

Crystallographic texture of light tinplate coatings made in various electrolytes

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Abstract. Two electrolytic tinplating processes are currently used in Europe: PSA (based on phenolsulfonic acid) and MSA (based on methanesulfonic acid). The Halogen Process is used in other parts of the world. The electrolyte composition and process parameters affect the electrodeposit and ultimately the tinplate appearance and performance. In order to better understand the impact of electrolyte composition on the crystallographic texture of tin coating tinplate, light tin coatings on single reduced, continuously annealed (CA) tinplate produced in three electrolytes: Halogen, PSA and MSA were analyzed. The crystallographic texture of thin tin coating ($<2.8\text{gm}^{-2}$) was analyzed by X-ray Diffraction and Electron Backscatter Diffraction. The effect of reflow (melting of the tin followed by rapid solidification) and ironing during drawn and wall ironed (DWI) can forming on the tin crystallography were evaluated. Both texture analysis by XRD and EBSD confirmed that all un-melted tin coatings, made in three different electrolytes, contain texture fibers. The effect of steel sheet crystallographic texture was investigated by comparing the tin crystallographic orientation on continuously annealed steel substrate (with α and γ fiber texture) versus batch annealed (BA) steel with a strong γ fiber texture. The main electrolytic parameters, current density and line speed, did not affect the texture formation of tin coating produced in MSA-based electrolyte within the commercial ranges. Un-melted tin coatings produced in the MSA-based electrolyte showed sharper texture than those produced in PSA and Halogen electrolytes. The FeSn_2 alloy structure was not observed in un-melted tin coatings; however, it was detected after ironing in the DWI process.

1. Introduction

Many performance attributes of polycrystalline materials (e.g. drawability, magnetic polarization or corrosion resistance) can be optimized by control of the crystallographic texture. Electrochemical tin deposition has two main processing parameters: current density (CD) and bath chemical composition, both of which affect the tin deposition's morphology and crystallographic orientation. The un-melted tin coating texture of laboratory-produced PSA electrolyte consists of (321) texture, of which the fraction decreases with increasing CD [1]. Girin established two axial texture components (110) and (100) for laboratory produced un-melted tin coatings, where the texture (110) influences the protective ability of the tin coating [2]. Ichiba et al., studied the effect of MSA bath chemistry and CD on the tin coating appearance [3]. On the basis of X-Ray texture analysis these authors concluded that tin coatings with a (101) crystal orientation have a beneficial effect on glossy appearance, while the (200) crystal orientation was formed by dendritic tin deposits. Most of the abovementioned papers used X-ray diffraction (XRD) for tin coating crystallographic orientation analysis. In the last decade, texture measurement of polycrystalline materials has increasingly been performed using EBSD, which enables analysis of individual grain orientation, while conventional XRD is more useful for bulk texture measurement [4]. The un-melted tin coating texture was analyzed using both XRD and EBSD. The crystallographic textures of the tin deposit are presented in Orientation Distribution Function (ODF) sections. The volume fractions of main fiber textures from ODF were calculated.



2. Materials and Experimental Procedures

The texture of commercial un-melted tin coatings, produced in three electrolytes (Halogen, PSA and MSA), was analyzed by XRD and EBSD to establish the effect of electrochemical bath composition on light tin coating texture formation. In addition to the electrolyte effect, the effect of steel substrate texture produced by continuous or batch annealing on tin texture was analyzed. The tinplate samples included in the analysis are summarized in **Table 1**.

Table 1 Analyzed commercial tinplate BA and CA samples produced in USS Corporation

Electrolytic tinning line Type	Electrolyte	Sample Name	Tin Coating weight [g.m ⁻²]	Line Location
Horizontal	Halogen	H	2.3	USA
	MSA	MSA-H	2.3	
Vertical	PSA	PSA	2.8	Europe
	MSA	MSA-V	2.5	

The crystallographic texture of un-melted tin coating was measured on the surfaces of the samples as produced without additional preparation. Five incomplete pole figures of un-melted tin coating, (200), (101), (220), (301) and (112), were measured by XRD with filtered Co radiation using a texture goniometer and a position sensitive detector (PSD). The XRD crystallographic texture was measured using point focus, which expands profiles of diffraction lines much more than line focus. ODF was calculated from the measured pole figures data using the Arbitrarily Defined Cells (ADC) method [5].

The tin coatings were also analyzed by EBSD. The samples were analyzed as-produced because the thin and relatively soft tin coatings precluded the use of the grinding and polishing typically used for EBSD preparation. All samples were analyzed at 200-2000x magnification with 0.15-1.5 μm step intervals, depending on the surface quality. The textures of the un-melted tin coatings were evaluated from measured points with a confidence index (CI) >0.1 that resulted in volume fraction in the interval of 5–16%, [6, 7]. Those small volume fractions are hardly satisfactory values for reliable texture evaluation. However, the EBSD texture of the Halogen and PSA, which showed the highest CI values, were compared with the XRD results.

