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Improvement in Adhesion Behavior of Aluminum Due to Surfaces Treatment with Arc Discharge

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Abstract

Adhesive bonding of aluminum requires activating of part surfaces to improve the adhesion process. In the present study, The influence of arc discharge on the adhesion of epoxy, polyurethane and acrylic adhesives to aluminum is investigated whereby the influence of arc discharge parameters (amperage, frequency, work distance and treatment speed) on the improvement of adhesive strength are examined. Changes in surface topography and chemical composition of the surfaces are also identified, using Scanning Electron Microscopy (SEM) and Energy Disperse X-ray analysis (EDX).The results indicated that, two-components epoxy and polyurethane adhesives enable high adhesive strength, in comparison to thermosetting of single component epoxy. Similar behavior was determined for cold setting of two-component acrylic adhesive. Cohesive rupture was found in the two component epoxy and acrylic adhesives to be predominant. The rupture occurred in the layer nearby the aluminum surface whereby the rupture took place cohesively in the center of the adhesive layer in the polyurethane adhesive joint. The adhesion improvement achieved can be attributed to increasing roughness, complete removal of organic layers and reduction of inorganic magnesium oxide layers

Keywords: Arc Discharge, Adhesive Strength, Surface Pretreatment, Epoxy Adhesives (One-Component, Two-Components), Acrylic and Polyurethane Adhesives.

1. Introduction

In industrial applications, surface pretreatment of Al samples is a must to achieve strong and stable adhesion. Chemical and electro-chemical pretreatment of Al surfaces exhibit favorable adhesion. Disadvantages regarding those pretreatment methods are the disposal of chemicals involved, long pretreatment times and high operating costs. For said reasons, the application of mentioned or similar pretreatment methods is not recommended in many industries. On the other hand, mechanical pretreatments result often in unsatisfactory adhesion and long-term stability. The results of adhesion and long-term behavior of excimer- and CO_2-laser treatments show also some restrictions. The application of arc-discharge pretreatment methods could be considered as an alternative technique. Research related to arc-discharge pretreatment is limited right now. This art of pretreatment could be considered to fulfill both requirements, environmentally friendly preparation method, and could be developed to be fully automated in the industry.

2. Literature Review

For initial strength bonding, degreasing of Al surface is sufficient, whereas long-term-steady joints require a mechanical, chemical or electro-chemical pretreatment. Chemical and electro-chemical pretreatment produces reliable adhesion if suitable adhesive and primer were selected [1]. In summary, an oxide coating must develop as a result of the pretreatment, which stabilizes and enlarges the joint surface area and thus increases the interactions between adhesive and Al surface [1-27]. Surface anodizing with phosphoric, sulphuric, chromic acid or pickling agents provides excellent results because the adhesive, with the oxide coating, forms a composite structure [1, 9]. After Digby and Packham [6], the penetration of adhesive depends on the wetting behavior and viscosity of the adhesive and cavity dimensions. Disadvantages regarding the disposal of chemicals, high operating cost and long pretreatment times oppose application in automobile and vehicle industry.

Environmental-friendly pretreatment methods include: Excimer laser [12], CO_2-laser [20, 21], cryoblasting [13], dry ice blasting [19], organosilane [22-26], warm or boiling water [15, 27] and arc-discharge [14]. The application of excimer laser leads to removal of organic contamination, to an increase of the surface roughness and porosity, which results in an increase of adhesive surface and supplies satisfactory long-term stability [12]. CO_2-laser treatment causes a removal of organic contamination and an increase of the oxide coating thickness from 10 nm up to 85 nm, and a reduction of the Mg:Al ratio [9, 10]. Adhesive strength and long term behavior of CO_2-laser pretreated surfaces is satisfactory compared with cryoblasting and dry ice blasting treated samples [13,19]

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whereas the long term stability of sandblasted Al surfaces is insufficient [11]. Adhesion and long-term endurance of Al surfaces treated with arc-discharge correspond to chemical pretreatments [14]. The use of organosilane pretreatment has shown to be effective in increasing the adhesive joint strength and the joint durability [22, 24]. Samples pretreated with warm or boiled water shows improvement in the adhesive performance due to the formation of hydroxyl layer. Those hydroxyl layers improve the molecular interactions with the adhesives. Furthermore, the layers show porous and highly rough surfaces that are responsible for mechanical interlocking with the applied adhesives, [15 and 27]. The chemical interactions resulting in a “micro/nano-composite” inter-phase leads to no appreciable loss in peeling resistance after aging in warm water or exposure to a corrosive environment [27].

3. Test Materials and Conditions

Throughout this project, Metallic partner's as used by automobile industry for body application was 1 mm thick aluminum sheet (AlMg4, 5Mn0, 4). Sheets were supplied by VAW Aluminum AG/Germany.

The adhesives were selected to fulfill industrial requirements as used by the automobile industry, like high strength, ductility, as well as high temperature and aging resistance. The two-component cold setting epoxy adhesives (Araldite 2011 (EP 1) and Permabond E 32 (EP 2)), the two-component cold setting polyurethane adhesive (Tivopur 1667+1600/07 (PU)) and the two-component cold setting acrylic adhesives (Permabond 6050 (AC 1) and Quickbond 5002 (AC 2)) were tested. In addition to the two components, single component thermosetting epoxy adhesives ESP 109 (EP 3) and ESP 104 (EP 4) were tested. Permabond/Germany provided us with the epoxy resin EP 2, 3, 4 and acrylic adhesives AC 1 and AC 2. Spezialitätenchemie GmbH/Germany provided the epoxy adhesive EP 1. PU was supplied by Tivioli Werke/Germany. The thermosetting epoxy adhesive ESP 104 is suitable because of its relativity to fast hardening at low temperature and its ability to glue plastics sensitive to high temperature. The adhesive EP 1 contains bisphenol A-epoxy resin with a molecular weight smaller than 700, 3-Dimethylaminopropyl and 1, 3-Propylenediamin. The adhesive EP 3 contains magnesium oxide filler. In the PU adhesive, the A-component consists of polyolen, fillers and 10-25% polyether modified bisphenol whereas the B-component contains a isocyanate hardener, Diphenylmethan, -4, 4`-diisocyanat (<75%) and Hexamethylen-1,6-Diisocyanat (0,1-1%). The acrylic adhesive AC 1 uses a multi-phase technology to reduce crack growth by embedding microscopically small rubber particles. **Table 1** indicates the adhesives selected that was investigated in this project.

