Long-time Stability of Electrochemical Ni-layers on Aluminium Applied with Different Pretreatments

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Abstract

Several differently plated types of nickel layers on aluminium substrates were studied with respect to their corrosion and diffusion barrier properties.

For the deposition, different acid one-step pretreatment methods were examined. It was found, that tensile strengths of more than 50 N/mm^2 can be achieved.

In addition, the long-time stability at elevated temperatures was determined. After heat treatment at different temperatures in the range of 350°C to 400°C, the formation of NiAl alloys was detected by X-ray diffraction.

The growth constants of the NiAl alloy was calculated for different temperatures from SEM and EDX measurements.

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Introduction

In spite of the fact that 100 years ago aluminium was as rare and expensive as gold, it is nowadays one of the most important technical metals.

In a modern automobile more than 100 kg (220 lb) of aluminium are built-in. This is because of its advantageous properties like its light weight, its good electrical and thermal conductivity and the corrosion stability of the pure metal[1]. However, the technically used aluminium alloys are more susceptible to corrosion. Therefore corrosion and diffusion effects are often the limiting factors for components made from aluminium. This is particularly important for devices which are exposed to elevated temperatures, like e.g. car engines.

One of the possibilities to prevent corrosion attacks is the application of metal over layers applied by different electrochemical processes. The metals used for corrosion protection are mainly nickel or chrome and their alloys. These layers may also be used as diffusion barriers between the substrate and additional functional coatings.

One of the problems of electroplating on aluminium substrates is the need of a special and expensive pretreatment of the surface to achieve useful peel strengths.

If the produced devices are used at elevated temperatures, alloys according to the binary alloy diagram (Fig. 1) can form through diffusion processes. Then, the life-time limitation is the time the aluminium needs to diffuse through the barrier.

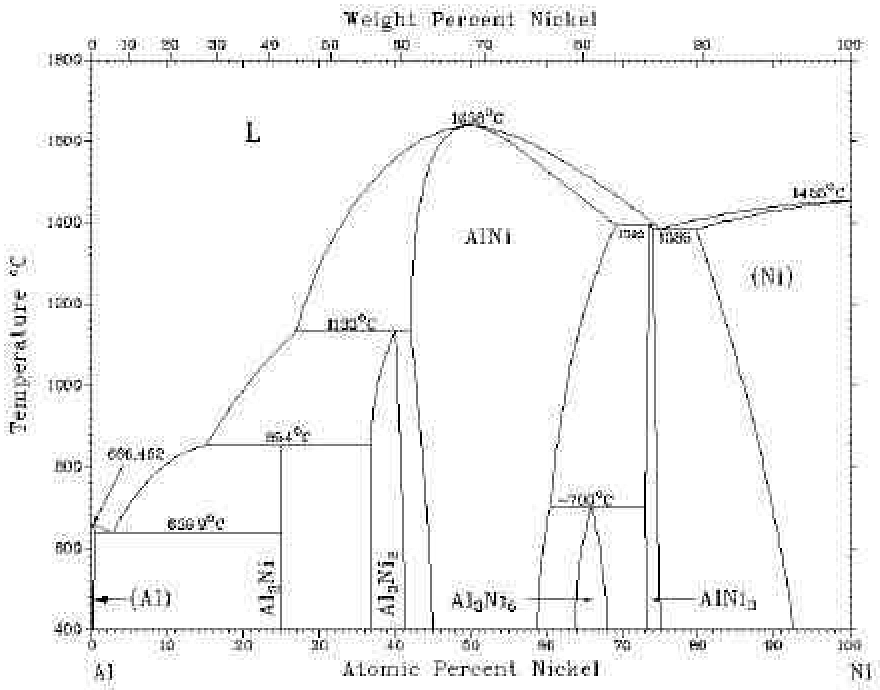

Fig. 1: Binary Alloy Diagram Nickel-Aluminium.

The scope of this work was to find

1. cheaper and easier pretreatment methods than the well known zincate process.
2. kinetic parameters for the Ni-Al diffusion couple to get an estimate of possible lifetimes for nickel layers used as diffusion and corrosion barrier at elevated temperatures.

Experimental

For the tempering experiments AlMg3 sheets of 5 x 8 cm (1,9 x 3,1 in) with a thickness of 1 mm (40 mil.) were used.

The plated samples were tempered in air in a filament heating furnace type HTK 8, Gero Hochtemperaturöfen, Germany.

Measurements of the occurring phases were carried out with a XRD spectrometer Siemens D-5500 Goniometer (Siemens AG, Munich, Germany).

