Application Report

Optimizing the pretreatment of metal surfaces for bonding in vehicle construction

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Industry section: adhesives, coating, car
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Method: 

Drop Shape Analyzer – DSA100

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Light metal, but difficult to bond

Abstract

Adhesives have poor bonding properties on aluminum. Aluminum alloys are therefore pretreated in conversion baths in order to prepare them for bonding. Such pretreatment methods are increasing in importance, particularly in vehicle construction. A current method is immersion bath treatment with the active substances hexafluorotitanic or hexafluorozirconic acid. The process parameters exposure time, temperature and concentration have a great influence on the surface free energy and its polar and disperse parts – quantities that are closely linked to the wetting and adhesion behavior of the surface and which therefore greatly influence the adhesive strength and the ageing behavior of the bonded joint. The Austrian Research Institute *ofi* has carried out a publicly funded study on the pretreatment of aluminum alloys in which KRÜSS participated. In addition to measurements of the adhesive strength and ageing behavior, contact angle measurements were made in order to investigate the effect of the bath parameters exposure time and temperature on the surface free energy and its polar and disperse parts.

Background

The industrial importance of aluminum bonded joints has increased considerably in recent years, particularly in the automobile industry. In some new vehicles the total length of aluminum bonded joints is three times that of older models. The long-term durability of light metal bonded joints has become an important quality and cost factor.

On exposure to the atmosphere, strongly reducing metals such as aluminum form a stable, passivating oxidation layer with a comparatively low surface free energy (SFE) and correspondingly poor wettability and adhesive strength. In order to improve these, aluminum alloys are treated in conversion baths.

The aim of the pretreatment is to increase the SFE of the alloy. The process is controlled by the exposure time, temperature and concentration parameters, which all influence the SFE. For wetting it is not just the SFE contribution that is important. The polar and disperse parts of the SFE also play a major role. Contact angle measurements can be used to check the effects of the treatment on the surface free energy and its polar and disperse parts.

Practical work

Within the framework of the study presented here various aluminum alloys were treated with the conversion bath active substances hexafluorotitanic acid and hexafluorozirconic acid and the effects of varying the above-mentioned process parameters were studied.

The exposure time and temperature parameters were varied for the contact angle measurements presented here. After the bath treatment the SFE of the samples and its polar and disperse parts were determined by the Owens, Wendt, Rabel and Kaelble method [2;3;4]. Water, diiodomethane and ethylene glycol were used as the test liquids.

After treatment the share of bound zirconium and titanium atoms was measured in parallel by energy-dispersive X-ray analysis (EDX); bonds were prepared and the initial mechanical strength and the strength after various ageing tests were measured. The results of these studies are shown in [1].

Bath control and adhesive strength

Measurements of the adhesive strength provided two important results with regard to the surface treatment [1]:

1) Whether the bond is ageing-resistant depends largely on the initial adhesive strength. The first contact between adhesive and metal already determines whether the bond will be resistant to ageing. The initial wetting of the surface therefore has a decisive influence.

2) No systematic relationship between the process parameters and the adhesive strength for all combinations of alloys and adhesives can be recognized. The dependency of the adhesive strength on the bath parameters was completely different with different samples. For example, with the alloy AW6016 and a single-component epoxy resin the greatest strength was determined at a relatively high bath temperature and a long exposure time. Alloy AW7020 with the same adhesive also showed the greatest strength at the higher temperature, but at short exposure times.

Surface free energy results

With the above-mentioned examples of samples the different influence of the exposure time could also be observed on the surface free energies: alloy AW6016 had the highest SFE at the longest exposure time, alloy AW7020 at the shortest. This correlates with the plot of the SFE against the exposure time shown below: for AW6016 (Fig. 1a) the slope is positive, for AW7020 (Fig. 1b) it is negative.