Table 1. Used adhesives and processing conditions

Adhesive basis	***two-component epoxy***		single component epoxy	
Manufacturer	Ciba Spezialitätenchemie	Permabond	Permabond	Permabond
Trade name	Araldite 2011	Permabond E 32	ESP 109	ESP 104
Abbreviation	EP 1	EP 2	EP 3	EP 4
Resin A	Aradite 2011A	Resin A	ESP 109	ESP 104
Hardener B	2011B	Hardner B	-	-
Mixing proportion A:B	100:80 (wt. parts)	1:1 (vol.-parts)	single-component	single-component
Pot life	85 min at 30°C	120 min at RT	-	-
Processing	Manually	Manually	Manually	Manually
Hardening conditions	30 min bei 80°C	45 min at 60°C	90 min at 120°C	60 min at 100°C

Adhesive basis	***Polyurethane***	Acrylic	
Manufacturer	Tivoli	Permabond	Permabond
Trade name	Tivopur 1667	Permabond 6050	Quickbond 5002
Abbreviation	PU	AC 1	AC 2
Resin A	Tivopur 1667	-	Harz A
Hardener B	Tivopur 1600/07	-	Härter B
Mixing proportion A:B	100:30 (wt. Parts)	1:1 vol. parts	1:1 (vol. parts)
Pot life	14 min bei RT	5 min bei RT	3 min bei RT
Processing	Manually	Static mixer	Bead on bead
Hardening conditions	48 h at RT + 3 h at 100°C	24 h at RT	24 h at RT

The Al sheets as received were contaminated and were covered with a layer of oil. Therefore the surfaces were cleaned and degreased with ultrasonic activated ethanol for 5 min and dried with oil-free compressed air. To achieve optimal adhesion, the surfaces were afterwards treated by spark discharge under argon. A Navigtor 240 AC/DC V-box 1 was used. **Fig. 1a** shows the experimental setup for the pretreatment. Variable pretreatment parameters were selected; amperage (5, 10 and 20 A), frequencies (100, 200 and 300 Hz), and the treatment speed (25, 50, 75, 100 and 150 cm/min). The distances between electrode and Al surface (2 and 4 mm) were chosen. Tungsten electrodes with a diameter of 1.6 mm were used, considering that the Al surface was acting as a cathode, whereby the electrodes were used as anode.

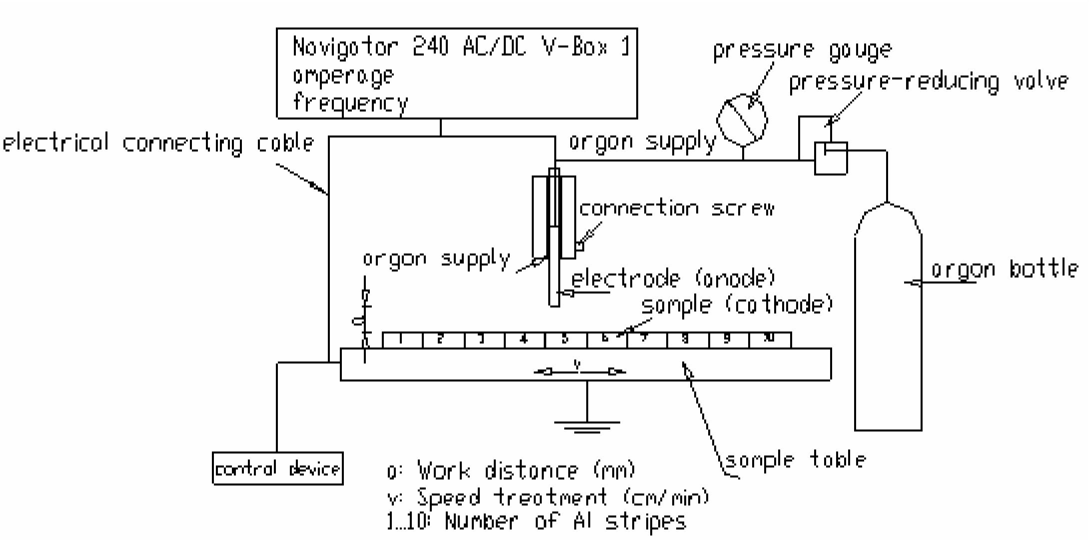


Fig. 1a. Experimental setup used throughout the investigations.

