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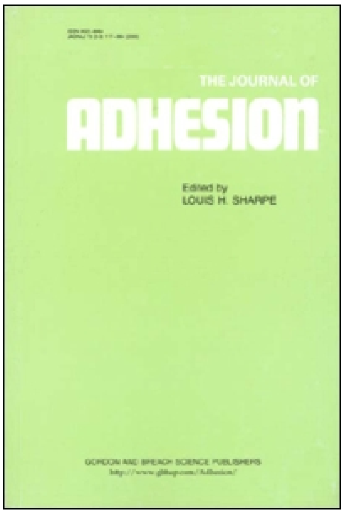

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Surface Morphology and its Influence on Adhesion

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Surface Morphology and its Influence on Adhesion

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Adhesively bonded airplane structures have sometimes failed in the past. Therefore we started an investigation to look for a comparison between strength and pretreatment of adhesive bonds. Materials used were the common airplane aluminium alloys 2024 T 3 and 7075 T 6 in bare and clad state. The methods of pretreatment were the European CSA-process, the European CAA-anodization, the FPL-process, the PAA-anodization, the SAA-anodization and some Chemoxal-processes. The adhesives we used were FM 123–5 and FM 73, both with primer BR 127. Micrographs from the surfaces prepared by the different treatment methods show, in all cases, a different microstructure which is in some cases more or less suitable for a connection with the polymer structure of the adhesive and, therefore, more or less suitable for good adhesion.

INTRODUCTION

Adhesively bonded airplane structures have sometimes failed in the past due to insufficient water stability of the adhesion between the adhesive or primer and the metal surface. One of the reasons for these failures was a lack of knowledge about the long term behaviour of epoxide-nitrile adhesives, in combination with chromic-sulphuric acid etched aluminium. Therefore, in the United States, an extensive research program was started—the Primary Adhesively Bonded Structures Technology program (PABST), to get more confidence in adhesively bonded aircraft constructions.[1]

The aim of this program was the development of new techniques of construction, new adhesives and new surface treatments for aircraft structures. But in this program the European surface treatments such as etching over 30 min in chromic-sulfuric acid (CSA) and chromic acid-anodizing (CAA), used in

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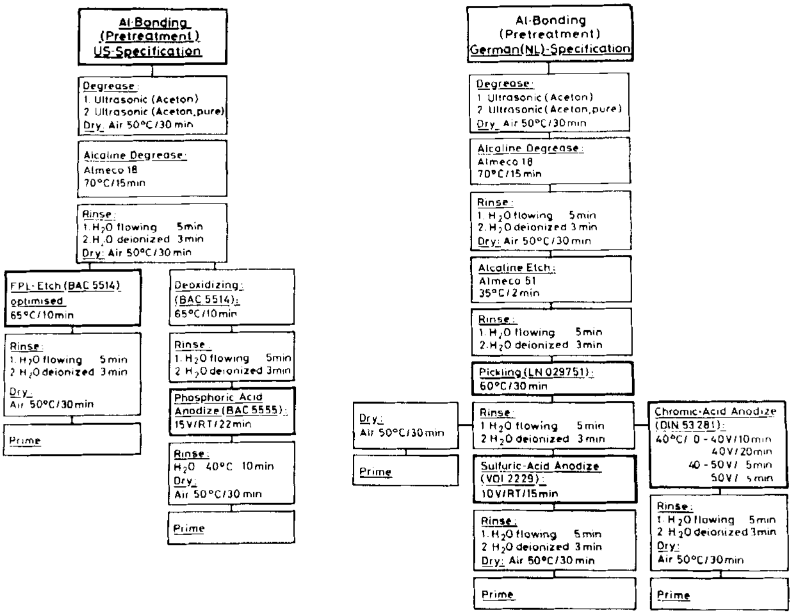

FIGURE 1 Pretreatment for Al-bonding.

Europe for more than 20 years, were not tested. Only the optimized FPL-Process, the newly developed phosphoric acid-anodizing (PAA) Process, and the CAA Process by Bell Helicopter and McDonnell Douglas are involved.[2] These methods of treatment are more economical than the European Processes—but it is not exactly known how much the durability of metal bonds produced with the US surface treatments exceeds those prepared by the European treatment methods. The results of the PABST program published to date lead to the conclusion that only the PAA pretreatment seems to be applicable for adhesive bonding of aircraft in the future.

Therefore, the aim of our study was to test and compare the strength and durability of adhesive bonds made with all known important surface treatments of aluminium alloys as shown in Figure 1.

There are:

1) The European CSA process, specified by German Standard DIN 53281 029751.[3]

2) European CSA process with chromic acid-anodizing (CAA), specified by LN 9368.[3]

3) FPL etch (optimized), specified by BAC 5514 (Boeing Airplane Company Specification).

4) Phosphoric acid-anodizing, specified by BAC 5555 (Boeing Airplane Company Specification).

5) In addition to these treatments, the sulphuric acid-anodizing (SAA) was also used (CSA etch and 15 min anod. in 11.4% SA at 10 V).

6) Chemoxal processes I, II, III, special pretreatments developed by Alu-Swisse (Switzerland).

MATERIALS AND TEST METHODS FOR BOND STRENGTH AND RESULTS

The aluminium alloys used for the comparison in our investigations were the four important alloys for aircraft structures: 2024 T3 (AlCuMg 2) and 7075 T6 (AlZnMgCu 1.6) which were treated and bonded in bare and clad state.

