base-material point of view but also galvanic-wise [33]. Moreover, since when it comes down to electroplating the base material roughness is a key parameter, both polished as well as unpolished aluminium samples were considered in the present work. For instance, low roughness is sometimes achievable only by means of time-consuming manual work. The latter, besides being challenging for tiny objects, is indeed expensive. Therefore, samples were double-zincated to thoroughly assess whether the setup process is able to produce well-adhered deposits regardless of the base material roughness [34]. Prior to SEM characterization, a thick layer of nickel was deposited both to shelter the underlying layer of zinc previously deposited onto the base material and to evaluate adhesion by performing an adhesion-evaluation test (ISO 2819:2018). Furthermore, the electrodeposition from a white bronze galvanic bath followed by a Pd-Ni bath were performed in order to carry out ageing test commonly employed within the fashion industry in order to assess whether a full galvanic electroplating cycle obtains durable plated Al6082 fashion items and accessories. Results showed that Al6082 can be exploited as innovative base material within the fashion-jewellery industry since a simple electroplating cycle can produce galvanized objects meeting sector standards. In addition, no constrains due to the intrinsic roughness of the object being galvanized were underlined.

2. Materials and Methods

High purity (for analysis, ISO) nitric acid (65%) was purchased from Carlo Erba Reagents (Milan, Italy). High purity (for analysis, ISO) sulfuric acid (96%) was purchased from PanReac AppliChem (ITW Reagents, Monza, Italy). The following commercial electroplating, etching, and degreasing solutions were all kindly provided by Valmet Plating Srl (Calenzano, Italy): Solution A, TOPCLEANLQ, a proprietary degreasing solution used to ultrasonically clean the samples; Solution B, ATMETPLUS, a proprietary degreasing solution to electrochemically clean the samples surface; Solution C, ATMET70, a proprietary fluoride-based etching solution; Solution D, ALUCHEMCF, a proprietary electroless alkaline cyanide-free zincate solution; Solution E, NILUXMU, a proprietary "Watts nickel" electroplating solution; Solution F, BROMETN05, a proprietary white bronze electroplating solution; Solution G, PALMET910, a proprietary Pd-Ni (85%–15%) electroplating solution. The workflow followed in this study is schematized in Figure 1.
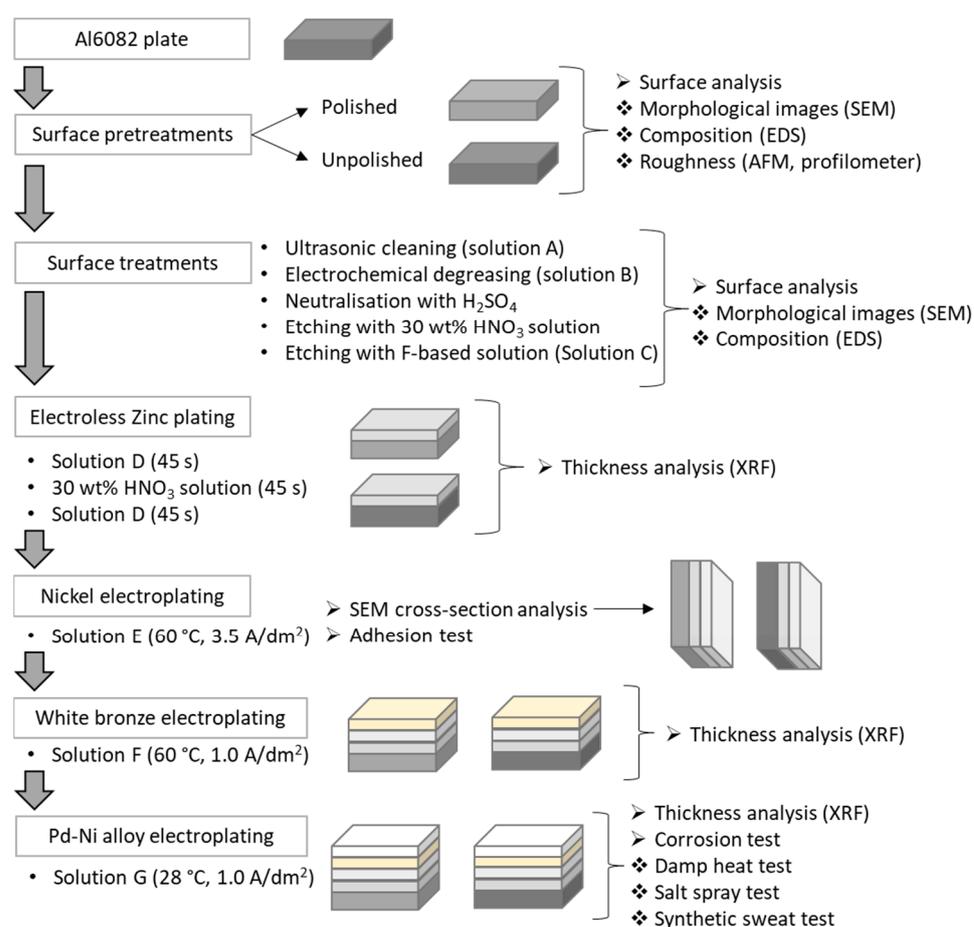