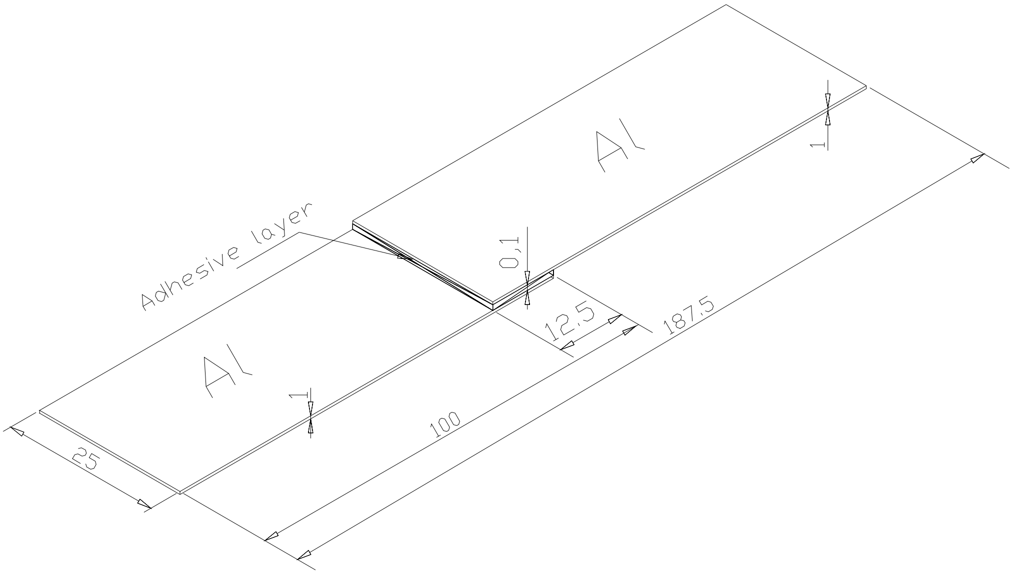


Fig. 1b: Sample dimensions and form

The two-component adhesives EP 1, EP 2, PU were mixed manually, degassed in vacuum for some minutes to avoid bubbles. The single component epoxy adhesives EP 3 and EP 4 were laminated by a cartouche pistol on the Al sheets. For keeping an even layer of 0.1 mm adhesive thickness, copper wires of 0.1 mm diameter were inserted. To keep a constant applied pressure, a device with constant weights was used. The adhesive joints were warm-hardened in a circulating air furnace, **Table 1**. Resin and hardener with the AC 1 were supplied in chamber cartouches with static mixer. The joining parts were fixed into appropriate device by means of pressure weights, so that they do not slide. The adhesive AC 2 was spread by double chamber cartouches in the "Bead on bead" procedure. The adhesive hardening by AC 1 and AC 2 took place at ambient temperature within 24 h, **Table 1**.

To determine adhesive strength, single overlapped tensile shear test specimens were used according to DIN EN 1465. **Fig. 1b** shows the specimen shape and dimensions. To measure the adhesion, strength mechanical test were conducted. The samples were pulled on an instron tensile testing machine with a test speed of 5 mm/min under normal climate. For each test series 5 samples were examined, from which the average strength was determined. To see the topographic structure of the differently pretreated Al surfaces as well as the fractured occurred on the fractured surfaces, Scanning Electron Microscopy (SEM) was used. EDX analyses were applied to determine the chemical composition of Al surfaces before and after treatment. Furthermore EDX was used to determine where fracture took place on the fractured samples

4. Test Results

The organic layers on Al surfaces represent residuals of the lubricating oil during the rolling process of Al sheets as well as contamination from the environment, which minimized the adhesion. Degreasing the samples with ethanol did not cause a complete removal of organic and hydrocarbon layers as well as inorganic MgO layers. After degreasing, the carbon concentration on sample surface (area integral) decreased up to 1%, and the oxygen decreased insignificantly, Table 2. Arc-discharge lead to the complete removal of organic hydrocarbon layers and reduced the inorganic MgO layers. Magnesium concentration was reduced independently of the treatment parameters approximately 3%. The reduction of oxygen concentration was influenced by the treatment parameters. The Al concentration increased in the outer surfaces after arc-discharge by 7% in relation to the delivered state. After arc-discharge the elements manganese and iron were found. This could be related to elements presents in the Al alloy. The concentration of these elements did not show significant dependence on amperage, treatment speed and work distance, **Table 2**.

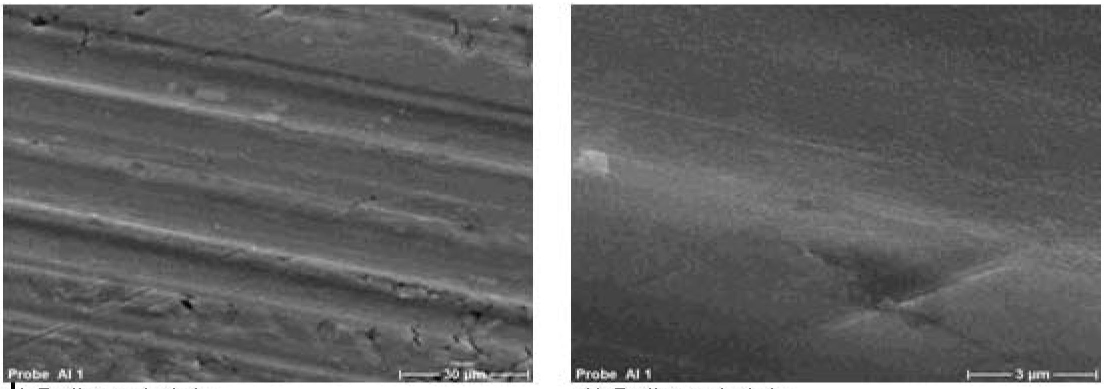
SEM photographs show that arc-discharge causes a strong surface roughness in relation to the delivered and degreased surfaces, **Fig. 2, 3**. Arc-discharge changes the topographic structures. The topography changes were strongly influenced by treatment parameters, work distance, amperage, frequency and speed; however speed was not significant as the other parameter. At a 4 mm work distance, the surface shows cotton wool-topographic structures. Magnification (10000) shows this microstructure very clearly, **Fig. 2d, f.** At 20 A current, the surface roughness is more pronounced with a pretreatment speed of 100 cm/min rather than with 50 cm/min, **Fig. 2g, h**. **Fig. 3 a and b** show the surface topography at 100 Hz and 2 mm distance. The structure was a homogenous fine grain structure. Increasing the frequency to 200 Hz influenced the structure and generated a semi fine-rough structure, **Fig. 3c, d**. At 4 mm distance, the structure was homogenous and rougher at 200 Hz than 100 and 300 Hz, **Fig. 3e, f, g**.

Fig. 4, 6-8 indicates the Influence of the treatment parameters of arcs on the determined average adhesive strength of Al surfaces bonded with epoxy adhesive EP 1, EP 2, EP 3, and EP 4, and polyurethane adhesive (PU), and acrylic adhesive AC 1 and AC 2. The adhesive strength of Al - arc-discharge pretreated surfaces depends strongly on adhesive type. In this report, it is clearly indicated that treatment parameters have low impact on the adhesion.