3. Results

None of the X-ray diffractograms of the four un-melted tin coatings revealed the presence of the FeSn_2 structure, which forms after the reflow process and can be detected in melted tin coating. However, the presence of FeSn_2 was confirmed after ironing during the DWI can production. The diffractograms were also evaluated by the Rietveld method, [8].

The ODF were calculated in orthorhombic sample symmetry because all the pole figures showed orthorhombic sample symmetry observed in the (200) and (101) pole figures. ODF section $\varphi_2=0^\circ$ of all the samples are summarized in **Figure 1**. All the ODF sections confirmed an incomplete fiber texture. The same ODF section $\varphi_2=0^\circ$ determined by EBSD analysis for the Halogen and PSA sample are shown in **Figure 2**, which correspond well to those calculated from the X-ray pole figures. In spite of the small texture fraction analyzed using EBSD, the fiber texture can be seen in both ODF.

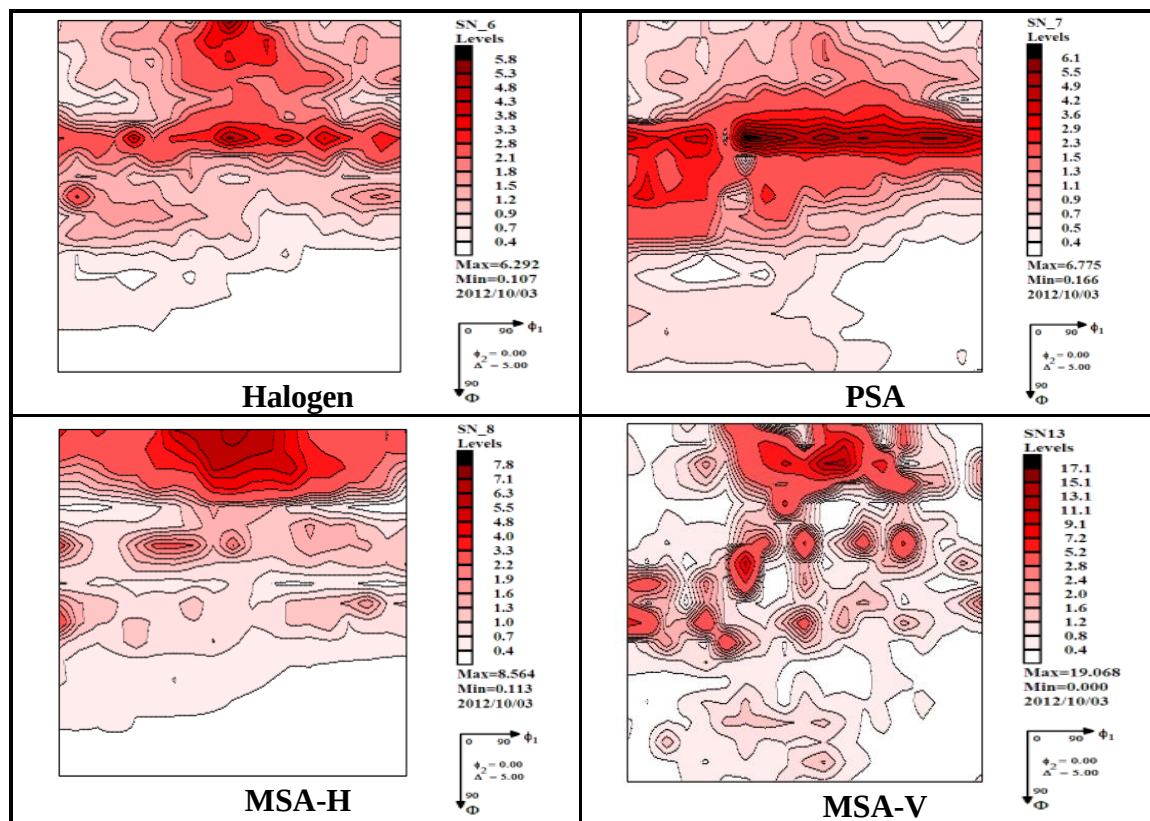


Figure 1 ODF section $\phi_2=0^\circ$ calculated from pole figure of X-ray texture analysis for all four samples of CA tinplate sheets