Figure 1. Flowchart of the depositions and characterizations performed in this study.

Samples to be plated were cut out of a Al6082 slab (thickness = 1 mm) kindly provided by Fulvio Casamonti Srl (Impruneta, Italy). A 1.5 mm diameter circular hole was mechanically made in the upper part of each 5.0×3.8 cm^2 aluminium sample to eventually tie them with copper thread prior to galvanization. Half of the samples were mechanically polished to diminish their surface roughness. Sample pre-treatments were performed using Solution A, Solution B, and Solution C. Zinc plating was performed after the pre-treatment procedure using an electroless immersion plating through Solution D.

EX354RD DUAL power supply (280 W) was used for all the experiments involving the use of current (i.e., cathodic alkaline electrochemical degreasing, nickel, white bronze and Pd-Ni electroplating). Electroplating was performed in a two-electrode electrochemical

cell consisting of 500 mL beakers. The counter electrode (anode) was a bare nickel plate in the case of nickel plating and a mixed metal oxide (MMO) mesh for the white bronze and palladium alloy depositions. Sample pre-treatments and plating necessary to obtain well-adhered galvanic coatings are given in Sections 3.2 and 3.3. The nickel coating was used both to shelter the underlying layer of zinc during the cross sectioning as well as to evaluate adhesion. Nickel deposits were obtained by depositing from Solution E at 60 °C and 3.5 A/dm^2 for a variable amount of time (10–40 min) in order to evaluate any possible impact of the thickness on the adhesion. White bronze deposit was obtained from Solution F at 60 °C and 1 A/dm^2 for a deposition time of 5 min. Pd-Ni alloy was electroplated from Solution G at 28 °C and 1 A/dm^2 for a deposition time of 8 min. During all the electrodeposition, the solution was kept in motion by means of a magnetic stirrer. Unpolished sample roughness was measured by means of a HOMMEL WAVE profilometer (OGP Hommel srl, Desio, Italy) whereas a Molecular Imaging PicoSPM Atomic force microscopy (AFM) with a triangular Si_3N_4 cantilever (Veeco, NP-S10, Munich, Germany) was used to measure the roughness of the mechanically polished samples. A Hitachi SU3800 scanning electron microscope equipped with an UltimMax Oxford instrument detector (Oxford instrument, Wiesbaden, Germany) was used both to gather data with respect to the composition of the Al6082 as well as to collect the energy-dispersive X-ray spectroscopy (EDS) signals to evaluate the composition of the samples. For SEM cross-section analysis, samples were cut and incorporated within a conductive polymeric resin. After resin curing, samples were polished with abrasive papers, following the typical procedure for cross-section analysis [35].

The software CASINO v2.51 [36] was used to simulate and evaluate the depth from which the X-ray was generated in the sample during the EDS analysis. The simulation was performed using 10^5 electrons with various accelerating potentials.

X-ray fluorescence (XRF) thickness measurements [37] were performed with a Bowman B Series XRF spectrometer (Schaumburg, IL, USA) using an acquisition time of 60 s, 50 kV tube voltage, 0.8 mA tube current, and a collimator of 0.6 mm in diameter.

ISO 2819:2018 standard was followed to assess the adhesion between layers. In particular, a TQC Sheen CC3000 cross-cut tester ISO-compliant was used to cut the plated surface of the objects and a TESA 4124 tape was employed to try to peel off the metallic deposits.

Eventually, damp heat test (ISO 4611:2011), salt spray test (ISO 9227:2017) and synthetic sweat test (NF S80–772:2010) standards were followed to evaluate electroplated items ageing resistance. In particular, a Haida International Equipment (HD-E808-90) chamber (Haida International, Dongguan, China) was employed to perform the salt spray test and a Ghumy Climatic Chamber (F.LLI GALLI G. & P. snc, Milan, Italy) was used when requested from standard procedures. Salt spray test was conducted by using a 5% NaCl (Merck, Ph EUR, BP, USP) solution (pH = 6.5–7.2) whereas synthetic sweat composition was 5% lactic acid (Fluka Analytical, Milan, Italy) and 10% NaCl (Merck, Darmstadt, Germany) in deionized water.