The samples coated with 1 µm (40 µin.) Ni-layer were heated with a temperature rate of 0,133°C / s. They were measured with a 2-θ-scan, beginning at 20° with a step size of 0,014265°.

The thickness of the intermetallic layers was detected with a scanning electron microscope XL 30 ESEM FEG (FEI Company, Hilsboro, OR/USA) and energy dispersive x-ray measurements (EDX). Since the intermetallic layers were not fully planar during growth, the thickness was determined as the average from the measurements of the growth distance at 10-15 chosen points. The ion beam etching of the cross sections was done in argon atmosphere in a precision etching coating system (PECS) Gatan model 682 (Gatan Inc, Pleasanton, CA/USA). The etching time was 6 min with an acceleration voltage of 6,5 kV.

Results and discussion

Pretreatment

The zincate process is state of the art in industrial electroplating on aluminium. In a first acid step, the oxide film of aluminium is removed. In a second step zinc is applied on the reactive surface to decelerate the formation of the oxide film and as a starting reagent for the deposition of electroless nickel. Best results are achieved when these two steps are repeated twice. This means that four steps are needed before nickel can be applied. Additionally, between every step a minimum of two rinsing steps are necessary.

The search for cheaper alternatives to this process ended in the late fifties, when different one step acid pretreatments were published [2-4].

Based on these findings, two pretreatment methods were investigated, which allow the deposition of electroless as well as galvanic nickel layers on aluminium (Tab. 1):

After degreasing in an alkaline solution at 65 °C for two minutes, the substrates were treated in the pickle tanks at several temperatures and for different periods of time. The deposition of the nickel layers has to be started within 30 s to avoid the reformation of the oxide film.

Tab. 1: Composition of the pickle for aluminium

Pickle 1		***Pickle 2***	
$FeCl_3$	60 g/l	$MnSO_4$	2,67 g/l
HCl	20 g/l	HCl	400 g/l

Due to the different thermal expansion coefficients of aluminium and nickel ($23{,}1 \cdot 10^{-6} K^{-1}$ and $13{,}4 \cdot 10^{-6} K^{-1}$, respectively) thermal stress causes problems with the adhesion of the applied nickel layers.

To test this, samples coated with galvanic or electroless nickel were tempered for one hour and subsequently quenched in cold water. The procedure was iterated with the undamaged samples at higher temperatures until damage occurred. Fig. 1 gives an overview of the results for the Fe-pickle. It can be seen, that after a pretreatment with Fe-pickle at 60 °C/30 s even after quenching from 500 °C specimens with undamaged nickel layers could be obtained.

The maximum temperatures where no damage occurred to the nickel layers were as high as with the zincate pretreatment.

With the so detected optimal conditions tensile strength tests were performed. For both pretreatments max. tensile strenghts of over 50 N/mm^2 (7250 lb/in^2) could be achieved.

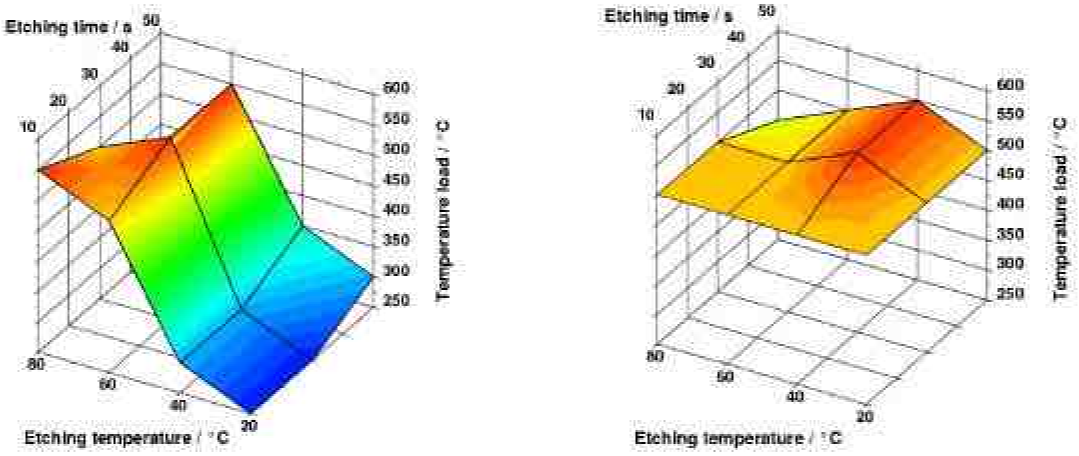

Fig. 2: Optimum Fe-pickling conditions for galvanic nickel (left) and electroless Nickel (right) on aluminium based on temper test results.