Adhesives were the one-component epoxide-nitrile systems FM 123–5 and FM 73 of American Cyanamid in combination with the corrosion-inhibiting primer BR 127 from the same company.

At first special peel tests were carried out. In this test a 0.1 mm thick metal foil bonded to a rigid metal plate was peeled off with a peeling angle of 180° which produces in practically all cases adhesional failures between the foil surface and the adhesive layer.[4]

Aging procedure in this case was storing the specimens in water vapour of 2 bar or 133°C over a time of 168 h. Figure 2 shows some results, they are similar for all tested metal and adhesive specimens in this investigation.

The decrease of peel strength by aging is greater for the FPL and CSA etched surface compared with the PA- and CA-anodized. In addition, the peel-test shows that CAA-pretreated surfaces have a much higher peel strength than PAA-pretreated surfaces. These very different results of the peel test are supported by similar peel tests with aluminium foils bonded onto polyamide 6,6 (through which water can diffuse at elevated pressures for accelerating the aging processes), as shown in Figure 3, and by the results of shear strength shown in Figures 4–7. Therefore, the peel test[4] used in this investigation is the only test with a rather short time of aging to give a differentiated answer on surface preparation properties for adhesive bonding. Of course, up to the present time, there is no known connection between the absolute values of peel strength and the durability of a structure; therefore, we have to do much work in investigation and testing in the future.

Nevertheless, the peel test can differentiate between various methods of pretreatment and that tendency is a basis for making predictions in durability. Surely, there are some inconveniences in the peel test. One is the fact that

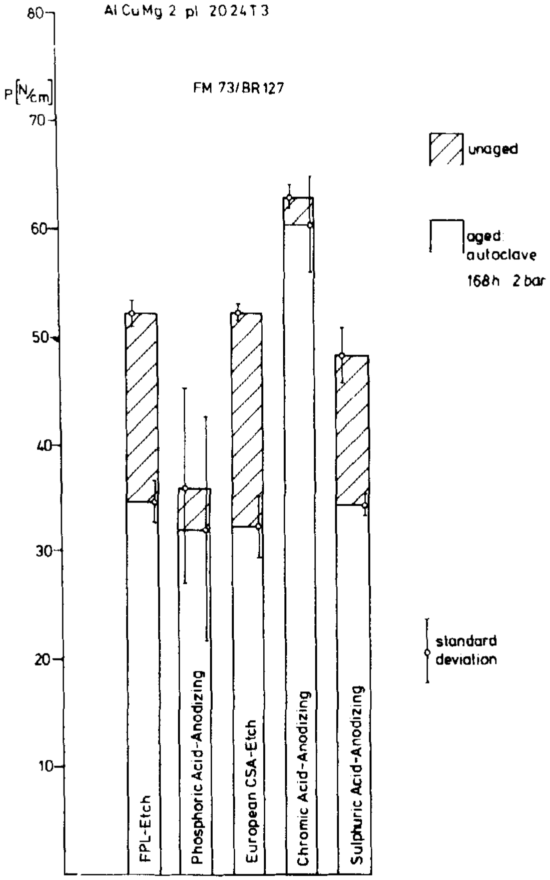

FIGURE 2 Peel strength of 2024 clad.

during the peeling process extremely high deformations in the thin foils occur. So in the case of brittle surface layers produced by some treatment methods, such as sulphuric acid anodizing, the results may lead to false interpretations. And, on the other hand, it is difficult to obtain thin foils of all alloys to be tested.

An alternative to the peel test is the well-known wedge test used as a process control.[5] But PAA anodized surfaces show no crack propagation if a primer is used.[6] In our investigations we got the same results. We produced wedge specimens of all alloys mentioned earlier with FM 123–5 and FM 73 and primer BR 127, storing them over a month in an artificial climate of 40°C and 95% relative humidity. Adhesional failure did not occur in any of the specimens. Only when the corrosion inhibiting primer was omitted did

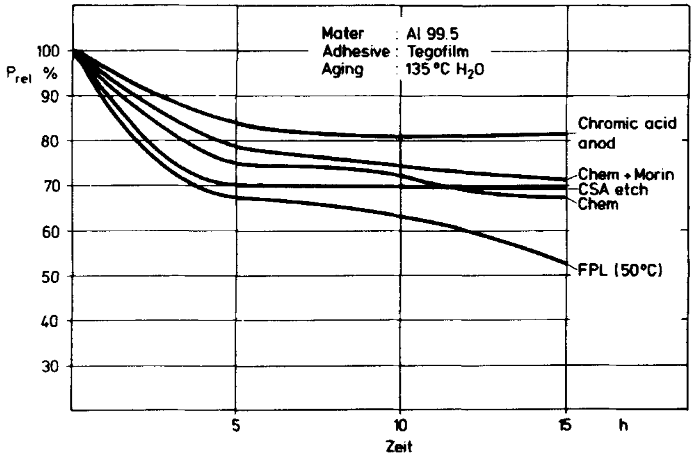

FIGURE 3 Peel strength of Al, 99.5% pure.

adhesional crack propagation occur. The same is true after preparing the surfaces by the old "non optimized" FPL process, *i.e.* without additives of aluminium and copper.[5] All these results show that the detection level of the wedge test is very low.

