

# Elucidating the effect of silicon on Fe-Zn phase formation in galvanized steel via advanced TEM

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## Introduction

Raising the bar for weight reduction, safety, and environmental protection in modern automotive and construction materials can be barely achieved without new types of Advanced High-Strength Steel (AHSS) [1] and must be guided by in-detail structural and chemical characterization. To meet safety and durability requirements, modern AHSS products additionally need effective corrosion protection, and the galvannealing process, which involves hot-dip galvanizing in a Zn bath followed by annealing, is considered to be one of the most efficient methods for achieving this goal. Such a well-balanced but complex process of interfacial interactions can be significantly affected by alloying elements, which are added in AHSS to augment its mechanical properties and achieve a superior combination of high tensile strength and good formability [1,2]. For instance, silicon affects the steel bulk properties enhancing the Fe-liquid-Zn interfacial reaction by solute Si in the  $\alpha$ -Fe phase. An additional effect is attributed to the formation of surface oxides on the steel sheet during annealing before immersion in the Zn bath [3,4]. One can conclude that the structural and chemical peculiarities of the steel/coating interface region including the so-called inhibition layer, e.g. [3], must be considered as a key factor governing the phase formation kinetics. Advanced transmission electron microscopy (TEM) can help us collect morphological, structural, and elemental information at the nanoscale. For a deeper understanding of phase evolution, it is necessary to study not only fully galvanized samples processed at different annealing times but also steel sheets at the outlet of the bath, coated with almost pure Zn.

## Methods

We optimized various TEM sample preparation techniques and showed that low-temperature FIB is a method of choice for dependable Zn-coated steel preparation [3], which can be further enhanced utilizing a plasma P-FIB operated with, for instance, Xe ions. Cross-sectional TEM lamellae were prepared using a CrossBeam 1540 XB SEM (Zeiss, Germany) Ga-FIB using W to form a protection capping layer. The final thinning was performed at -60°C applying a Micro Heating Cooling Stage (MHCS) (Kleindiek Nanotechnik GmbH, Germany) based on the thermoelectric effect and 5 kV acceleration voltage to minimize the invasive influence of the Zn-Ga eutectic formation. The investigation was carried out in a JEOL JEM-2200FS (JEOL, Japan) operated at an acceleration voltage of 200 kV. The TEM is equipped with an in-column  $\Omega$ -filter and a TemCam-XF416 (TVIPS, Germany) CMOS-based camera. HRTEM data processing was done with Gatan Microscopy Suite. Crystal structure simulations were performed via JEMS software. STEM EDX analysis was fulfilled in a scanning (S)TEM mode for qualitative elemental characterization of the specimens with an X-MaxN 80 T detector from Oxford Instruments (United Kingdom).

## Results

Employing complementary TEM techniques (HRTEM, SAED, STEM EDX), we traced the formation of Zn-Fe phases in AHSS with high Si content at different stages of galvannealing process along with as-galvanized reference specimen [4]. In particular, it has been disclosed that the Si-based surface oxide layer, formed on steel during the recrystallization annealing step before dipping into the Zn bath (460°C) remains stable, separating the coating from the reaction zone (Figure 1). This efficiently hinders the desired reaction of Fe with Al in a Zn bath at the early stage of hot-dip galvanizing and complicates the formation of the Fe<sub>2</sub>Al<sub>5</sub>-xZn<sub>x</sub>

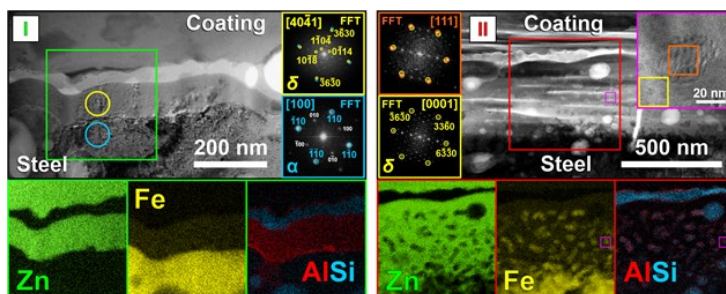
inhibition layer. One can reveal that liquid Zn can penetrate local disruptions in this film forming a  $\delta$  phase layer below, while Fe diffusion into the coating is suppressed. The  $\delta$  layer supersaturates with Fe and Si from the steel during long-term annealing at 480°C and decomposes forming a  $\delta$  phase [5] matrix with Fe-Si-Al-based nanoprecipitates with a cubic structure (Figure II). The phases were identified via HRTEM and STEM EDX. Based on experimental STEM EDX data, the achieved phase configuration was refined via Thermo-Calc Fe-Zn-Si-Al system simulation. It must be emphasized again that the observed Si-based oxide layer remains stable even after long-term annealing, thus Si, which constitutes this membrane, was not actively involved in the Fe-Zn reaction.

### Conclusion

Our results indicate the following evolution of phases at the steel/coating interface of AHSS subjected to an industrial continuous hot-dip galvannealing process. During dipping in a liquid Zn bath, Zn penetrates the gaps in an existing oxide film and forms a layer below directly reacting with the Fe. This layer was identified as the  $\delta$  phase. Thus, the desired Fe<sub>2</sub>Al<sub>5</sub>-based inhibition layer cannot be formed as intended. Mentioned  $\delta$  phase layer can grow during subsequent annealing being, however, efficiently constrained by the mixed oxide membrane. While long-term annealing, Si dissolved in the steel destabilizes the  $\delta$  phase supersaturated with Fe and Al, triggering its decomposition into the  $\delta$  phase and Fe-Si-Al-based nanoprecipitates. The challenges and solutions on the way toward a fruitful and dependable TEM analysis of galvanized industrial steels will be also discussed in detail.

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### Graphic:



### Keywords:

Fe-Zn, phase formation, galvanized steel

### Reference:

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