3. Results

3.1. Al6082 Aluminium Plate Surface Analysis

3.1.1. Unpolished Aluminium Samples

Unpolished 6082 series aluminium samples were manually degreased by means of a common soap, thoroughly washed with deionized water and then with isopropanol. SEM analysis was performed both to collect surface images as well as to check aluminium alloy composition (Figure 2a,b). Regular longitudinal marks due to the manufacturing of the metal are visible on the surface of the aluminium plates using a medium-high magnification (×5 k, Figure 2a). EDS spectrum was collected with a ×100 magnification to minimize any compositional inhomogeneities; the analysis was performed at two different acceleration potentials: 5 kV, to obtain the surface composition of the alloy, and 20 kV, to evaluate the bulk composition (Figure 2b).
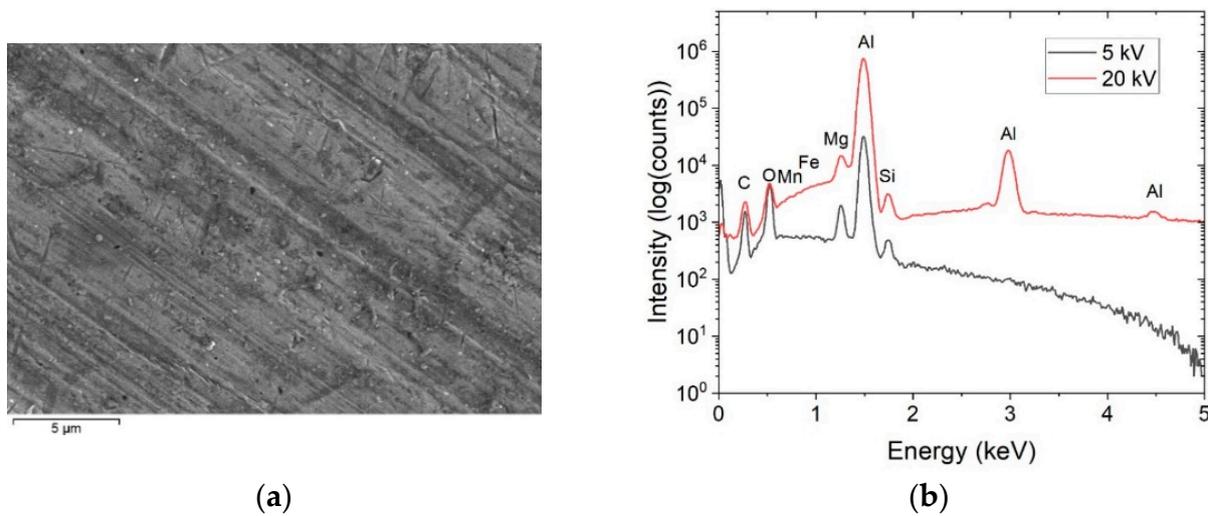
(a)

(b)

Figure 2. SEM analysis of unpolished Al6082 aluminium plate surface: (**a**) ×5 k magnification image; (**b**) EDS analysis of the sample by using a 5 kV and 20 kV acceleration potential at a magnification of ×100.

EDS measurement performed with 5 kV and 20 kV on aluminium element was simulated using CASINO software. Results show that the 99.99% of the X-rays produced by the samples comes from a maximum depth of 320 nm in the case of the 5 kV measurement, while the depth for the 20 kV measurement is 3.9 μm. For this reason, it is evidence that the measurement performed at 5 kV certainly produces a more superficial compositional result than the one at 20 kV.

Table 1 reports a comparison between the theoretical composition of 6082 aluminium series alloy [38] against the aluminium slab used in this study measured with EDS. Adventitious carbon and oxygen contaminations detected on the surface of the sample have been excluded from the quantification and the normalized composition is also reported. The EDS analysis shows that the measured and normalised compositions agree with the theoretical one. On the surface (5 kV measurement) higher amounts of silicon and magnesium with respect to the bulk material (20 kV measurement) were detected. These elements are mainly responsible, together with the oxide layer, for the difficulties encountered in the plating of aluminium.