The problem is to differentiate between the pretreatments of higher performance in combination with today's adhesive systems. The question is : in which way is it possible to realize and test bonds with a flight lifetime higher than 30,000 hours, as the airplane industry has to give a guarantee. A selection between adhesive bonds made with primer or without primer is a decision

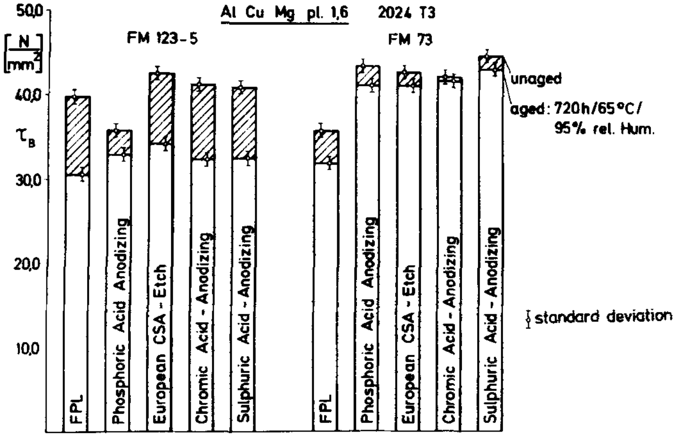

FIGURE 4 Shear strength of overlapped bonds of 2024 clad.

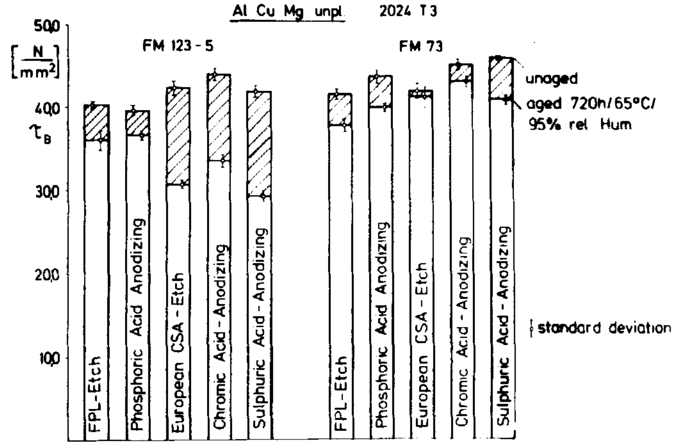

FIGURE 5 Shear strength of overlapped bonds of 2024 bare.

involving a lifetime above or below about 5000 or 10,000 flight hours. In consequence, the wedge test is unsuitable to support a development in adhesive bonding.

Further test specimens for evaluating the bond-strength and the aging behaviour were single overlapped joints with a sheet thickness of 1.6 mm and an overlap length of 12.5 mm, specified by ASTM D1002-72. Aging procedure was to store the specimens in the unloaded state for 720 h in an artificial climate of 65°C and 95% relative humidity.

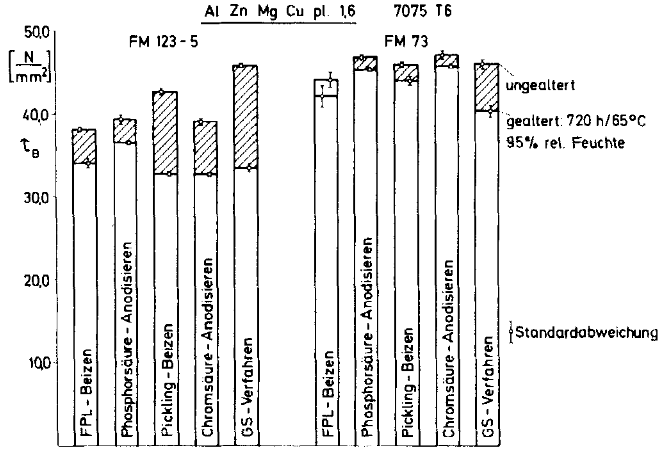

FIGURE 6 Shear strength of overlapped bonds of 7075 clad.

The results of the bond-strength and the behaviour by single overlapped joints are to be seen in Figures 4–7. Plotted in Figure 4 is the shear strength of 2024 T3 clad bonds in the unaged state and after aging. For FM 123–5 the European treatments seem to be slightly better, whereas in the case of FM 73 PAA, CSA, CAA and SAA lead to good results.

Figure 5 shows the results obtained with the bare 2024 alloy with FM 123–5. The US treatments lead to better results because the effect of aging is less than for the European treatments. In combination with FM 73, however, the European treatments are better than the US processes. Figure 6 shows the results for 7075 T6 clad. Here the US treatments lead to somewhat better results with FM 123–5. For FM 73, with the exception of SAA, no differences between the treatments are to be seen. In Figure 7 are plotted the results obtained with this alloy in the bare state. Of interest here is that in combination with FM 73 the aging influence in the case of European treatments is less and the best aging behaviour is reached by sulphuric acid-anodizing (SAA).

