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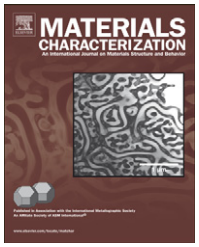

Microstructural characterization and quantification of Zn–Al–Mg surface coatings

C. Commenda, J. Pühringer*

Department of Microstructure and Surface Analysis, voestalpine Stahl GmbH, voestalpine-Strasse 3, 4020 Linz, Austria

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ABSTRACT

The microstructure of Zn–Al–Mg coatings on steel sheets is characterized with the energy dispersive X-ray technique. Optimum parameters on the scanning electron microscope with a field emission gun have been found in order to laterally resolve the fine structure of the individual phases. A quantification of the microstructure is done with a mean shift algorithm that is usually applied for image segmentation in pattern analysis. This nonparametric technique is here based on the chemical composition and the spatial domain. The measured area is partitioned by a quantitative feature space analysis into phases with similar chemistry. A backscattered electron image is compared with the results of the X-ray point map of the same area. As an application the influence of the chemical composition of the melt on the resulting microstructure is compared for two different alloys.

1. Introduction

In order to increase the corrosion resistance of steel sheets, Zn–Al–Mg alloy coatings were developed [1] for industrial application. From the thermodynamic point of view the zinc rich part of the ternary system [2] is of interest. Besides the zinc matrix phase, a phase rich in aluminum, the stoichiometric phase $MgZn_2$, and the binary intermetallic phase Mg_2Zn_{11} can be expected from the equilibrium diagram. The rapid solidification of the Zn–Al–Mg coating results in a deviation in the chemical composition of the phases compared to the equilibrium values. Furthermore the high cooling rates result in a very fine and complex microstructure. Macroscopic properties such as the formability, fracture- and corrosion resistance depend on the microstructural details. The analysis and quantification of the phases, their chemical composition and structure have to be based on an analytical method with high lateral resolution. Besides the technical relevance of the Zn–Al–Mg surface coating this ternary system serves as a perfect example to demonstrate an experimental technique and quantification procedure, that can generally be applied to different microstructures. An important precondition is a measureable quantity that is necessary to distinguish different phases.

2. Experimental Procedure

The cold rolled steel sheets are coated with a Zn–Al–Mg surface layer. In order to suppress topographical contrast on the SEM the surface of the samples was polished with polycrystalline diamond grains with a size of 1 μm. The final polishing was done with a silicon oxide suspension for 5 min. The oxidation of the Zn–Al–Mg layer can be avoided by increasing the acidity with 0.5 vol% of *ortho*-phosphoric acid (>85%).

Since focus is centered around the chemical composition of the phases the energy dispersive X-ray technique on a SEM with a field emission gun has been chosen. Monte Carlo simulations were carried out in order to predict the optimal settings of the SEM. The output of the software Casino [3] predicts that the lateral resolution can be increased by

* *Corresponding author*. Tel.: +43503041573084.
E-mail address: chris.commenda@gmx.net (C. Commenda).

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lowering the acceleration voltage of the incident electron beam. Fig. 1 shows typical electron trajectories for an acceleration voltage of 15 kV (left) and 5 kV (right) starting at the center of a narrow 100 nm vertical section of aluminum adjoined by zinc at both sides. In terms of the X-ray intensities the comparison for different acceleration voltages is less dramatic than in the image of electron trajectories depicted down to an energy of 0.05 keV. Fig. 2 shows the results for a horizontal line scan starting at the center of the aluminum section. The vertical line at a position of 50 nm marks the boundary between aluminum and zinc for the chosen geometry. Higher aluminum X-ray intensities in the zinc substrate indicate a lower lateral resolution for an incident electron energy of 15 keV.

A measurement of a quadratic point map at an acceleration voltage of 5 kV and a step size of 150 nm detecting and quantifying the elements aluminum, zinc and magnesium is shown in Fig. 3. The bright regions correspond to a high content of the elements. The microstructure can be qualitatively characterized by a zinc rich phase with small precipitations of aluminum, a dendritic aluminum rich phase, a binary phase rich in zinc and magnesium with hexagonal symmetry and a very fine structured ternary eutectic phase. The images in Fig. 3 are zoomed by applying a bicubic interpolation scheme [4].