Table 1. Comparison between theoretical composition of Al6082, and the measured composition with EDS at 5 kV and 20 kV.

	wt%		
Element	**Theoretical**	**5 kV**	**20 kV**
Al	Remaining	95.5 ± 0.2	97.4 ± 0.1
Si	0.7−1.3	1.3 ± 0.1	0.8 ± 0.1
Fe	0.5	-	0.3 ± 0.1
Mg	0.6−1.2	3.2 ± 0.1	1.0 ± 0.1
Mn	0.4−1.0	-	0.6 ± 0.1
Cr	0.25	-	-
Cu	0.10	-	-
Zn	0.20	-	-
Ti	0.10	-	-

The surface roughness of unpolished samples was evaluated performing five measurements perpendicularly to the visible scratches. The results are reported in Table 2. The surface of the Al6082 unpolished sample is highly rough; indeed the linear roughness parameters Ra (arithmetic average of profile height deviations from the mean line) and Rz (maximum peak to valley height of the profile) values are within the μm range.

Table 2. Unpolished Al6082 aluminium surface roughness: values are intended as an average of 5 measurements.

Roughness Parameter	Average (μm)	Standard Deviation
Ra	0.40	0.01
Rz	1.98	0.04

3.1.2. Polished Aluminium Samples

To perform surface analysis, polished samples followed the same characterization of the unpolished ones (compare Section 3.1.1). SEM analysis was performed to collect surface images and to check aluminium alloy composition, and ×5 k magnifications were used to observe the surface of the sample (Figure 3a). SEM images show that the polished aluminium has a uniform and smooth surface. The EDS analyses were performed with an acceleration potential of 5 kV and 20 kV at a magnification of ×100, confirming the results obtained for the unpolished sample (see Figure 2b and Table 1). Since the low roughness of the polished sample did not allow for a profilometer analysis, AFM investigation was adopted (Figure 3b).
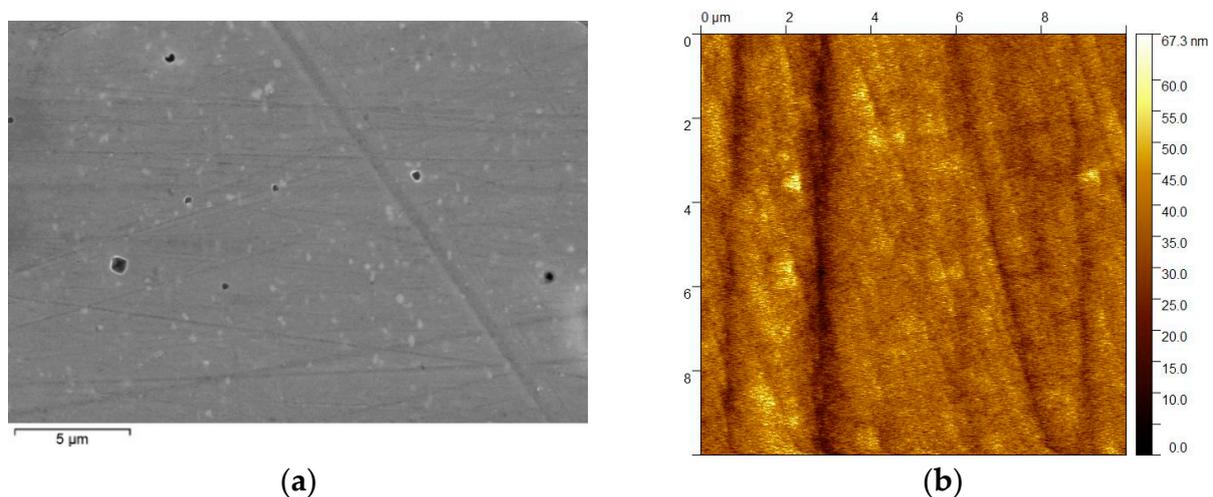

(**a**) (**b**)

Figure 3. Polished Al6082 aluminium plate surface: (**a**) 5 k magnification SEM image; (**b**) AFM image.

The roughness results are reported in Table 3 in terms of the surface roughness parameters Sa (root mean square average of profile height deviations from the mean plane). The SEM and AFM images show that the polishing does not completely eliminate all the scratches present on the aluminium surface, however it does reduce roughness by two orders of magnitude (compare Tables 2 and 3), resulting in a very smooth surface.

Table 3. Polished Al6082 aluminium surface roughness, values were obtained from AFM analysis.

Roughness Parameter	Value (nm)
Sa	5.09
Sq	6.55

3.2. Samples Pretreatment

Both unpolished as well as polished aluminium samples followed the same preparation procedure:

1. Each aluminium sample was tied with copper wire and soaked into an ultrasound bath filled with Solution A at 65 °C for 3 min.