These aging tests were done without sustained load, because results of earlier investigations carried out in our institute,[12] lead to the conclusion that sustained load up to 50% of the initial strength does not accelerate the deterioration of adhesion in a marked manner over an aging time of a month. Aging under load is only a suitable method to evaluate the load capability of the adhesive itself and not for the adhesion. Results up to one year aging time in natural and changing climate with low sustained shear stress (0.7 N/mm^2) are plotted in Figures 8, 9, 18. As can be seen, there is no clear difference between stressed and unstressed aging results for different adhesives and

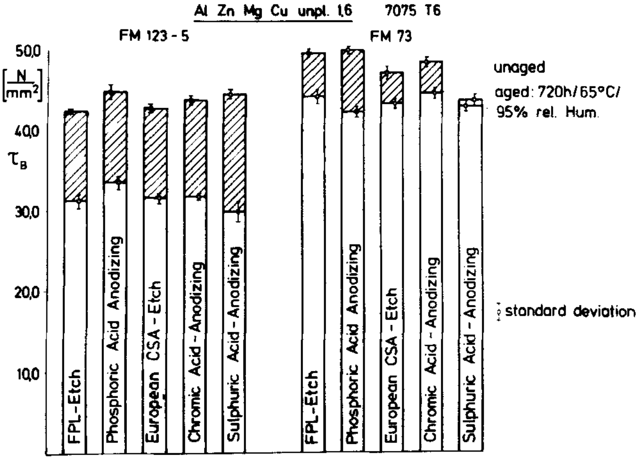

FIGURE 7 Shear strength of overlapped bonds of 7075 bare.

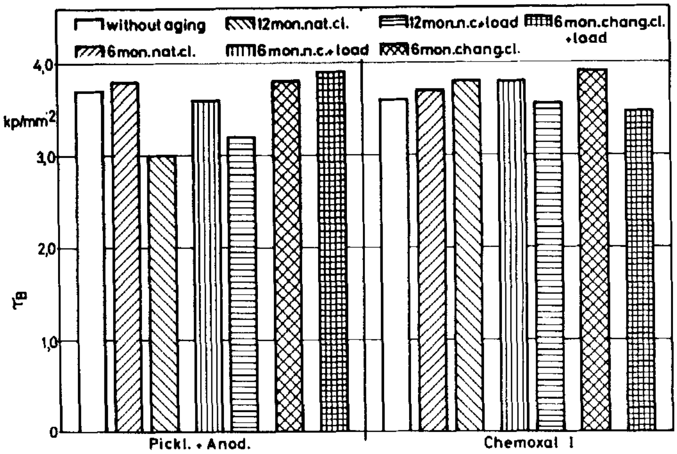

FIGURE 8 Shear strength of aluminium bonds: adhesive Tegofilm M 12 B.

different pretreatments. The first differences in strength occur upon aging with and without stress only after two years of aging, as Cotter and Kohler[7] have shown.

Generally speaking, there must be an influence of stress on the aging behaviour, but in what way and how great is the influence is still unknown; however, a change should not be expected before two years of test time. Of interest is that despite the relatively short aging time in the case of the overlapped joints, the results are similar to those of the peel tests carried out under very severe conditions.

The conclusion from the results discussed here is, that today there does not

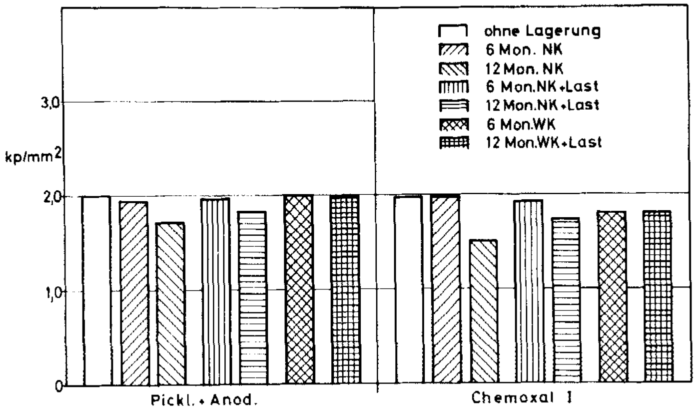

FIGURE 9 Shear strength of aluminium bonds: adhesive FM 34.

exist only one surface treatment with outstanding properties for producing bonded aluminium structures.[8] Generally, it seems to be true that the anodizing processes lead to better results than the etching systems. But the main problem is to develop a test which is able to give a more reliable answer as to whether a pretreatment, used in connection with a given adhesive system, results in good adhesive bonds with long lifetime.

MICROSTRUCTURE OF ALUMINIUM-SURFACES

The question arising in this state of knowledge is, which properties of the surface layers produced by the different treatment methods are responsible for the differences in the aging behaviour of metal bonds. One tool to evaluate the surface state is scanning electron microscopy.

As a first step this measurement technique was used in our investigations without special coating of the oxide layers to reduce charging. So the danger of damaging the oxide by a sputtering process was avoided. As a result, we learned that up to magnifications of 20,000 × under careful handling, sputtering is not necessary.

Figure 10 shows the change of the surface morphology after particular steps of the pretreatment. The as received state is not structured but contaminated. After degreasing, a still not really clean surface with some loose particles is to be seen.

The alkaline degreased surface shows an irregular structure with pits, but without any micromorphology. These changes in surface morphology up to

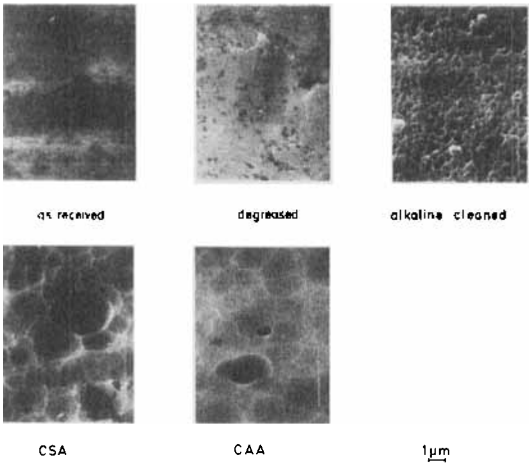

FIGURE 10 Steps of pretreatment for 2024 clad.

