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Influence of Surface Treatment on the Surface Energy of an Aluminium Substrate

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Abstract

The mechanisms by which adhesion occurs are known. In all cases, the search for an adequate surface condition is decisive in achieving a good adhesion. For this reason, the researches usually work on modifying the surface roughness or improving the thermodynamic characteristics of the surface. The objective on this work is to analyse influence of different attack types (chemical, mechanic, with laser ...) which are used to improve surface finish, roughness and surface energy. We have analysed the effects that have produced in the contact angle, measuring the surface energy by the Zisman method. The results revealed that the method of attack has more influence on the value of surface energy than the values of roughness obtained, which can make rethink the type of surface treatment to improve adhesion.

Keywords: Surfaces; Surface treatment; LSP; Roughness; Contact angle; Zisman.

1. Introduction

The analysis of the strength characteristics of an adhesive joint is usually studied from a phenomenological point of view. The results obtained in the tests performed on the adhesive bond are explained as one of the various mechanisms involved in the adhesion. The one that best explains their behaviour is looked for.

However, in recent years there has been the need for a better understanding of the physical and chemical interactions in the adhesive-substrate interface and their consequences on the outcome of the adhesive bond [1]. This requirement has been caused by the use of polymers as components such as semiconductors and electronic and optoelectronic devices [2, 3].

Adhesion is a surface phenomenon. The thickness in which interactions adhesive substrate (known as adhesive interface) has an order of magnitude of intermolecular distances [5, 6, 7], therefore it is necessary to control the state in which is the surface on which to apply the adhesive. Before performing an adhesive bonding, the substrate surface is treated, not only to clean off any impurities adhering at the same but to optimize adhesion. At other times the surface treatment has the function to facilitate the crosslinking of the adhesive, performing the function as an activator [8], or protecting the substrate surface, especially in the case of metals [9].

There are many surface treatments for preparing surfaces for each adhesive [10, 11, 12]. Each of these treatments acts on the surface differently. In general, they modify surface topography, which can lead to structural changes and, as a result, thermodynamic changes [13, 14, 10].

In different studies the effect of surface roughness on adhesion has been considered [15, 16, 17, 18]. The way to get this surface roughness is varied but, as said, in all cases aggression occurs to the grain

structure of the metal [19]. Studies on the effects of these attacks are analysed by considering the mechanical effects that come about at the adhesive bonding [20, 21, 22]. However, the study of the effects they cause on the crystallographic structure of the surface is very scarce.

On the other hand, the wetting of the surface by the adhesive represents the relationship between the surface energy of the substrate and the surface tension of the adhesive. Wetting can be described by two processes: spreading and penetration of the fluid adhesive into the surface cavities, characteristics of surface roughness. The first process is regulated by the relative surface energies of the adhesive and the substrate. The second is regulated mainly by the viscosity of the adhesive and the time remaining in the liquid state.

In this work, different attacks and treatments are carried out, both chemical and mechanical. These will modify the surface crystalline structure, which will produce modifications simultaneously, both in the surface topography and in the thermodynamic characteristics of the interface.

Therefore, these changes will have an influence on the adhesion characteristics between the adhesive and the substrate. In this way, the influence of different attacks on the mechanical mechanism of adhesion and thermodynamic adsorption will be seen.

2. Methodology

As has been mentioned previously, for the realization of this article, roughness tests, crystallographic and thermodynamic characterization of the surfaces have been carried out. For this purpose, the choice of surface treatments to be made to the test pieces was first made. The selected treatments were manual sanding, alumina blasting, Laser Shock Processing (LSP) and two chemical processing consisting of immersion in hydrochloric acid with two different concentrations. Besides, a piece in furnished conditions was analysed.

2.1. *Materials and Surface Treatments*

For the achievement of this study, samples of a laminated aluminium alloy of the series EN AW 6060 in dimensions 100 x 40 x 8 (mm) were used to perform the surface treatments. Of the six different surface treatments, four have been mechanic and two have been chemical. The mechanical treatments have been: sand blasting, manual sanding with two different grades and Laser Shock Processing (LSP). Two chemical treatments have been performed: acid attack 0,5M and 0,6M.

The sandblasting was performed on two specimens in the delivery state. The used equipment has been a Guyson, model Euroblast 25Fc. Artificial corundum of 120 μm grain was used as an abrasive, with a pass at 10 cm.

The mechanical abrasion by manual sanding was performed in two specimens, using two different grades: emery paper 40 and 1000 grit, with average roughness of 2 μm and 0,2 μm respectively.

The LSP treatment was performed with a Spectra-Physics Nit: YAG Quanta-Ray PRO 350 laser device pulsed with a maximum energy of 2850 mJ/pulse at the fundamental harmonic. The equipment used comprises an electro-optical Q-switch that generates pulse widths of approximately 10 nanoseconds, achieving a peak power supplied in each pulse of the order of GW. The emission frequency of the laser is fixed and equal to 10 Hz (10 pulses/s) [24]. Figure 1 shows the experimental setup

Figure 1. (a) LSP Experimental Assembly. (b) LSP in operation

In this case, the LSP treatment was programmed to give the specimen 625 pulses/cm².