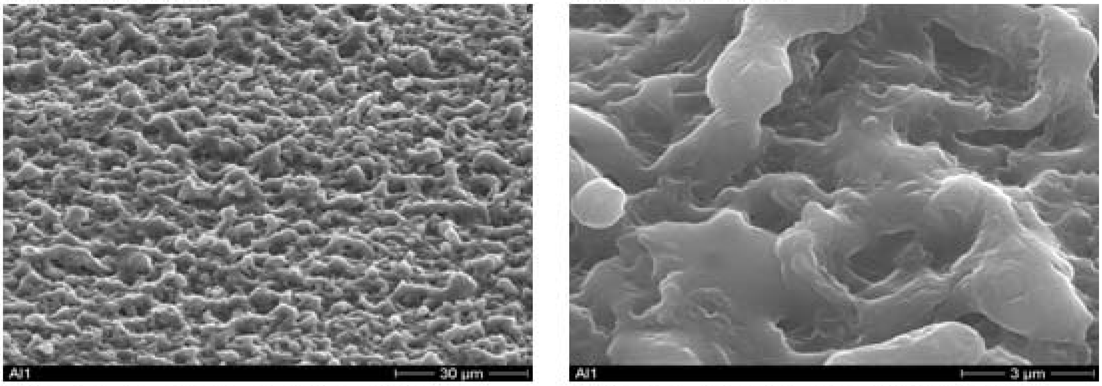
Table 2. Chemical composition (area integrals) of differently pre-treated aluminum surfaces

Pretreatment	Area integrals [COUNTS of the x-ray quanta in %]					
Elements	C	O	Mg	Al	Mn	Fe
None (Delivered state)	2.045	3.345	8.857	85.75		
Ethanol degreased	0.928	2.834	8.279	87.96		
5 A, 200 Hz, 50 cm /min, 2 mm		0.959	5.612	92.83	0.316	0.286
5 A, 200 Hz, 100 cm/min, 2 mm		1.067	5.812	92.58	0.301	0.240
5 A, 200 Hz, 50 cm/min, 4 mm		2.092	5.100	92.21	0.311	0.284
5 A, 200 Hz, 100 cm/min, 4 mm		1.651	5.428	92.21	0.333	0.378
10 A, 200 Hz, 50 cm/min, 2 mm		1.089	5.233	93.14	0.287	0.249
10 A, 200 Hz, 100 cm/min, 2 mm		1.002	5.581	92.82	0.315	0.283
10 A, 100 Hz, 100 cm/min, 2 mm		0.958	5.708	92.71	0.289	0.335
10 A, 300 Hz, 100 cm/min, 2 mm		1.245	5.426	92.71	0.298	0.322
10 A, 200 Hz, 50 cm/min, 4 mm		1.208	5.045	93.04	0.337	0.367
10 A, 200 Hz, 100 cm/min, 4 mm		1.243	5.302	92.78	0.314	0.362
10 A, 100 Hz, 50 cm/min, 4 mm		1.212	5.616	92.48	0.325	0.370
10 A, 300 Hz, 50 cm/min, 4 mm		0.999	5.269	93.13	0.331	0.270
20 A, 200 Hz, 50 cm/min, 2 mm		1.476	5.532	92.41	0.317	0.264
20 A, 200 Hz, 100 cm/min, 2 mm		0.938	5.354	93.03	0.353	0.323

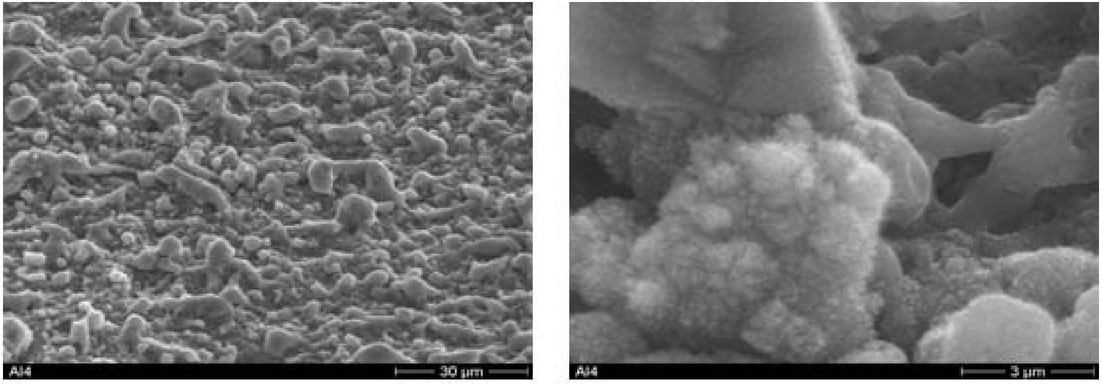
The adhesion of the two-component epoxy cold setting was improved approximately by 9-29% when the surface was arc treated for EP 1 type and 40-77% for EP 2, respectively, **Fig. 4**. The Adhesion depended strongly on the amperage but slightly on work distance and treatment speed applying EP 1. The adhesion values for samples treated with 5 and 10 A are 2-2.5 MPa, higher than samples treated with 20 A. Degreasing the samples with ethanol, the adhesive strength decreases in relation to the delivered state approximately 40%. The same sample pretreated by arc-discharge, the adhesion increased to double as compared to degreased sample, **Fig. 4**. Visual inspections show that the samples glued with EP 1 and EP 2 failed independently of pretreatment parameters in the boundary layer between adhesive and Al surface. Fig. 5 a and b show the SEM photographs of fractured Al joint glued with EP 1 and EP 2. SEM photograph of fractured joint glued with EP 1 shows, when samples pretreated at 10 A, 2 mm and 50 cm/min, traces of cohesive rupture in the adhesive layer, **Fig. 5a**. EDX analysis of the fracture surface showed the elements carbon, oxygen, magnesium,