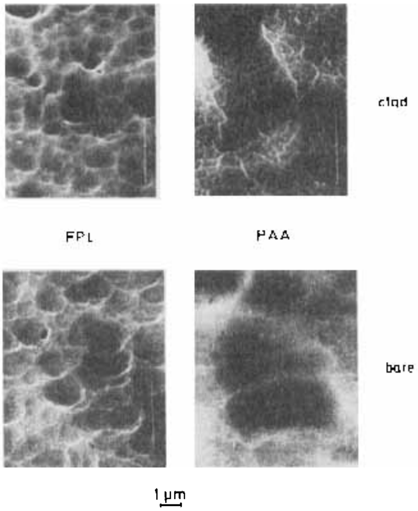

FIGURE 11 Surface morphology of treated 2024 clad and bare.

this step are characteristic for all chemical cleaning processes of aluminium alloys. The other two pictures in Figure 10 show an etched (CSA) and an anodized (CAA) surface, with developed oxide structures in more detail. Clearly visible here at a magnification of 20,000 × is the change in morphology after etching and anodizing.

In Figure 11 an optimized FPL-treated surface of a 2024 clad specimen is to be seen and compared with equally treated 2024 T3 bare specimens below. A concave, hilly overstructure and a hint of a micromorphology with oxide pits are to be seen. The pictures on the right side show surfaces treated by PAA. The clad state shows a highly structured oxide morphology while the bare state is much less structured. In both cases of PAA a very filigree morphology like an "oxide-wood" remains.

Figure 12 shows surfaces of the alloy 7075 T6 clad and bare, after the same treatments, with structures similar to 2024 T3. On the one side a hilly overstructure and on the other side a rather "filigreed-wood" type.

Figure 13 contains micrographs of the same aluminium alloys in the clad and bare state but pretreated by European chromic acid-anodizing (CAA) with stepwise increasing of voltage. The CSA-etching may be compared with the optimized FPL but the etching time is much longer, about 30 min instead of 10 min for the optimized FPL. The European chromic acid-anodizing (CAA) differs from those of the American ones. In this case, a bath temperature of 40°C is used and the voltage is increased from 0 to 40 Volts within 10 min. After a further 20 min the voltage is increased from 40 to 50 Volts within 5

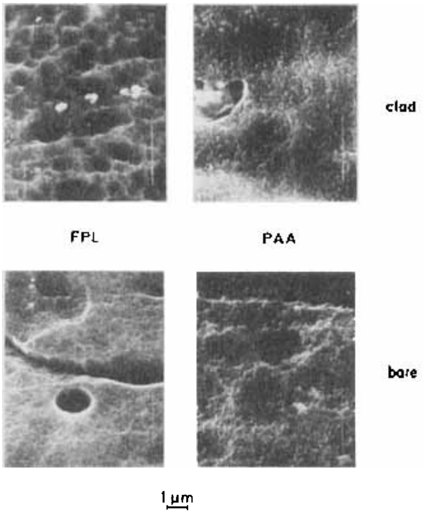

FIGURE 12 Surface morphology of treated 7075 clad and bare.

min followed by anodizing for another 5 min. On the left in Figure 13 are to be seen the CSA-etched surfaces, with nearly the same oxide morphology obtained in the optimized FPL-process. On the right are the micrographs of the anodized surface with a clearly visible overstructure as well and a form like a fine honeycomb structure.

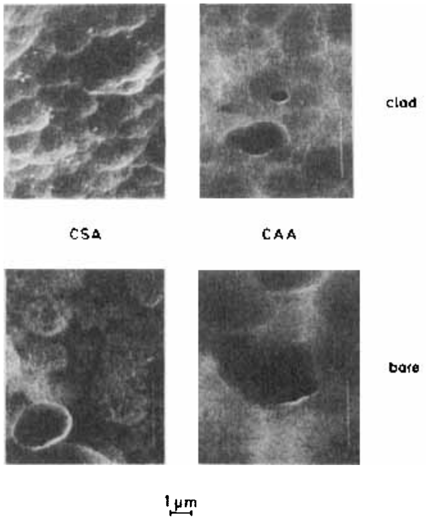

FIGURE 13 Surface morphology of treated 2024 clad and bare.

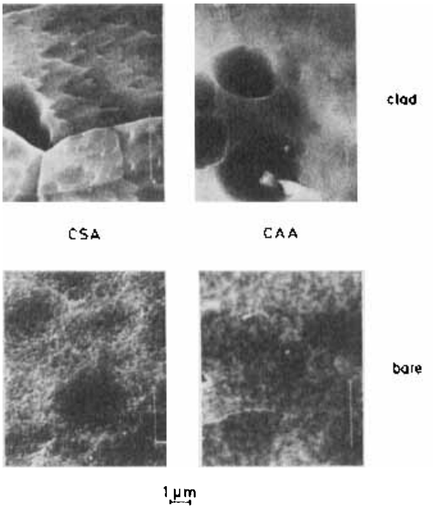

FIGURE 14 Surface morphology of treated 7075 clad and bare.