2. After thoroughly rinsing the sample with deionized water, a cathodic alkaline electrochemical degreasing was performed by immersion for 10 s into a two-electrode electrochemical cell containing Solution B applying 25 V.
3. Samples were again rinsed with deionized water and neutralized into a 3 wt% H_2SO_4 solution.
4. After deionized water rinsing, 30 wt% HNO_3 solution was used to etch aluminium surface (45 s at room temperature).
5. After water rinsing, a fluoride-based solution (Solution C) was used to reduce the presence of silicon on the surface of the samples (45 s at room temperature).

The decrease in the presence of silicon (the last step of treatment) is particularly important for the subsequent plating step; indeed, the higher is the percentage of silicon within aluminium alloy, the more difficult is the object to be plated, since silicon does not react when aluminium is soaked into the zincate solution [39].

The pre-treated surface was characterised by SEM analysis before electroplating the galvanic layers. Figure 4a shows the SEM image of the surface of the unpolished sample surface after the last step of the pre-treatment with Solution C. Figure 4a, compared with Figure 2a, clearly shows that the surface has been attacked by the chemicals agents used during the pre-treatment steps. EDS analysis at 5 kV and 20 kV were repeated on this sample (Figure 4b).
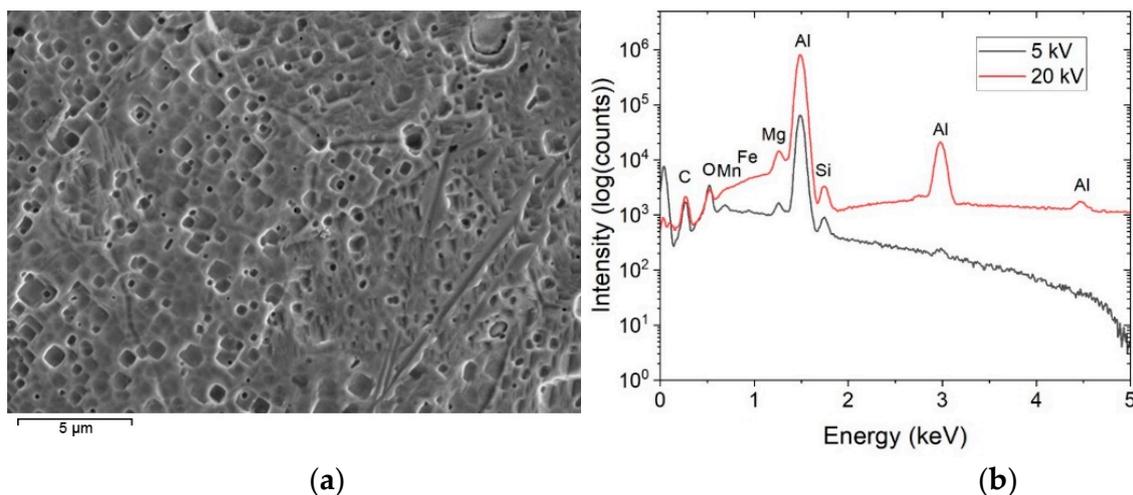

(a)   (b)

Figure 4. SEM analysis of unpolished aluminium sample after fluoride-based solution treatment: (**a**) ×5 k magnification image; (**b**) EDS analysis of the sample by using a 5 kV and 20 kV acceleration potential at a magnification of ×100.

The composition of the sample obtained from EDS is reported in Table 4. Comparing the results with Table 1, it can be seen that the treatment decreased the silicon content from 1.3% to 0.5% and the magnesium content from 3.2% to 0.3% from the surface (5 kV analysis). On the other hand, the composition obtained with the acceleration potential of 20 kV (bulk analysis) remains almost unchanged.

Table 4. Composition of the of Al6082 aluminium after the activation treatment measured with EDS at 5 kV and 20 kV.

Element	5 kV	20 kV
Al	99.2 ± 0.1	97.7 ± 0.1
Si	0.5 ± 0.1	0.8 ± 0.1
Fe	-	0.2 ± 0.1
Mg	0.3 ± 0.1	0.8 ± 0.1
Mn	-	0.5 ± 0.1

3.3. Zinc Plating

Electroless immersion plating through Solution D was performed for 45 s at room temperature immediately after the pre-treatment procedure. Magnetic stirrers ensured good mixing during all the passages carried out. Thanks to the pre-treatment, a thin layer of zinc was deposited onto the aluminium surface [40–42]. Nevertheless, to ensure better adhesion between layers, a double zincate step was preferred despite the fact that the literature is still controversial with regards to this point [41,43–46]. Therefore, by again rinsing with water in between each step, the zincate sample was soaked in 30 wt% HNO_3 solution for 45 s (room temperature) and a new layer of zinc was deposited by means of the cyanide-free zincate solution (45 s at room temperature).