Diffusion processes

Diffusion processes between a substrate and an overlayer are highly depending on the used materials and the application process. In contrast to recent assays (e.g. [5,6]) not the pure metals but technically used alloys (i.e. AlMg3) were examined in this study. The electroless nickel layers applied from hypophosphate baths contain up to 10 % P, whereas the galvanic nickel layers we used are relatively pure. In addition, due to the application process kinetic inhibition caused for example by residual very thin oxide layers between substrate and coating can affect the diffusion process.

As a result of these technical conditions, normal diffusion controlled processes following a parabolic law of second order were not expected.

In-situ high temperature X-ray diffraction was used to study the formation of intermetallic phases at elevated temperatures.

Apart from the primary and terminal solid solutions five intermetallic compounds are present in the phase diagram of Ni-Al (Fig.1): Al_3Ni, Al_3Ni_2, AlNi, Al_3Ni_5, and Ni_3Al. At the relatively low temperatures employed only the aluminium rich intermetallic Al_3Ni was detected in both nickel layers.

Fig. 3 shows that the Al_3Ni phase is formed at approximately 400 °C.

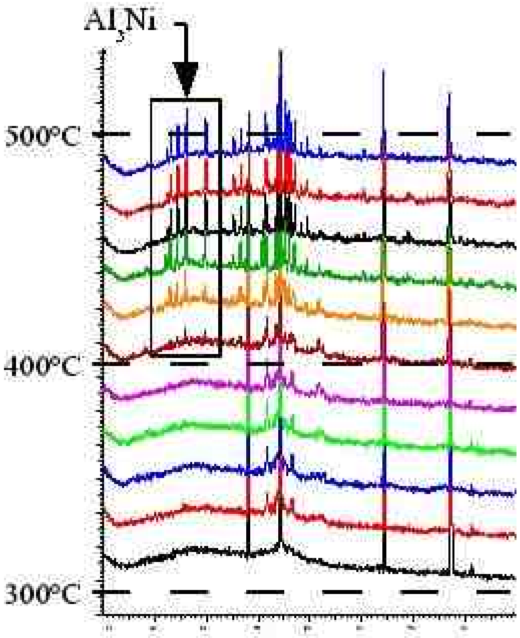

Fig. 3: In-situ high-temperature XRD measurement of the Ni-Al boundary

Cross sections were made and analysed by means of light microscopy, SEM and EDX to measure the thicknesses of the layers. To remove smeared material, the cross sections were finally treated by ion beam etching (Fig. 4)

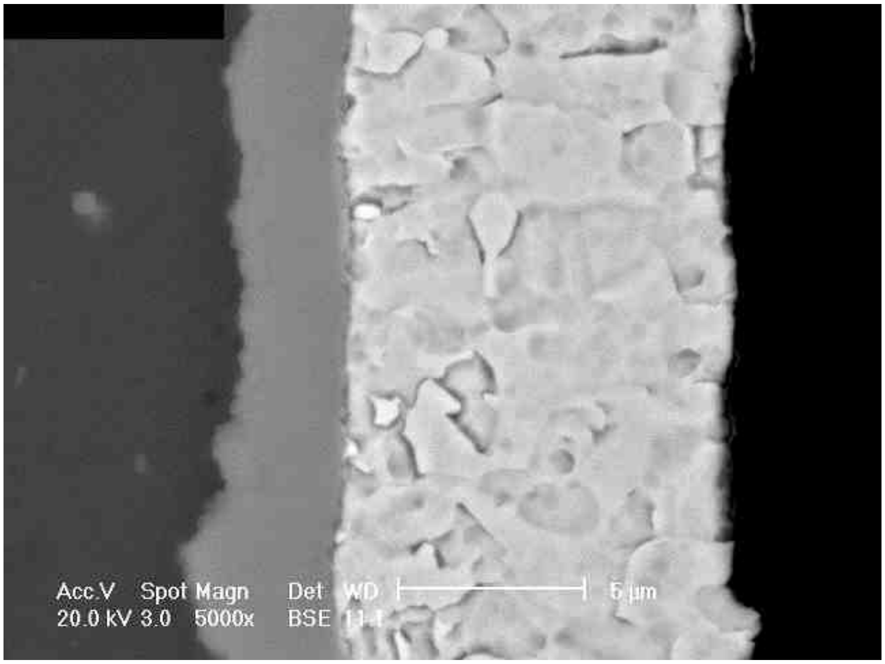

Fig. 4: Cross-section of a galvanic nickel layer (bright, on the right) on aluminium (dark, on the left) after heat treatment. The diffusion layer between them is clearly visible (grey)

The isothermal growth kinetics of the intermetallic layer were analysed using a general empirical power law which describes the average intermetallic thickness ($\bar{h}$) as a function of time (t) and temperature (T)[7]

$$\bar{h}(t,T) = h_i + k_h \exp\left(\frac{-Q_h}{RT}\right) t^{\left(\frac{1}{n}\right)} \qquad (1)$$

where h_i is initial intermetallic thickness, k_h and n are constants, and Q_h is the apparent activation energy for the growth process.