Figure 14 shows 7075 surface treated in the same way. The macroscopic structure is quite different but the microstructure is comparable to that of 2024 alloys.

To get more information about the microstructure of the oxides, higher magnifications are needed. They can only be realized after sputtering the surfaces, for example, with gold.[9] Before starting these investigations, tests were carried out to see how much the sputtering process could change the initial oxide structure.

Figure 15 shows scanning electron micrographs of CSA treated 2024 clad alloys in an unsputtered and in a sputtered state. One was sputtered for 30 sec under 8 Volts and the other one was sputtered for 180 sec under 30 Volts. It can easily be seen that the sputter process for 30 sec under 8 V does not change the oxide morphology, whereas the other sputtering process leads to changing and inability to form conclusions. So we used for the following investigations the 30 sec under 8 V sputter process, leading to better contrast at high magnifications.

Figure 16 shows at first a quite different method of chemical pretreatment for aluminium alloys, the Chemoxal process developed in Switzerland by Alu-Swisse. There we have to differentiate between these three alkaline processes, Chemoxal I, II and III. The remaining surface structure is comparable to that of a chromic-sulfuric acid-etched (CSA) surface but the microstructure is less fine as can be seen by comparing them with the fourth picture (below right) of a CSA-etched surface. In Figure 17 the microstructure of Chemoxal II treated 2024 can be seen in more detail by high magnifications.

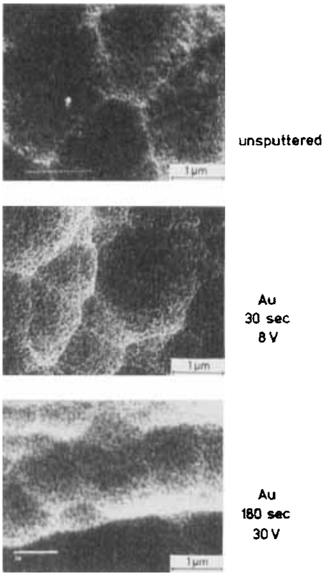

FIGURE 15 Influence of sputter conditions of 2024 clad CSA-etched.

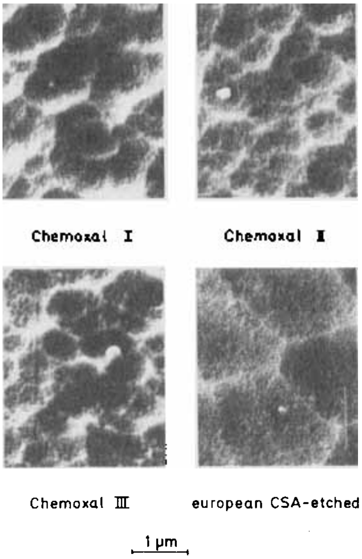

FIGURE 16 Etched surface of 2024 clad.

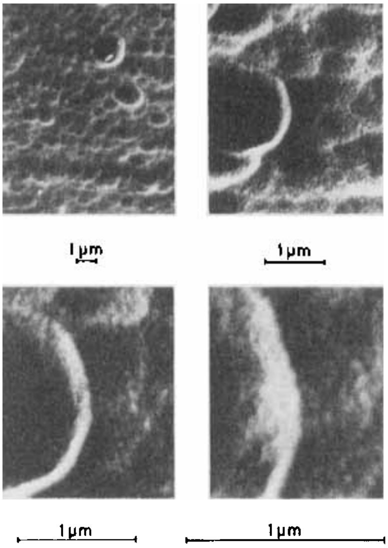

FIGURE 17 Chemoxal II treated surface of 2024 clad.

Without doubt the size and structure of the oxide layer must be very important for strength and durability of adhesive bonds. But if that is true, then different treatment methods producing the same morphology must lead to comparable properties on adhesion strength and durability.

To demonstrate that, lap-shear bonds of CSA and Chemoxal II treated 2024 alloys in the clad state were produced with a phenolic resin and tested for strength and durability.

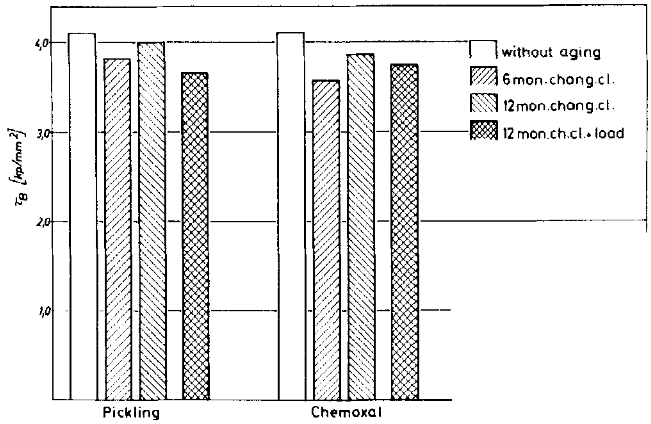

FIGURE 18 Shear strength of aluminium bond. Adhesive: Tegofilm M 12 B.