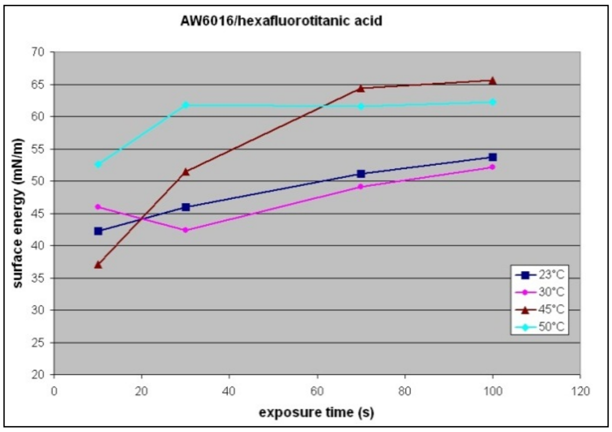

Fig.1a: SFE of AW6016 as a function of the conversion bath exposure time

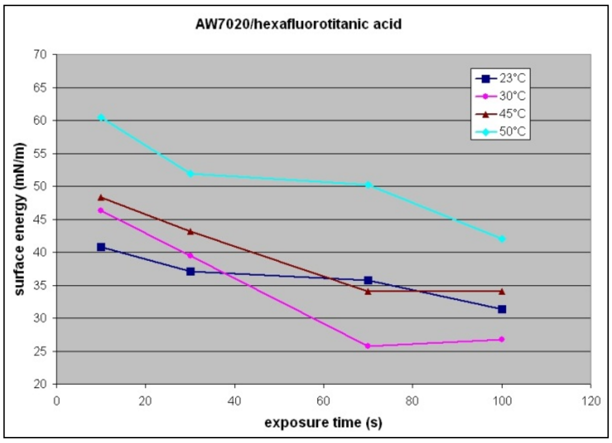

Fig.1b: SFE of AW7020 as a function of the conversion bath exposure time

However, it is not just the absolute value of the SFE of the alloy that is decisive. Investigations into the adhesive strength [1] showed no agreement of the maximum strength with the maximum SFE of the alloy for all adhesives used. As a possible cause of this the different forms of the particular polar and disperse interaction parts at the metal-adhesive boundary are discussed.

Polar and disperse interactions

The surface free energy of a phase can be described as being the sum of the polar and disperse interaction parts. On contact with a surrounding phase the rule is that the same interacts with the same: the polar parts of a phase interact with the polar parts of the adjacent phase, the disperse parts with the disperse parts. The bonding of an adjacent phase depends on how similar the phases are with respect to the polar and disperse parts of the SFE. For example, despite a high SFE an alloy can have a low affinity to adhesives if the solid forms strongly polar and the adhesive primarily disperse interactions. The best adhesion can be expected when the high SFE of the alloy simultaneously coincides in its polarity with that of the adhesive. A simple wetting test on the alloy is often not sufficient to be able to estimate the bonding result in advance – it does not allow a breakdown into the SFE components.

A plot of the percentage part of the polar interactions of the total SFE ("surface polarity") for the sample AW7020, for example, shows that this quantity does not follow such a uniform trend as the total contribution of the SFE. Depending on the temperature, as the exposure time increases the polarity can either decrease, increase or pass through a minimum value.

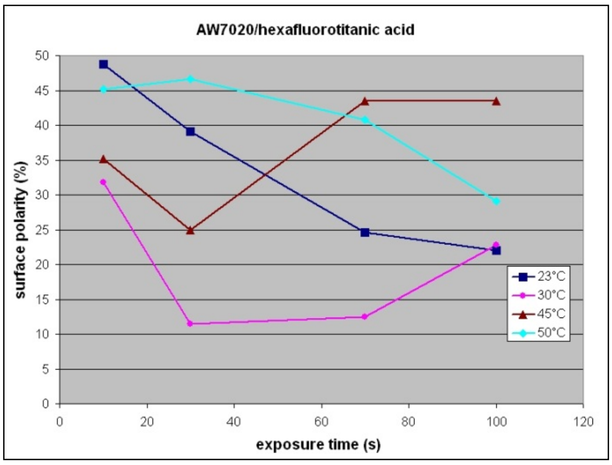

Fig. 2: The surface polarity of sample AW7020 as a function of the exposure time

For the sample AW7020 the highest measured value for the total SFE was achieved at a exposure time of 10 s and a temperature of 50°C (see Fig. 1b). For these bath parameters the surface polarity was 45% (see Fig. 2).

For the alloy AW7020 an adhesive whose surface polarity was 45% would be ideal. Polar parts of organic adhesives usually have lower values, so that the maximum strength often does not lie at the same bath parameters as the maximum total SFE of the alloy.

If the surface free energy properties of the adhesive are known then, by using the SFE results of the alloy and the calculated polarities, an estimation of the degree of affinity between the adhesive and the surface can be made.

Summary

Contact angle measurements within the framework of this study show that the alteration of the exposure time and the temperature can lead to an increase or also a reduction in the SFE and the polarity for different alloys. A systematic trend cannot be demonstrated; the particular system must be investigated separately with respect to the SFE and the polar and disperse parts.

Contact angle measurements are ideal sensors for optimizing the bath control for a particular alloy and the use of a particular adhesive. In principle it is important to achieve as high a surface free energy of metal and adhesive as possible, with polar and disperse parts that are also as similar as possible. These two quantities – high SFE and similarity of the percentage polar parts between alloy and adhesive – are the precondition for high initial adhesive strength and long-term stability of the bonded joint.

Literature

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