The chemical attacks were performed by immersion in hydrochloric acid of two different concentrations: 0,5M and 0,6M, for a time of 30 h 30 min [9, 15]. Treatment previously used in P.S. Desai works [27] as well as in other works of the author's working group [18] [22].

In the general reaction of aluminium pitting corrosion produces the dissolution of aluminium for the formation of Al³⁺ ions that in the lower part of the cavity creates an electric field that moves towards the interior of the cavity the ions Cl⁻, which neutralize the solution and form the aluminium chlorides.

The hydrolysis of aluminium chlorides occurs in accordance with:

This will lead to acidification of the lower part of the cavity. Thus, the medium becomes very aggressive, producing self-propagation of the sting. The overall reaction that takes place in this attack is:

2.2. Roughness analysis.

The roughness was measured with a roughness tester Time Group model TR200, with a measuring range between 0,005 and 16 µm. Ra is the roughness parameter which is used in its measure.

2.3. Crystallographic and thermodynamic characterization.

The visual inspection by digital microscopy was performed with a Leica stereomicroscope model EZ4 D model. The objective of this visual analysis was to observe if the treatment was homogeneous or otherwise, there were spot surface defects.

The critical surface energy (γ_c) was measured using the Zisman method according to the UNE-EN ISO 828. With this aim, three of the chemicals mentioned in the standard were chosen whose values of surface tension are shown in the Table:

To determine the critical surface energy and the influence of viscosity, the contact angle of the products must be measured with each of the test pieces, the same procedure being used in both cases.

For the measurement of the contact angle, a profilometer with RAMA 300V optical goniometer was used, adapting to it a tool to redirect the light beam of the profilometer, make it go through the drop and return it to the detector. The system can be seen in Figure 2.

Figure 2. Useful and profilometer used for the measurement of contact angles

On the tool designed to deposit the drop of each liquid, was deposited a drop of 2ml of each of the products. The image was captured, after 10 seconds, and processed using the AutoCAD 2016 graphic design software (Figure 3)

Figure 3. Measurement of contact angle by AutoCad

The balance of forces between the liquid and the solid is expressed by the Young equation [28]:

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL}$$

being γ_{LV} the liquid-vapor interfacial tension, θ the contact angle, γ_{SV} the solid-vapour interfacial tension and γ_{SL} the solid-liquid interfacial tension. Zisman's method has been used to determine the surface energy of solids [29, 30].

3. Results and Discussion

3.1 Roughness obtained for each treatment

Once the surface treatments were performed on the different specimens, the values of the surface roughness were determined, with the following results (Table 2):

Aluminium alloy EN AW 6060					
Surface Treatment	Ra1(μm)	Ra2(μm)	Ra3(μm)	$\bar{Ra}$ (μm)	σ
0,6M HCl	1,195	1,321	1,968	1,495	0,415
0,5M HCl	0,222	0,371	0,200	0,264	0,093
Shot blasting	1,330	1,096	1,188	1,205	0,118
Sanding Grain 40	1,673	1,865	2,018	1,852	0,173
Sanding Grain 1000	0,242	0,172	0,285	0,233	0,057
LSP	2,512	2,648	2,655	2,605	0,081
As furnished conditions	0,054	0,043	0,065	0,054	0,011

In table 2, roughness values to different directions (Ra1, Ra2 and Ra3), average value of surface roughness ($\bar{Ra}$) and its standard deviation (σ) are shown for all treatments. Besides, it can be observed that the treatments that provide the highest roughness values are the LSP, followed by grinding with grain 40 and attack with 0,6M HCl.

In Figure 4, all surfaces of every treatment can be observed on Metallographic microscope images.

Figure 4. Metallographic microscope images 1000x of all samples: (a) 0,6M HCl, (b) 0,5M HCl, (c) Shot Blasting, (d) Sanding Grain 40, (e) Sanding Grain 1000, (f) LSP and (g) As furnished conditions.

In the pictures of Figures 5a) and 5b), it's observed that the surface in the samples treated with attack 0,6M HCl and shot blasting the topography is very similar.

Figure 5. Metallographic microscope image 1000x of a sample of treated aluminum: (a) with 0,6M HCl during 1830min ($R_a \approx 1,495 \mu\text{m}$); (b) with shot blasting ($R_a \approx 1,205 \mu\text{m}$)

In both cases it can be seen that the surface has undergone crystalline grains, those with weaker bonds, either due to the orientation of the crystalline planes, or because they are more exposed to the impact of the abrasive product of the shot blasting.