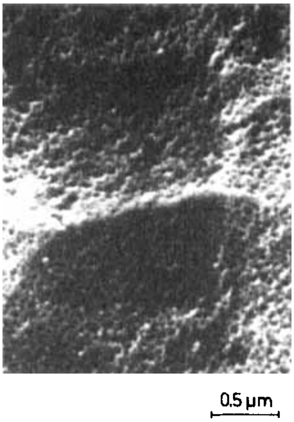

FIGURE 19 Sulphuric acid-anodized (SAA) 2024 clad.

Figure 18 shows some values of the strength of bonds with CSA- and Chemoxal-etched metal parts. It is remarkable that the strength of Chemoxal treated bonds without aging and after aging is similar to that of CSA etched. This result leads to the conclusion that firstly, the aircraft industry is not the only industry using techniques to pretreat aluminium surface for good bonds. Secondly, there is a correlation between surface morphology and bondability. But that is only true if the adhesive is able, after wetting the surface, to invade the oxide morphology.

This possibility is demonstrated by Figures 19 and 20. Figure 19 is a micrograph of a sulphuric acid anodized 2024 surface with a typical well developed honeycomb structure. Figure 20 is a SE-micrograph of the surface

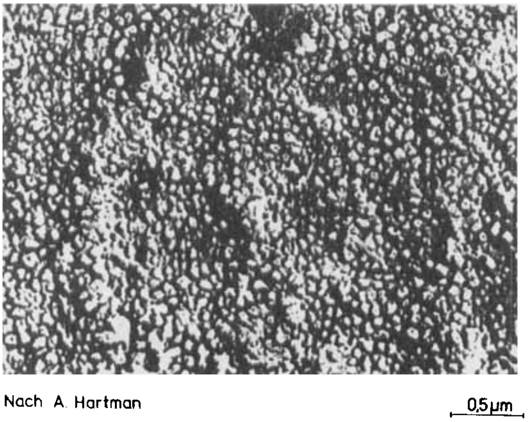

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FIGURE 20 Phenolic resin replica of an SAA surface, 2024 clad.

of a phenolic adhesive cured on a SAA treated aluminium surface after etching the aluminium away. Easily visible are the characteristic pits on the resin's surface setting before in the pores of the oxide layer.[10] This example demonstrates that the adhesive can creep into the formed oxide structures if its molecular weight in the uncured state is small enough, which is true in the case of phenolic resin.

The remaining question is, how deep does it creep into these small honeycombs and how good is the resulting chemical or micromechanical connection and its resistance against aging.[11] But it is not enough to take a look only at the outer submicroscopic topography of a metal surface to get a reliable answer on the question of bondability. That is demonstrated by Figure 21. To be seen are pictures made by transmission electron microscopy (TEM) with a high magnification of CSA and optimized FPL-etched surfaces and CAA and PAA surfaces. The etched surfaces always have the typical cellular oxide structure with small areas of about 300 Å, fenced by tiny oxide walls with a much smaller thickness of about 50 to 100 Å. The anodized surfaces have a very different structure:

On the one hand a honeycomb structure with cell areas of about 300 Å in the case of CAA, on the other hand a very filigree down after PAA. There a single pit has a diameter of about 100 to 200 Å, from one to another there will

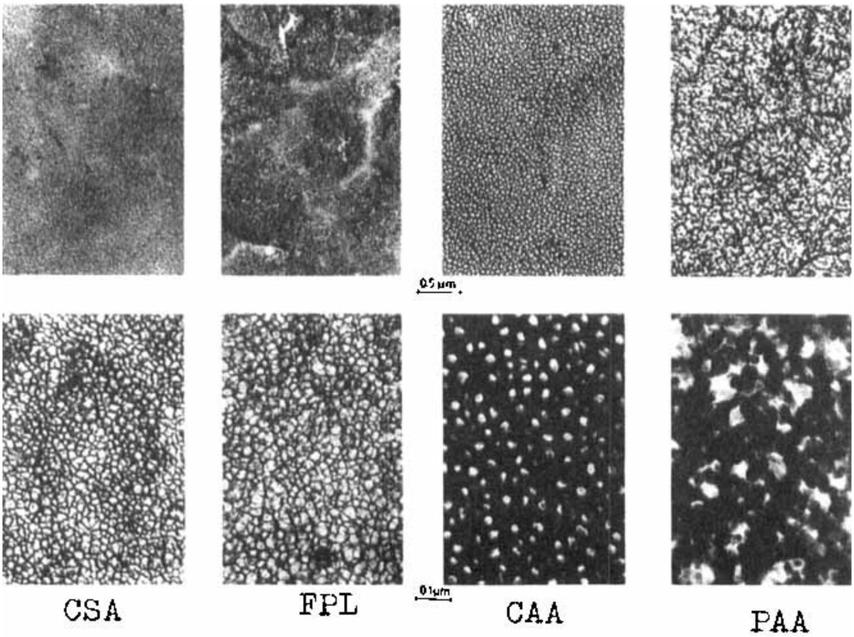

FIGURE 21 TEM micrographs of treated 2024 clad.