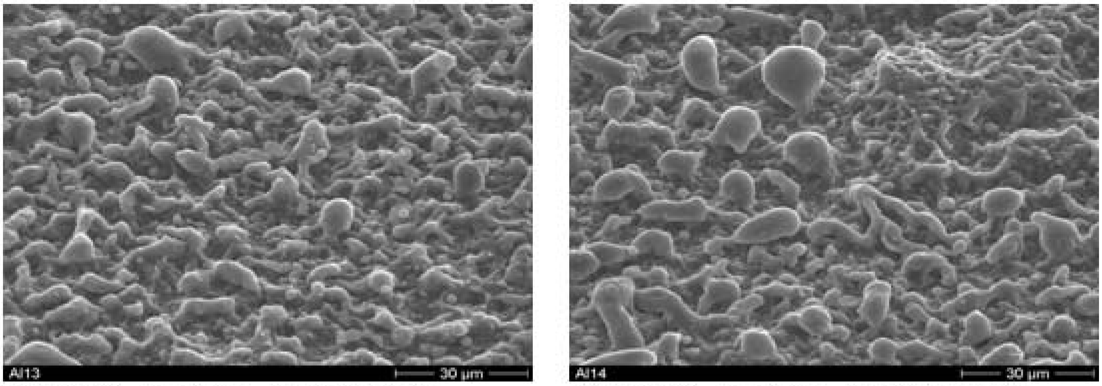
a) Delivered state b) Delivered state



c) I = 5 A, a = 2 mm, v = 50 cm/min d) I = 5 A, a = 2 mm, v = 50 cm/min

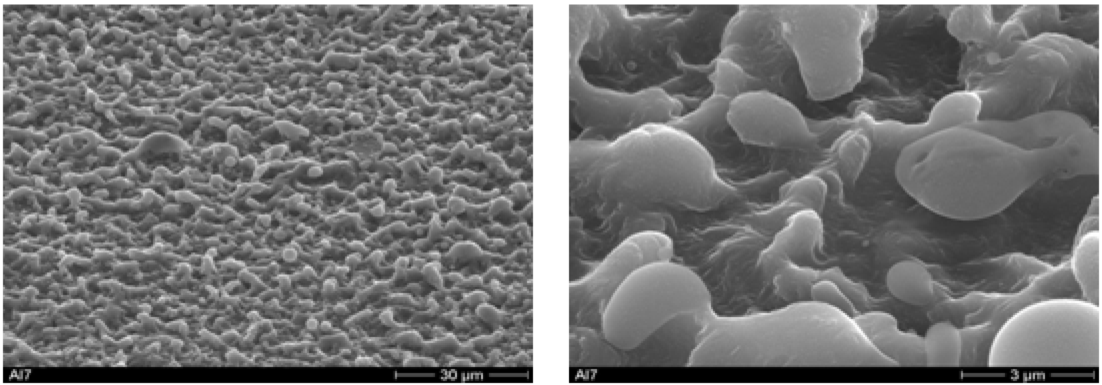


e) I = 5 A, a = 4 mm, v = 100 cm/min f) I = 5 A, a = 4 mm, v = 100 cm/min

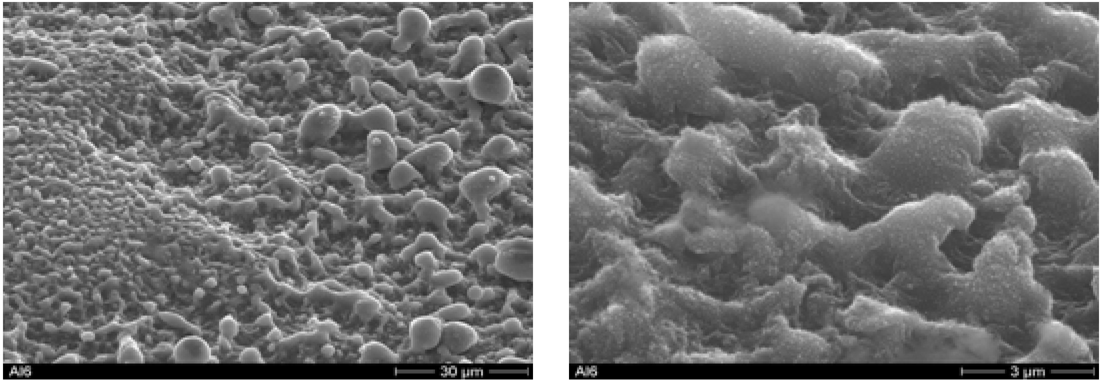


g) I = 20 A, a = 2 mm, v = 50 cm/min h) I = 20 A, a = 2 mm, v = 100 cm/min

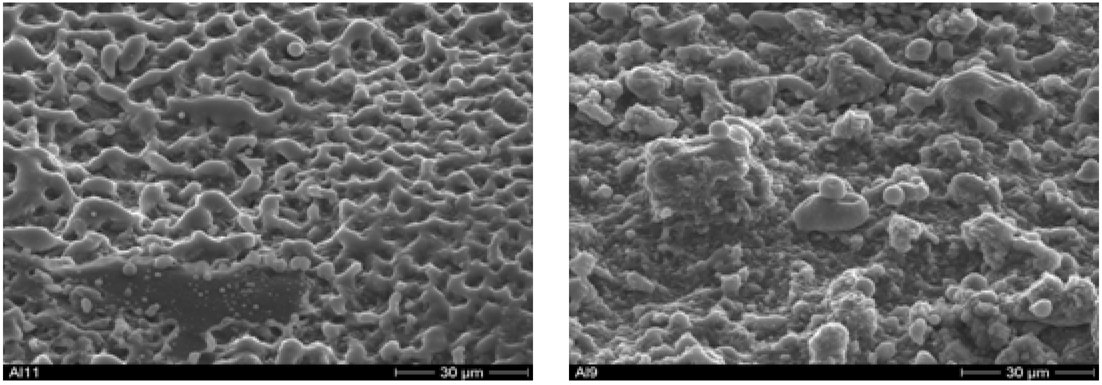
Fig. 2. Topographic structures of aluminum surfaces pre-treated with arc discharge. Frequency = 200 Hz. I: Amperage, a: Work distance, v: Treatment speed