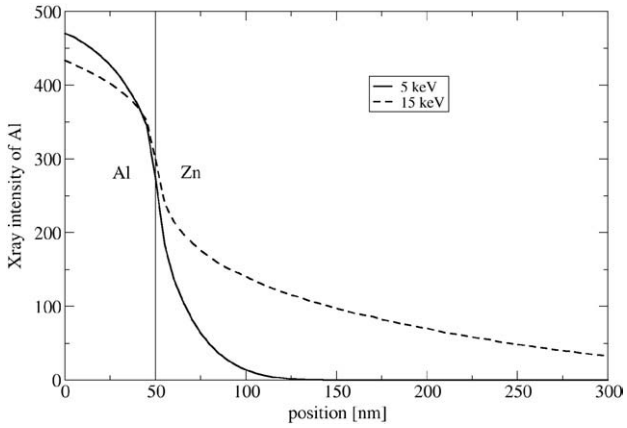

Fig. 2 – Comparison of Al X-ray intensities: acceleration voltage 15 kV, 5 kV.

3. Quantification of the Microstructure

The chemical composition of the ternary Zn–Al–Mg system has two independent variables, e.g. the atomic fractions of aluminum x_{Al} and magnesium x_{Mg}. From the conservation relation

$$x_{Al} + x_{Mg} + x_{Zn} = 1$$

the dependent atomic fraction of the matrix element zinc x_{Zn} can be calculated. The map in Fig. 3 is a grid of 256×256 points with a spacing of 150 nm. For each point the chemical composition is known from experimental data of the energy dispersive X-ray measurement. The atomic fractions of magnesium and aluminum of all these points are plotted in Fig. 4. Since the number of counts for each element is finite, the calculated concentrations are rational numbers, which explains the discrete nature of the represented data.

Many phase analysis tools are based on thresholds with respect to the chemical composition. As can be seen in Fig. 4 the experimental data is not heavily clustered and the chemical compositions are much more spread than can be expected from the ternary equilibrium phase diagram. Choosing certain boundaries in the chemical composition for individual phases introduces bias, which is strictly avoided here.

In order to find phases with similar chemical composition it is useful to analyze the density of measured points in the area spanned by the contents of aluminum and magnesium. In general the density $f_{h,k}(x)$ can be computed with the *kernel density estimator*

$$f_{h,k}(x) = \frac{1}{nh^d} \sum_{i=1}^{n} K\left(\frac{x - x_i}{h}\right) \quad (1)$$

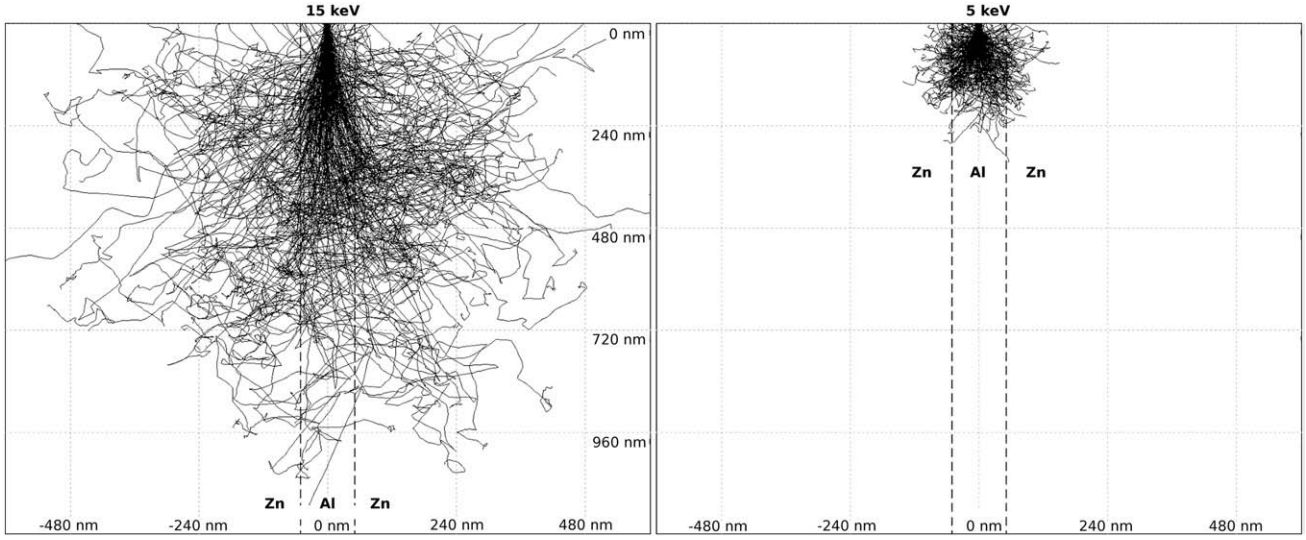

Fig. 1 – Comparison of interaction volumes: acceleration voltage 15 kV (left), 5 kV (right).