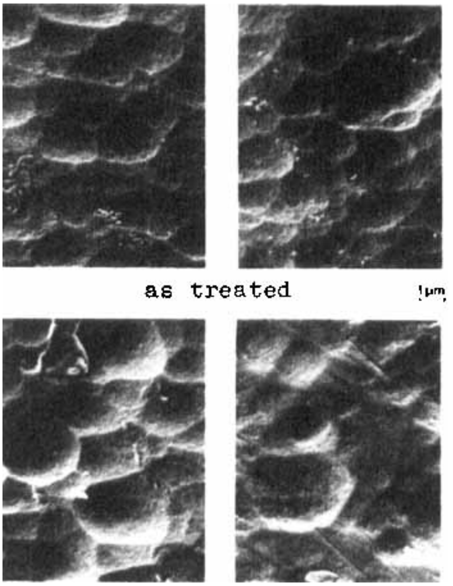

FIGURE 22 Pretreated and contaminated 2024 clad.

be a distance of about 300 to 400 Å. These differences must have an influence on the adhesional properties especially when metal parts are handled prior to primer application. One point is the mechanical stability of the oxide structure and its influence on the bondability under industrial conditions. That the stability of different oxide layers is different, is easy to demonstrate, by simple tests as shown in Figures 22 and 23.

In Figure 22 the upper pictures are micrographs of 2024 surfaces in the as treated state; below is the same surface but wiped with lens cleaning paper. For CAA there is no change; for CSA the top areas of the overstructure are marked by grooves. Figure 23 shows the same alloy pretreated by PAA and FPL. After wiping there is almost no structure left.

The question arising from that effect is, how do such different changes in the oxide morphology influence the adhesional properties, especially under hostile environments. To get more information, special peel specimens with fresh and wiped surfaces were bonded for testing the initial and residual peel strength after aging for 168 h in water vapour at 133°C. In these specimens, in all cases, the adhesional zone between metal and primer or adhesive is destroyed, so that the peel strength gives a direct hint as to the quality of the adhesion.

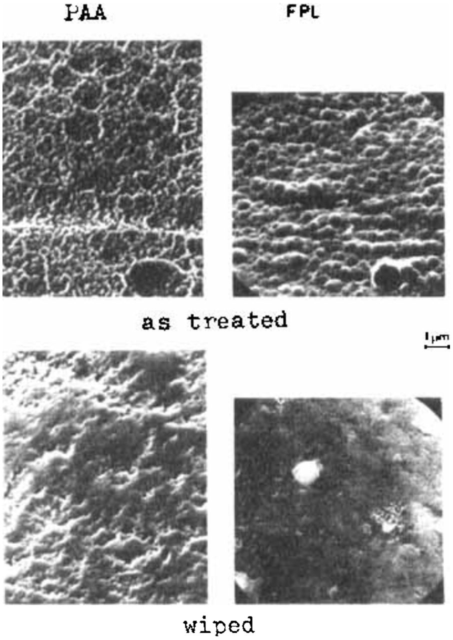

FIGURE 23 Pretreated and contaminated 2024 clad.

In these tests, only in the case of FM 123–5 was the superiority of phosphoric acid-anodizing lost by wiping the surface. In combination with FM 73, after wiping no reduction of water stability occurred if a primer was used. If we worked without a primer, the mechanical wiping reduced the adhesion stability on FPL- and PAA-surfaces in an extreme manner, whereas on CSA and CAA surfaces practically no reduction of adhesional quality was observed.

These results lead to the conclusion that the primer in its low molecular state invades the oxide cells, remaining undestroyed under the destroyed and equalized top of the surface layer. Only the molecules of the adhesive itself, with its higher molecular weight, remain still on the equalized top of the upper surface layers. The adhesive cannot invade the oxide morphology and has therefore mainly no mechanical connection to the oxide. The result is, we have bad adhesional bonds.

The aim of future investigations should be to prepare an oxide morphology being more suitable to the polymer structure of the adhesive or to formulate an adhesive with a polymer structure more suitable for an oxide morphology.

References

1. E. W. Thrall, Jr., *Primary Adhesively Bonded Structure Technology* (*PABST*), Technical Bulletin No. 1–19, March 28, 1975–January 11, 1979. (McDonnell Douglas Corporation, USA, 1975.)
2. E. W. Thrall, Jr., *Primary Adhesively Bonded Structure Technology* (*PABST*), Douglas Paper 6539.
3. NL: Normstelle Luftfahrt, DIN-Deutsches Institute für Normung e.V.
4. W. Brockmann, *2nd National SAMPE Technical Conference Proceedings*, Dallas, October 1970, pp. 477–490.
5. J. C. McMillan, AGARD Lecture Series No. 102, April 1979. Oslo, Norway and the Hague, The Netherlands.
6. V. S. Srinath, Structural Adhesives and Bonding Conference, March 1979, pp. 24–47. El Segundo, California, Technology Conferences.
7. J. L. Cotter, *International Journal of Adhesion and Adhesives* **1,** 23–28 (1980).
8. W. Brockmann and O.-D. Hennemann, *Comparison of Surface Treatments of Aluminium and Their Influence on Long Term Strength of Metal Bonds*, 11th National SAMPE Technical Conference Proceedings, Boston, November 13–15, 1979, pp. 804–816.
9. J. D. Venables *et al.*, *Appl. of Surface Science* **3,** 88–98 (1979).
10. A. Hartmann, *An Investigation on the Effect of the Pretreatment of the Metal and the Strength and Adhesion of Adhesive Bonded Joints Making Use of Electron Microscopy*, National Luchtwaart Laboratorium, Amsterdam, July 1961.
11. D. Marton and A. Csaudy, *Nederlands tidschrift voor Vacuumtechniek* **16,** 47–48 (1978).
12. W. Brockmann, *Z. Werkstofftechnik* **8,** 259–267 (1977).