The thickness of the zinc layer was measured by means of XRF for both the unpolished as well as the polished samples obtaining 29 ± 6 nm and 23 ± 1 nm values respectively. Results are expressed as the average of three measurements.

Eventually, a thick layer of nickel from an acid Watts bath (Solution E) was electroplated onto the galvanized aluminium, as described in Section 2. Unpolished sample was plated for 20 min, while two polished samples was nickel plated one for 40 min and the other for 10 min.

3.4. Cross-Section Analysis of Nickelated Samples

3.4.1. Unpolished Samples

SEM cross-sectional analysis of the samples was carried out. The unpolished sample shows a good interlocking between layers with no detachment of the coating from the substrate as a consequence of the cross-sectioning procedure and lapping (Figure 5a). EDS profile analysis was performed (red arrow Figure 5a): the intensity of the Al, Zn and Ni signals is reported in Figure 5b. A good overlapping is present between the Al and Ni signals, confirming the good adhesion of the coating. The nickel coating thickness after 20 min of deposition was approximately 15 μm, whereas the Zn signal turned out to be too weak to be observed. The reason could lie in the low thickness of this layer, below the lateral resolution of EDS together with the partial dissolution of Zn when the sample is being immersed in Solution E for the nickel plating, in the instants preceding the application of the potential.
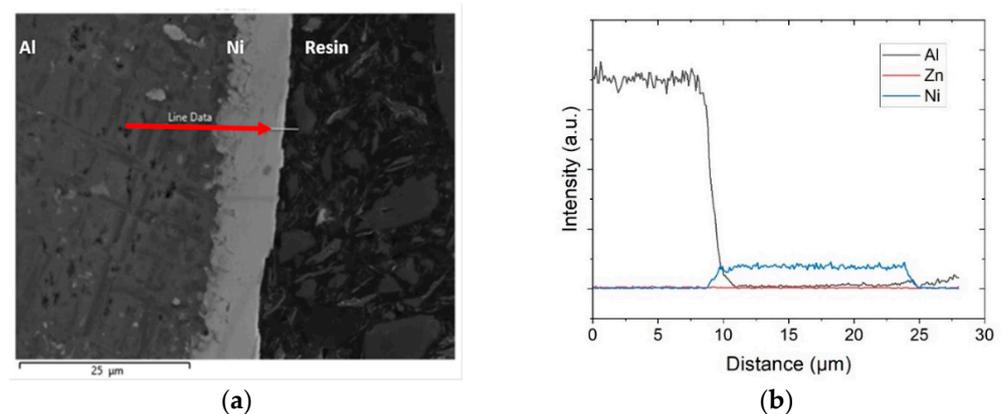

| (a) | (b) |

Figure 5. Unpolished sample subjected to the pre-treatment, zinc immersion plating and nickel electroplating for 20 min: (**a**) cross-section being analysed, red arrow indicates the area and the direction of the EDS measurement; (**b**) EDS profile analysis along the red arrow of Al, Zn and Ni.

3.4.2. Polished Samples

SEM and EDS profile analyses were repeated for the nickel-plated polished samples (Figure 6). Figure 6a,b refer to the polished sample plated through solution E for 40 min, resulting in a nickel coating of almost 35 μm. Figure 6c,d refer to the polished sample plated by means of solution E for 10 min, resulting in a nickel coating approximately 5 μm

