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ADSORPTION OF A FATTY ACID ONTO A DEFORMED ELECTROGALVANIZED STEEL SHEET

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ABSTRACT

During forming operation of electrogalvanized steel sheets, the crystallographic orientation of the zinc coating may evolve from a pyramidal texture to a basal one. As a consequence, the adsorption of lubricant additives onto the zinc surface may be altered. Plane-strain compression tests and XRD analysis are carried out to study the texture evolution. After deformation, the samples are cleaned and their reactivity versus fatty acids are measured by ToF-SIMS analysis. It is shown that fatty acids adsorb much more strongly on a pyramidal oriented zinc surface than on a basal one.

KEYWORDS

Zinc-coating, crystallographic orientation, adsorption, plane-strain compression test, XRD, Tof-SIMS.

INTRODUCTION

Electrogalvanized coatings are very efficient for the protection of steel against corrosion and have good mechanical properties. For these reasons, they are widely used in automobile industry.

The formability of zinc coated steel sheets has widely been studied for several years: In the boundary lubrication regime, it has been shown that the adsorption of additives is a key parameter for friction. During deformation, the zinc crystal orientation is affected but the influence of zinc crystal orientation on the adsorption of a fatty acid has not yet been studied. The purpose of the present work is to study the consequences of the zinc coated steels deformation on the zinc coating orientation and on the adsorption of a fatty acid.

EXPERIMENTAL PROCEDURE

Deformation tests were conducted using the plane strain compression test. The procedure is to compress the sample between two platens with a given load and speed. The deformation ε can be obtained by measuring the initial (e_i) and final (e_f) thicknesses:

$$\bar{\varepsilon} = \frac{2}{\sqrt{3}} \ln \frac{e_i}{e_f}$$

The orientation of zinc coatings was determined by X-ray diffraction (XRD). The relative orientation was estimated by comparing the orientation of the sample with a powder of zinc. The orientation of powder is random. The relative texture coefficient (RTC) was calculated via the measurement of diffracted intensities for the {hkil} plans. 9 Zn peaks were monitored. The percentage of each plan was used to characterize preferred orientation, similar to the procedure used by Shaffer [1]. The normalized intensity of each peak was then divided by the sum of the normalized intensities to yield an approximate fraction of each plane orientation (RTC).

After indentation, the sample was cleaned in four solvents ultrasonic bath in order to entirely remove the lubricant used during the compression test. It was then immersed in a solution of oleic acid in hexadecane. Oleic acid ($C_{18}H_{34}O_2$) has been chosen because it is one of fatty acid additives of usual lubricants. The concentration of oleic acid in hexadecane was adjusted at 1%. The sample was immersed vertically during 1 minute. It was finally rinsed in hexane to remove excess of hexadecane, just before ToF-SIMS analysis (time-of-flight secondary ion mass spectrometry).

The ToF-SIMS analysis was already used to quantify the adsorption of organosilanes on aluminum surfaces [2]. The interaction between fatty acid and zinc coating surface was also studied by ToF-SIMS [3]. Thanks to the low primary ion dose impinging the surface (static mode), the uppermost layers are analyzed: surface reactions and molecular fragmentation could be studied. The experiments were performed on a Charles Evans TRIFT machine. Positive and negative secondary ion spectra were recorded at several locations of the sample: Thanks to the positive mass spectra, the quantity of zinc could be controlled. Negative mass spectra was used to study the adsorption of acid oleic because the de-protonated oleic acid molecular ion $(C_{18}H_{33}O_2)^-$ is easily detected on them, whereas protonated ions $(C_{18}H_{35}O_2)^+$ exhibit very low intensities on positive mass spectra. Each analyzed area was 120 µm*120 µm. The peak intensities given below are normalized over the total number of counts, to account for experimental variations from one sample to another.

RESULTS

The initial preferred orientation of "as-received" electrogalvanized coating is pyramidal with a low basal component. XRD analysis show that the texture evolved under the deformation. With a deformation larger or equal than 2, the predominant orientation was basal and no more pyramidal. Mean values obtained for 10 samples of each kind can be seen on Table 1.