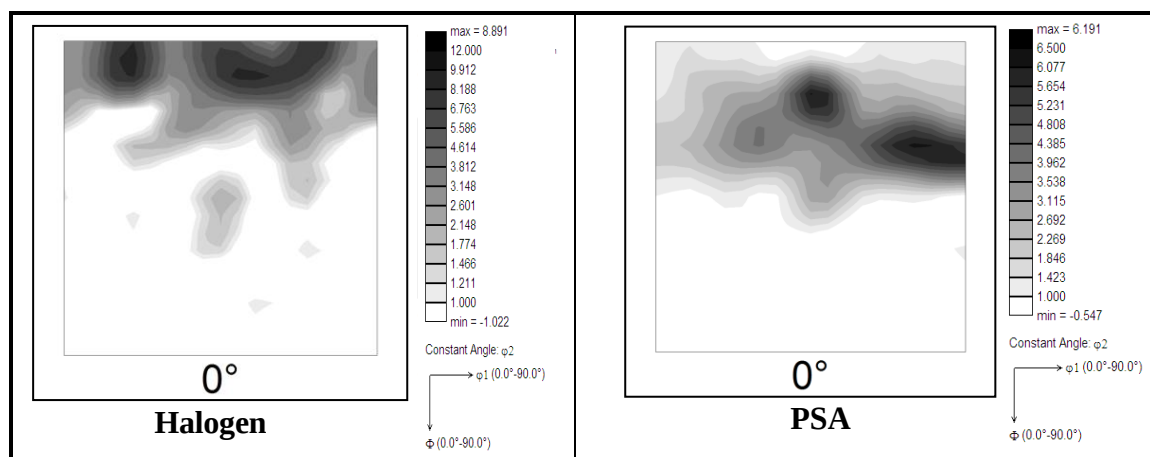


Figure 2 ODF section $\phi_2=0^\circ$ calculated from pole figure of EBSD texture analysis for Halogen and PSA samples of CA tinplate sheets

The main texture fibers with a volume fraction greater than 4% from the XRD ODF were calculated using LaboTex software. The main texture fiber components of all four CA samples are summarized in **Figure 3**. Analysis of the texture fibers processed from ODF showed that approximately 70% of the total crystalline volume of the un-melted tin coatings is textured, while the remaining volume is randomly oriented.

In spite of being plated on lines with different configurations and with different processing parameters, in terms of line speed and CD value, both MSA tin coatings showed very similar

crystallographic texture. Those textures consisted of fibers: (321), (221), (213), (011) and (001) with similar volume fraction, see **Figure 3**, with the strongest fiber of (321) plane which is in agreement with the literature [1]. All five of the analyzed fibers of the MSA-V and PSA un-melted tin coatings have similar volume fractions with highest (321) and lowest (001) fibers. MSA-H and Halogen samples showed weaker (321) fibers than PSA and MSA samples. No significant difference was seen in the tin coating crystallographic texture between CA and BA tinplate steel strip coated in the MSA and PSA electrolyte bath as shown in **Figure 3**.

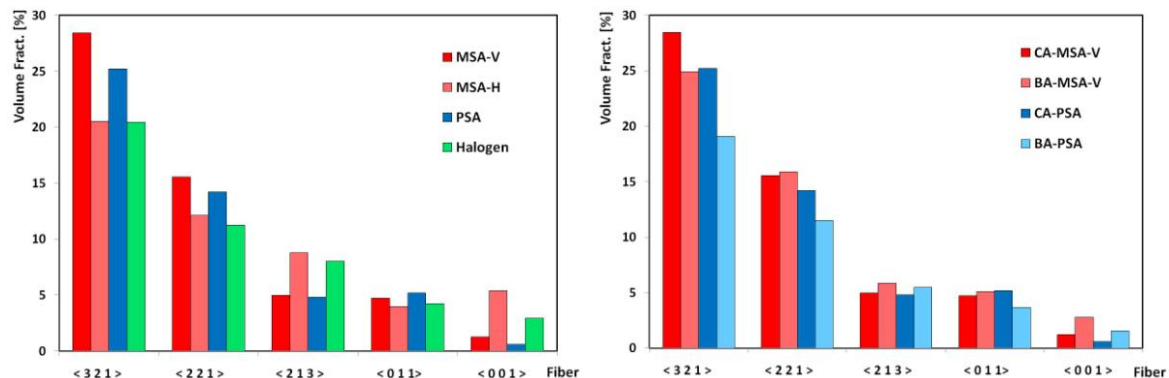


Figure 3 Volume fraction (>4%) of the main fiber texture of un-melted tin coatings. Four different electrolyte bath of CA tinplate (left). MSA vs PSA samples of CA and BA tinplate (right)

4. Conclusion

X-ray diffraction phase analysis of un-melted tin coatings did not reveal the presence of a FeSn_2 phase. However, such intermetallic phase was detected after ironing during DWI can production. All un-melted tin coatings, made in three different electrolytes, contain incomplete texture fibers, mainly (321)<uvw> fiber. Crystallographic textures of the both continuously and batch annealed tinplate strips have the same effect on the crystallographic texture component of the tin coating which is slightly influenced by the electrolyte.

References

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