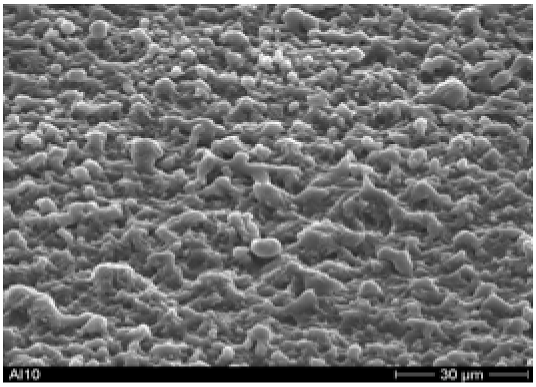
a) F = 100 Hz, a = 2 mm, v = 100 cm/min b) F = 100 Hz, a = 2 mm, v = 100 cm/min



c) F = 200 Hz, a = 2 mm, v = 100 cm/min d) F = 200 Hz, a = 2 mm, v = 100 cm/min



e) F = 100 Hz, a = 4 mm, v = 50 cm/min f) F = 200 Hz, a = 4 mm, v = 50 cm/min



g) F = 300 Hz, a = 4 mm, v = 50 cm/min

Fig. 3. Influence of the treatment parameters of arc discharge on the topographic structures of aluminum. Amperage = 10 A. F: Frequency, a: Work distance, v: Treatment speed

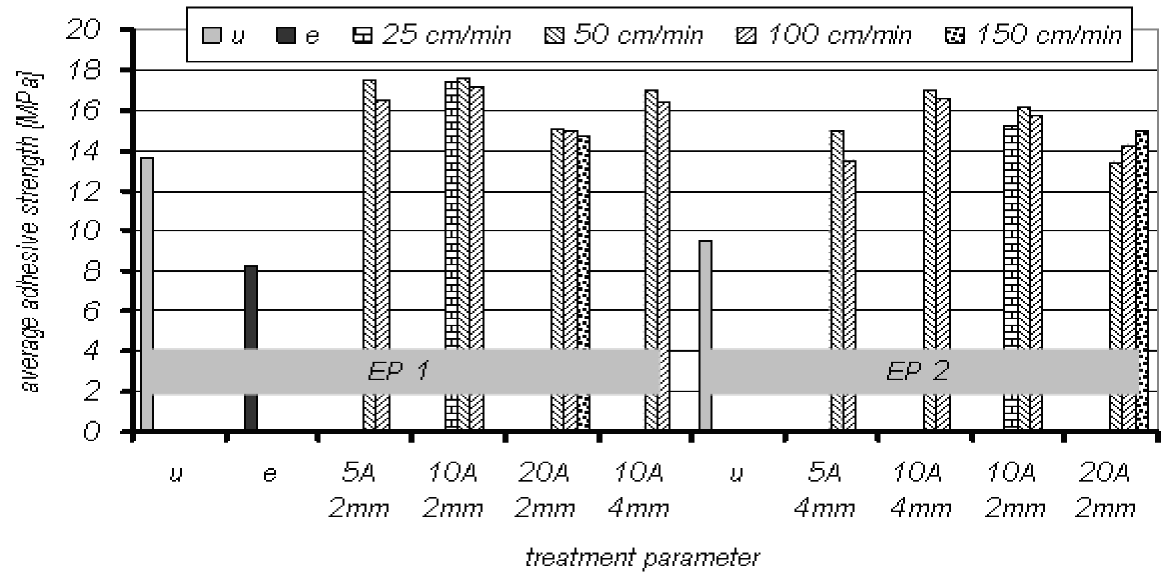


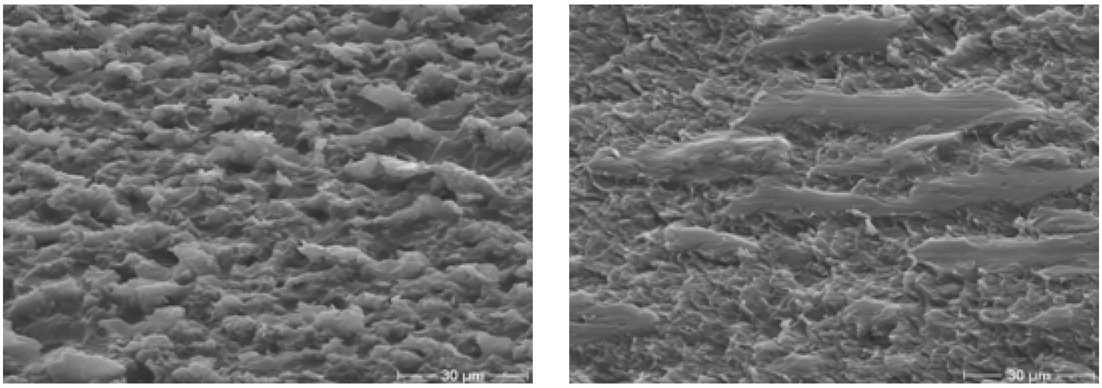
Fig. 4. Influence of the treatment parameters of arcs on the determined average adhesive strength of aluminum surfaces bonded with epoxy adhesive EP 1 and EP 2. u: untreated, e: ethanol degreased.

Al and silicon, **Table 3**. From SEM photographs and EDX analyses, it can be concluded that the rupture was cohesively in the adhesive layer and took place closely to the Al surface and in the oxide layer. SEM photographs of fractured Al joint glued with EP 2 indicate that oxide layers were pulled out partially from the aluminum surface, **Fig. 5b**. Further it could be concluded that the fracture was adhesively between oxide and adhesive layer. EDX analysis indicated that Al oxide on both fracture surfaces was available, that is to some extent responsible for the increase of adhesion **Table 3.** The rupture occurred cohesively in the adhesive layer since on both fracture surfaces carbon and calcium were present, **Table 3**.