thick. For these samples, as observed for the unpolished sample, no detachment of the coating from the substrate and a good interlocking between the layers are observed. These results suggest that the studied procedure is valid for a wide range of substrate roughness and coating thicknesses.
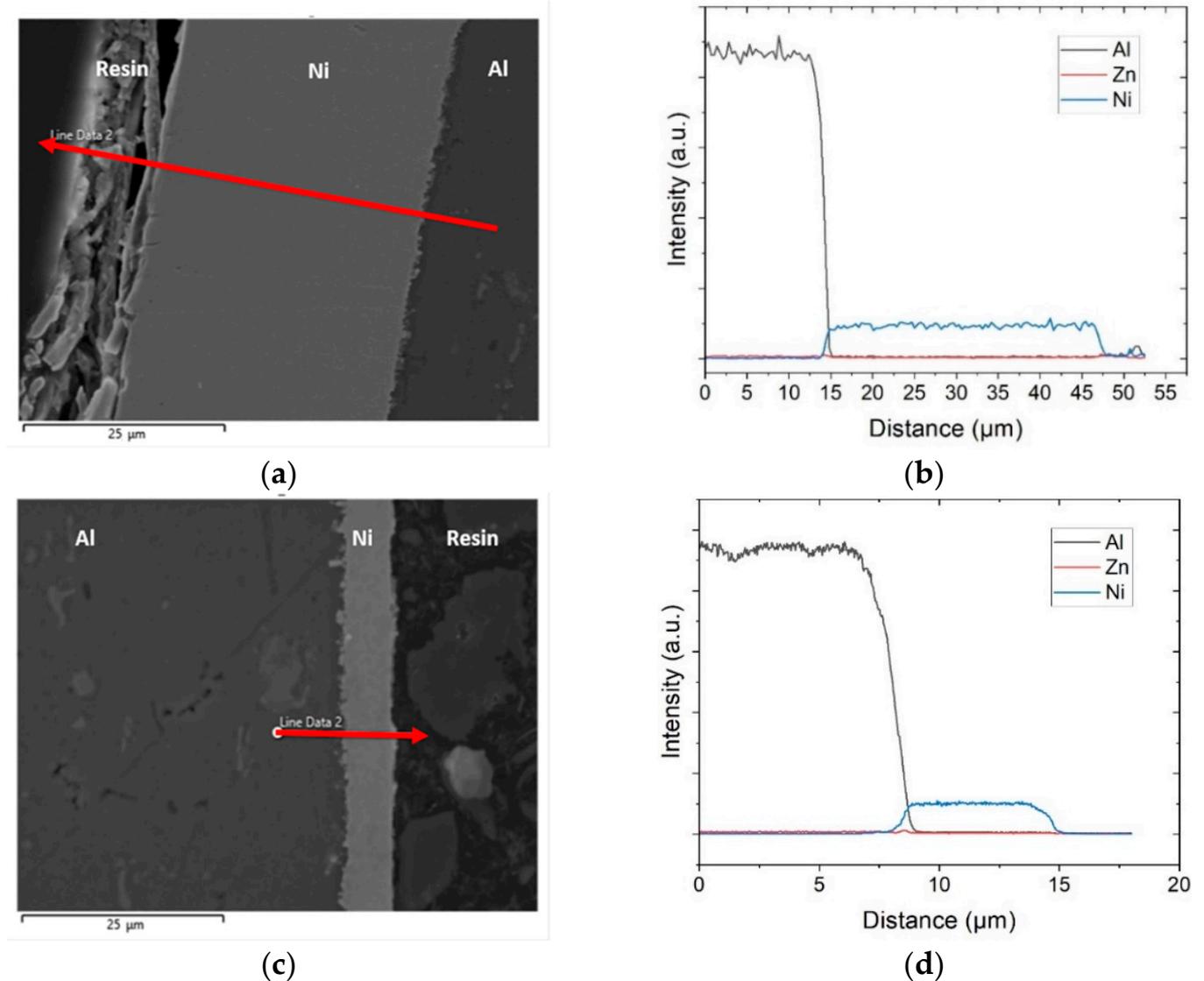

Figure 6. Polished samples subjected to the pre-treatment, zinc immersion plating and nickel electroplating: (**a**) cross-section being analysed, red arrow indicates the area and the direction of the EDS measurement for a sample nickel-plated for 40 min; (**b**) EDS profile analysis along the red arrow of Al, Zn and Ni; (**c**) same as (**a**) but for a sample nickel-plated for 40 min; (**d**) same as (**b**) but for a sample nickel-plated for 40 min.

3.5. Adhesion Test

Adhesion between the nickel, zinc coatings and the aluminium substrate was tested following ISO 2819:2018 standard criteria: outer nickel coating were all cross-cut and pieces of TESA 4124 tape were manually applied onto each sample surface. Prior to peeling off the tape it was left attached to the metallic surface for five minutes. None of the plated samples showed detachment of the nickel layer (Figure 7), confirming that the coatings were all well bonded to the substrate.
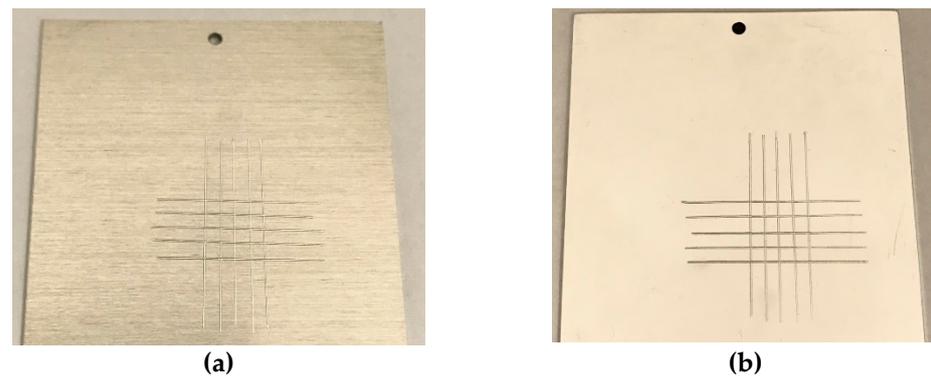
(a)   **(b)**