(a)

(b)

Figure 6. Metallographic microscope image 1000x of a sample of treated aluminum: (a) with sanding grit 40 ($R_a = 1.852 \mu\text{m}$); (b) treatment LSP ($R_a = 2.605 \mu\text{m}$)

However, in the images of Figure 6 the effect of the treatment on the surface is different. While the attack of HCl has eliminated crystalline grains, with the sanding surface texture is produced (Figure 6a), the grains that are in the path of the abrasive are eliminated and the treatment with LSP brings on plastic deformation by compression, eliminating grains that are not able to adapt to crystalline restructuring (Figure 6b).

3.2 Values of the wetting angles of reference liquids

Figures 7 and 8 are an example of the forms that the drops of DIIM and glycerine acquire when deposited on the aluminium samples with LSP, 0,6M HCl, Sanding grain 1000 and 0,5M HCl.

In Figure 7, the images of the DIIM drops deposited in the aluminum specimens with the most representative treatments are presented. The angles are greater in the treatments with lower values of roughness, i.e., with the attack 0,5M and sanding grain 1000

(a)

(b)

(c)

(d)

Figure 8. Image Glycerine drops on treatments (a) LSP, (b) 0,6M HCl, (c) grinding grain 1000 and (d) 0,5M HCl

Figure 8 shows the angles formed by glycerin in the same substrates and with the same treatment as in the previous figure. In this case it is more clearly seen that the angles are more different depending on the treatment. The mechanical treatment produces the lowest values, while the LSP, 0,5M HCl and 0,6M HCl are the ones that produce, in that order, the highest values, always close to 90° .

Finally, with the DMSO treatment, the values of the angles repeat those of the DIIM except in the two sanding treatments, where both values increase.

The values of the wetting angles, corresponding to the standard reference liquids, dimethylsulfoxide (DMSO), diiodomethane (DIM) and glycerine, respectively, for each of the treatments are listed in the table and represented in the Figure 9

Figure 9. Wet Angle Values in Sexagesimal Degrees

The Figure 10 shows the obtaining of the critical energy (γ_c) for the untreated aluminium

Figure 10. Obtaining critical energy (γ_c) by the Zisman method for the untreated aluminium

The values of the surface energy obtained by the Zisman method [30] for each of the treatments are listed in the following table. Also, you can see the relationship between the critical energy of Zisman and the surface roughness:

As can be seen in the table, the highest roughness values correspond to highest critical surface energies (brown values), although not proportionally. It is observed that in the case of sanding grain 1000, with a very low roughness, the energy obtained is similar to treatments with six times greater roughness.

In this table, it can also be seen that the highest value of the critical surface energy is obtained for the treatments with 0,6M HCl, with shot blasting and with LSP, whereas the values of lower critical surface energies are obtained for the less aggressive treatments (blue values), as sanding with 1000 grit or grain 40, or attack with 0,5M HCl.

These variations can see graphically in the Figure 11:

Figure 11. Representation of Surface energy and Roughness to all treatments

The Figure 12 shows three treatments (0,6M HCl, shot blasting and LSP) that provide a very similar critical energy (values less than 5% variation). However, the Ra value obtained is very different (variation values greater than 100%), which indicates the importance of the treatment to activate the surfaces. Even in two impact treatments, such as Shot blasting and LSP, the Ra value is very different.

Figure 12 Representation of " γ_c " and "Ra" vs three treatments (0,6M HCl, Shot blasting and LSP)

4. Conclusions

- The obtaining of a surface roughness can be associated with different values of surface energy depending on the applied treatment.
- There is no direct correspondence between the values of the roughness and those of the surface energies, namely, the roughness, by itself, does not define the surface energy, since it has been seen that the type of treatment also influences.
- The value of the concentration of HCl in the chemical attack has much impact on the value of surface roughness, as well as on the values of the critical energy.
- Considering the value of the critical energies obtained by the Zisman method, one can observe that the most aggressive attacks, such as LSP, Sandblasting or chemical attack with 0,6M HCl, are the ones that cause greatest surface energy, which suggests that the adhesion forces should be higher in the samples attacked with these treatments.

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Figr-19

Figr-20

Figr-21

Table 1. Reference compounds and values of their surface tensions

Liquid	γ (mJ/m ²)
Glycerol	59,40
Diiodomethane	50,80
Dimethyl sulfoxide	43,5

Table 3. Values of the critical surface energy (γ_c in [mJ/m²]) in the specimen, obtained by the Zisman method

Superficial treatment	γ_c	R_a (μm)
0,6M HCl	44,72	1,495
0,5M HCl	39,06	0,264
Shot blasting	42,4	1,205

Sanding Grain 40	39,7	1,852
Sanding Grain 1000	40,47	0,233
LSP	43,06	2,605
As furnished conditions	33,54	0,054

Table 1. Reference compounds and values of their surface tensions

Liquid	γ (mJ/m ²)
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Table 2. Roughness values according to surface treatment.

Aluminium alloy EN AW 6060					
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