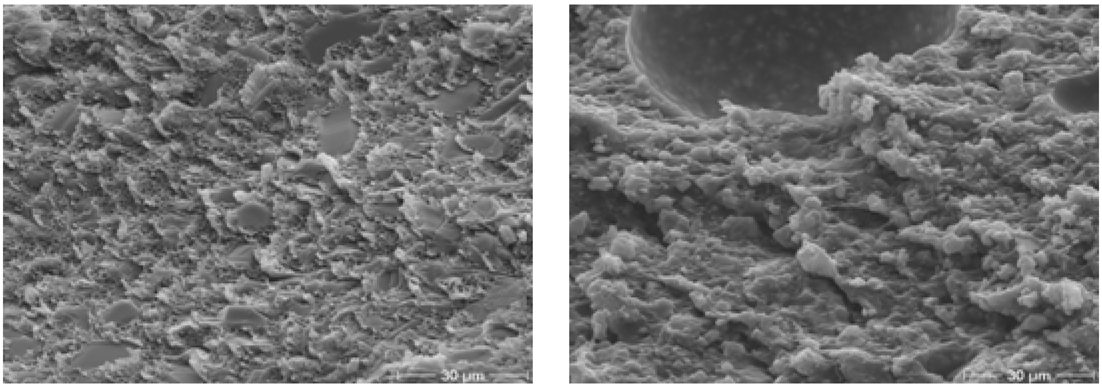
Table 3. Chemical composition of the fracture surfaces with different adhesives after arc discharge pretreatment of aluminum surfaces

Pretreatment parameter / Adhesives		Area integrals [COUNTS of the x-ray quanta in %]							
		C	O	Mg	Al	Si	Ca	Cl	K
10 A, 200 Hz, 2 mm, 50 cm/min, EP 1	A	5.823	2.084	7.01	84.47	0.614			
	B	87.18	9.553		0.911	2.352			
10 A, 200 Hz, 4 mm, 50 cm/min, EP 2	A	27.51	6.650	6.558	53.87	4.917	0.492		
	B	66.98	13.17	3.078	3.021	9.713	3.442	0.593	
20 A, 200 Hz, 2 mm, 75 cm/min, EP 3	A	29.39	14.36	51.14	0.508	4.165	0.426		
	B	31.83	8.090	7.705	48.79	3.400	0.184		
10 A, 200 Hz, 4 mm, 50 cm/min, PU	A	53.70	18.24		1.077	5.098	21.41		0.475
	B	58.21	18.39		1.703	4.866	16.47		0.356
5 A, 200 Hz, 2 mm, 50 cm/min, AC 1	A	45.47	10.48	2.967	38.68	2.402			
	B	77.84	17.02		0.569	4.577			
5 A, 200 Hz, 2 mm, 50 cm/min, AC 2	A	31.47	8.669	4.370	54.84	0.653			
	B	80.34	17.59	0.246	1.285	0.529			

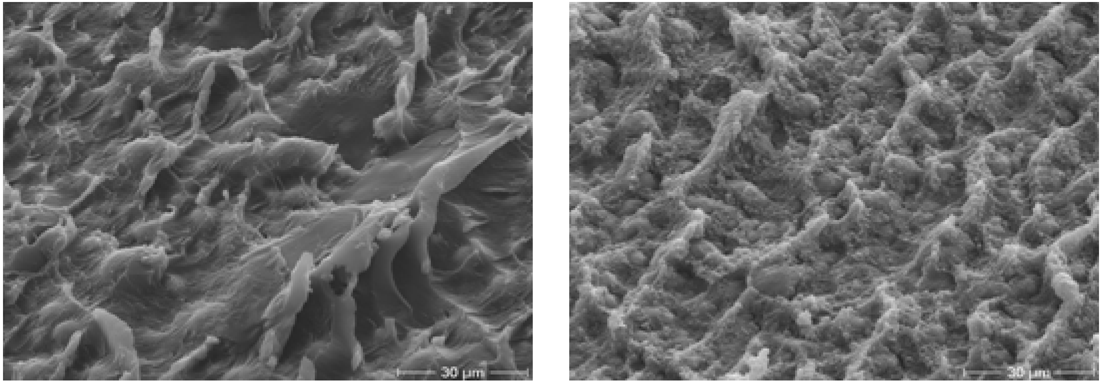
A and B are the opposite fracture surfaces for each sample



a) EP 1; I = 10 A, a = 2 mm, v = 50 cm/min, F = 200 Hz   b) EP 2; I = 10 A, a = 4 mm, v = 50 cm/min, F = 200 Hz



c) EP 3; I = 20 A, a = 2 mm, v = 75 cm/min, F = 200 Hz   d) PU; I = 10 A, a = 4 mm, v = 50 cm/min, F = 200 Hz



e) AC 1; I = 5 A, a = 2 mm, v = 50 cm/min, F = 200 Hz   f) AC 2; I = 5 A, a = 2 mm, v = 50 cm/min, F = 200 Hz

Fig. 5. Fracture surfaces of aluminum bonded with different adhesives. I : Amperage. F : Frequency, a : Work distance, v : Treatment speed.

For the single component epoxy adhesive EP 3, the adhesive strength is approximately 30% lower after sample treatments with arc-discharge in relation to the sample as delivered, **Fig. 6**. The adhesive strength is higher with 10 A compared to 20 A. Degreasing the Al sheets with different solvents before arc-discharge has small influence on adhesion. The rupture took place independently of the treatment parameters in the boundary layer between adhesive and Al surface. SEM fracture analysis exhibited fine porous surface texture, **Fig. 5c**. The presence of carbon on both fracture surfaces demonstrated that the rupture in the adhesive layer took place. EDX analysis of the fracture surface (**Table 3**) provided higher magnesium concentration as compared with the pretreated Al surface (**Table 2**), since MgO was added as filler in the formulation of the adhesive. After [16] heat curing of adhesives causes a drastic increase of magnesium concentration in the surface due to diffusion of Mg^{2+}-Ions from the adhesive mass. According [18] less adhesion rupture occurs with thermosetting adhesives because the deposit of magnesium in the boundary layer during hardening process reduces the adhesion, so that the fracture occurs partially in the magnesium-rich layer. Further, magnesium can favor the electro-chemical dissolution of Al [16].