Fig. 5 shows the temporal evolution of the diffusion layers for electroless and galvanic nickel, respectively. The results were fitted by means of equation (1).

Fig. 5 shows, that electroless nickel layers initially have a higher growth rate for Al_3Ni than galvanic nickel. This could be caused by the high concentration of grain boundaries which form during the recrystallisation of the initially amorphous nickel-phosphorus layer at approximately 320°C.

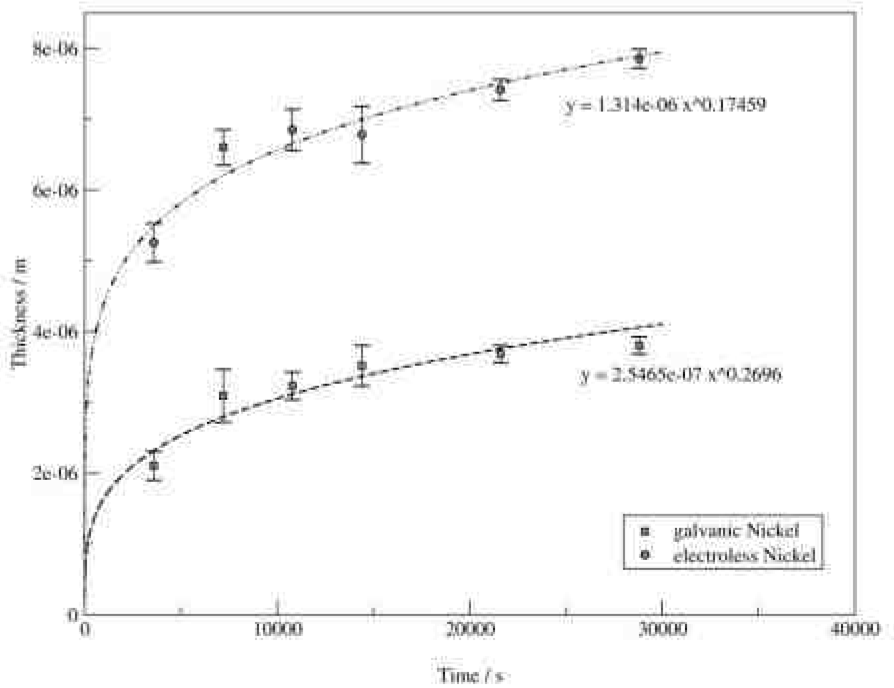

Fig. 5: Growth process of Al_3Ni-layers during temper experiments at 500 °C

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However, the time-dependence of the Al_3Ni-growth in electroless nickel is of an order of 5,72 whereas the galvanic layer shows only a dependence of 3,71.

This difference can be explained with the simultaneous displacement of phosphorus by aluminium. EDX analyses of the cross-sections show a phosphorus content in the Ni-Al-diffusion layer of approximately 3 % P whereas the concentration in the remaining nickel layer has increased from initially 10 to 16 % after the heat treatment.

This displacement probably slows down the growth process and therefore increases the order of the time-dependence for electroless nickel.

Conclusion

Pretreatment methods different from the widely used zincate process were studied. In only one step the aluminium surface can be prepared for the deposition of an electroplated nickel layer. This result in lower manufacturing costs.

The diffusion behaviour of galvanic nickel and electroless nickel-phosphorus layers was studied. After recrystallization nickel-phosphorus layers initially show a growth rate for the Al_3Ni phase higher than galvanic nickel. The growth process decelerates with time. It is assumed that the slowdown is caused by the simultaneous displacement of the phosphorus in the nickel layer. Galvanic nickel layers exhibit a slower initial rate for Al_3Ni. This is probably due to the lower concentration of grain boundaries in the galvanic coating. The deceleration, however, is not as strong as in the case of the nickel-phosphorus layer. As mentioned above, this can be understood by the absence of phosphorus in the pure nickel deposit.

Acknowledgements

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