Figure 7. Photo of the nickel-plated (**a**) unpolished and (**b**) polished samples after the adhesion test. The cross-cuts are evident but no detachment of the coating was observed.

3.6. Corrosion Test

A typical industrial electroplating cycle [3,47] was carried out both for zinc-plated aluminium-based polished and unpolished samples. The samples were nickel-plated with Solution E for 15 min obtaining a nickel deposit of $\approx$ 10 µm. Solution F was used to deposit $\approx$ 2 µm of white bronze onto nickel coating. On top of the white bronze deposits, a $\approx$ 0.8 µm thick layer of Pd-Ni (Solution G) was electroplated in order to provide corrosion resistance to the objects. The thickness of the layers was measured by XRF. Damp heat test (ISO 4611:2011), salt spray test (ISO 9227:2017) and synthetic sweat test (NF S80–772:2010) standards (the most used and representative in the fashion-jewellery industry) were performed. A 24 h synthetic sweat led to partial corrosion—pitting—of all the samples tested but to a low extent (<10% of the surface). A 24 h dump heat with leather (40 °C, 93% RH) did not lead to any visible alterations. A 48 h salt spray test left some salt traces on the samples surface but upon rinsing with deionized water no visible alterations were highlighted. The results confirm that the employed galvanic cycle is able to produce durable items for both polished and unpolished aluminium. In general, the use of rough substrates (i.e., unpolished metal surfaces) leads to bad adhesion between the layers and consequently to unsatisfactory results in corrosion tests (stains and detachments of coatings are often observed). In this work, a suitable approach was developed. Pre-treatment of aluminium and subsequent electroless deposition of zinc provide a suitable base substrate for the electrodeposition of common metal coatings used in the fashion-jewellery industry. Corrosion tests show that mechanical pre-treatment of the substrate is not paramount: the developed galvanic process can provide excellent results even by making use of unpolished substrates. Once the corrosion tests have been carried out, no major defects can be seen on the surface of the external coating (Pd-Ni), which proves the good corrosion resistance and excellent interconnection between the lower and upper layers.

4. Conclusions

The Al6082 alloy was characterized and plated by means of an innovative alkaline cyanide-free solution kindly provided by Valmet Plating Srl. In particular, both polished and unpolished aluminium samples were evaluated: profilometer and AFM measurement were used to determine their roughness. Polished Al6082 had a lower roughness (1.98 µm) compared to non-polished aluminium (6.55 nm). By means of SEM analysis, surface images and composition were collected. Al6082 contains minor percentages of Si, Fe and Mg. Prior to galvanization, samples underwent a pre-treatment with the purpose of cleaning and activating their surface in order to improve the adhesion between the base material and the very first layer of zinc being deposited. A fluoride-based solution turned out to be effective in decreasing the number of shallower silicon atoms, the high presence of which is otherwise detrimental when it comes to zinc-aluminium adhesion. The fluoride-based treatment decreased the surface silicon content from 1.3% to 0.5%. A double zincating step followed by nickel-plating was performed for each sample using different nickel-

plating times. The thickness of the zinc layer was measured by means of XRF for both the unpolished as well as for the polished samples, obtaining 29 ± 6 nm and 23 ± 1 nm values respectively. Cross-section analysis shows interlocked layers and both unpolished as well as polished plated samples surpassed the ISO-compliant adhesion test; indeed, detachment phenomena were not observed for any of the samples being electroplated. Therefore, the samples pre-treatment and the cyanide-free zincating step are suitable for Al6082 substrates of different roughness. In particular, mechanical preparation of the items prior to electroplating turned out not to be mandatory since no influence in the adhesion has been highlighted. In addition, the further electroplating through white bronze and Pd-Ni galvanic baths underlined that producing Al6082-based fashion items able to withstand the main ageing tests employed within the decorative electroplating sector is feasible.

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