The thermosetting single component epoxy adhesive EP 4 increases adhesion of arc-treated Al surfaces only slightly compared to untreated ones, **Fig. 6.** The samples failed predominantly adhesively.

PU adhesive causes an increase adhesion after arc-discharge of approximately 10-23%. The adhesion is only slightly dependent of the treatment parameters, **Fig. 7**. The rupture changed from the mixed fracture in the delivered state to coherence rupture after arc-discharge, **Fig. 5d**. Closed bubbles were seen, generated during the hardening process.

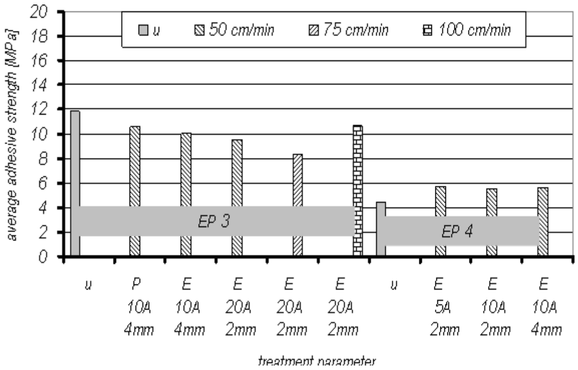


Fig. 6. Influence of the treatment parameters of arcs on the determined average adhesive strength of aluminum surfaces bonded with epoxy EP 3 and EP 4 adhesive. u: untreated, E: ethanol degreased, P: Permaclean degreased

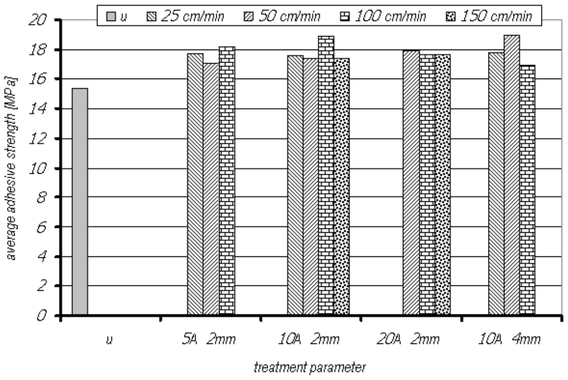


Fig. 7. Influence of the treatment parameters of arcs on the determined average adhesive strength of aluminum surfaces bonded with polyurethane PU adhesive. u: untreated

The adhesive strength for the two-component acrylic adhesives AC 1 and AC 2, increase after arc-discharge treatment up to 17% and 23%. The adhesive strength values differ slightly in relation to the different treatments parameters, **Fig. 8**. Samples with AC 1 adhesives failed in the delivered state adhesively in the boundary layer between the Al and adhesive. With increasing adhesive strength, the samples show both adhesive and cohesive rupture, **Fig. 5e**. Samples with AC 2 adhesives exhibit in delivered state and after arc-discharge adhesion rupture in the boundary layer between Al and adhesive, **Fig. 5f**. AC 1 shows higher adhesive strength than with AC 2.

Change the arc-discharge frequency from 100 to 200 and 300 Hz, the adhesive strength increases with EP 1, EP 2 and AC 1 slightly, whereby the adhesive strength increases with PU obvious more, **Fig. 9**.

Table 4 shows the differences between the measured maximum and minimum adhesive strength values for each adhesive as a function of the pretreatment parameters

5. Conclusions

Arc-discharge of Al sheets causes a strong improvement of adhesion on Al surfaces, which exceeds the adhesive strength of sand-blasting. **This fact was investigated and reported by Anagreh, etc [18].** This was related to the strong roughening of the surface topography, and thus an increase of the surface area. The adhesive penetration in the porosity, the removal of organic contamination layers (lubricating oil and contamination) and the strong reduction of inorganic magnesium oxide layers contribute to the increase in adhesive strength. The cold setting two-component epoxy adhesives show strong adhesive strength compared to the thermosetting single component epoxy adhesives. Maximum adhesive strength was achieved using polyurethane adhesive. Two-component acrylic adhesives indicate lower adhesive strength than the two-component epoxy and polyurethane adhesives. SEM photographs and the EDX analyses of fracture surfaces point out that the rupture occurred with the epoxy and acrylic predominantly cohesively in the adhesive layer closely to the Al surface. Polyurethane adhesive shows different behavior, and the sample failed cohesively in the center of adhesive layer.

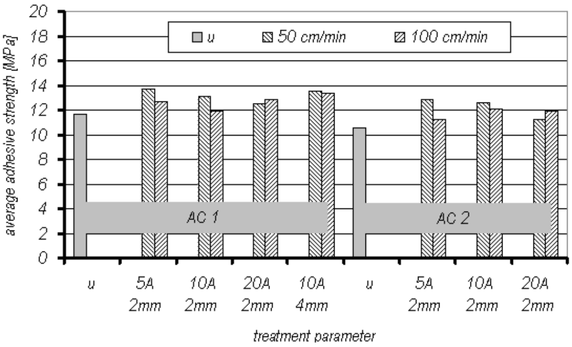


Fig. 8. Influence of the treatment parameters of arcs on the determined average adhesive strength of aluminum surfaces bonded with acrylate AC 1 and AC 2 adhesive. u: untreated

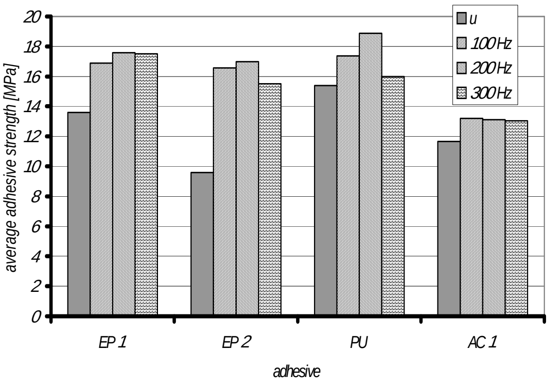


Fig. 9. Influence of the frequency on the determined average adhesive strength of aluminum surfaces bonded with different adhesives. u: untreated.

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