RTC (%)	before deformation	deformation ε = 2
basal	3	**65**
low angle pyramidal	**39**	16
high angle pyramidal	**39**	11
prismatic	19	8

Table 1: Relative texture coefficient (RTC) values for the two samples: as received and after deformation – XRD analysis

The role played by the orientation of zinc coating on the adsorption of fatty acid has been studied on these deformed samples. The Tof-SIMS technique is not a quantitative one, but it is possible to compare relative intensities for similar samples.

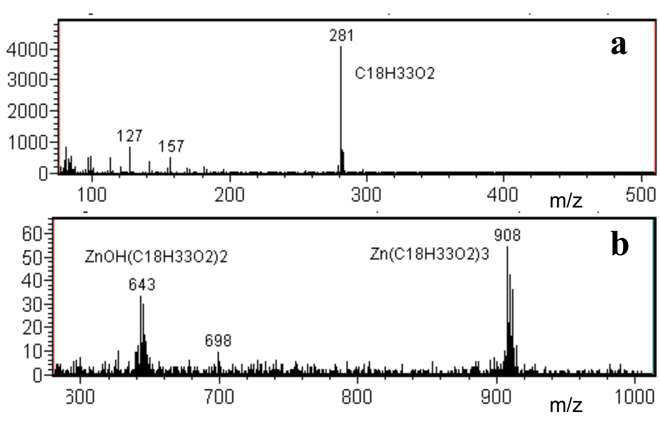

Figure 1: Portions of negative Tof-SIMS mass spectra showing the most characteristics peaks of adsorption

On negative mass spectra (Fig. 1a), the relative intensity of the de-protonated oleic acid peak $(C_{18}H_{33}O_2)$ shows the reactivity of the fatty acid with the zinc coating. Moreover, on the negative mass spectra, the presence of zinc carboxylates compounds (Fig. 1b) can be seen and show the association between zinc and one, two or three fatty acid molecule: respectively $ZnO(C_{18}H_{33}O_2)$, 361 amu, $ZnOH(C_{18}H_{33}O_2)_2$, 643 amu and $Zn(C_{18}H_{33}O_2)_3$, 908 amu.

The normalized intensities of these peaks are given in Figure 2 for the electrogalvanized samples as-received (pyramidal orientation) and after deformation (basal orientation). All pyramidal peaks show higher intensities which can be traduced by a higher reactivity of fatty acid onto a pyramidal orientation zinc substrate than for a basal one.

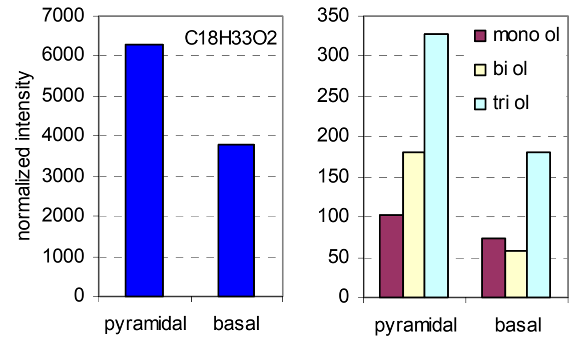

Figure 2: Intensities of oleic acid, mono, bi and tri-zinc oleates normalized by the total number of counts, versus the sample orientation. Immersion for 1 minute, in 1% oleic acid – hexadecane bath (mean values for 10 experiments)

CONCLUSION

One of the consequences of the deformation with the plane strain compression test was the change of the zinc electrodeposited orientation from a pyramidal to a basal orientation. The effect of the orientation on the adsorption has been studied. Such work has shown that a pyramidal orientation is more favorable on the adsorption of a fatty acid than basal orientation.

When large deformations of electrogalvanized steel sheet are necessary, it seems that good lubrication need other additives than fatty acids.

ACKNOWLEDGMENTS

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