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Outbursts formation on low carbon and trip steel grades during hot-dip galvanisation

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Abstract. Low carbon and TRIP grade steels have been hot dip galvanised in order to study outbursts formation. Microstructure and texture of intermetallic phases have been observed after selective electrochemical etching by scanning electron microscopy. Potential versus time (chronopotentiometric) characteristics were recorded in order to monitor surface modifications. This combination of techniques enable to quantify and observe intermetallic phase one by one. The overall thickness of coating on both substrates are similar. However, microstructures of Fe-Zn intermetallic phases are very different on both grades. In particular, the Σ phase is dense on standard steel but develops a highly branched filament structure on TRIP steel. The transformation of Σ phase to ι and B_1 are limited on TRIP steel. Differences of texture provide clues for understanding mechanisms of formation of outbursts. They can account for the differences of mechanical properties and corrosion resistance. Silicon from the substrate influences the reactivity of TRIP steels due to capping and local reactions.

Résumé. La formation des outbursts a été étudiée sur un acier bas carbone et sur un acier TRIP galvanisés. Les épaisseurs des revêtements sont similaires. Néanmoins, les observations microscopiques et les érosions électrochimiques montrent que la répartition des phases intermétalliques et leurs microstructures diffèrent sensiblement en fonction de la nature du substrat. Ces différences expliquent les propriétés mécaniques et anticorrosions. L'encapsulation de la surface par les oxydes de silicium freine la transformation de la phase dzêta en delta et gamma sur l'acier TRIP.

1 INTRODUCTION

Outbursts are microstructures made of Fe-Zn phases developing within anticorrosion coatings during hot-dip galvanisation. They evidence violent local reaction between the galvanisation alloy and steel. They impair mechanical and anticorrosion properties of the coating not only because intermetallic phases are brittle and offer a poorer resistance to corrosion, but also because their dispersion produces grain boundaries which are paths for corroding molecules. Finally outbursts deteriorate the visual aspect of the coating due to pitting when they reach the surface. This paper compares outbursts grown on standard low carbon steel and TRIP (transformation induced plasticity) grade steel aiming at understanding mechanisms of triggering and growth.

Reactivity of galvanisation alloy with low carbon steels is usually regulated by aluminium addition above 0.15 wt. % in the alloy. Aluminium reacts rapidly with iron and produces a thin Fe_2Al_5 layer inhibiting momentarily the formation of Fe-Zn phases during hot dipping. Silicon from the substrate also increases reactivity when concentration in steel ranges of some tenths of wt. %. This is known as the Sandelin effect. In high resistance steels like TRIP's, silicon concentration reaches about ~1 wt. % (~2 at. %) and causes contradictory effects on reactivity due to the formation of a SiO_2 protective layer. This layer results from segregation to the surface and preferential oxidation during hot rolling and surface preparation. It prevents contact between the galvanising bath and steel. Vigorous reactions forming outbursts start at cracks in the oxide layer. For these reasons high silicon grade steels are difficult to galvanise and studying the formation of outbursts deserves special attention.

2 EXPERIMENTAL

The 2 mm sheets of low carbon (hot rolled and cold rolled) HE400M and (hot rolled) TRIP steels were similarly prepared by alkaline degreasing and acid etching. A 500 g/l zinc and amonium chloride solution was used for fluxing at 70 °C. After drying in air at 95°C, hot-dip galvanising was performed at 450°C (without preheating) in a zinc alloy containing 1.1 wt.% tin, 0.1 wt.% bismuth and 0.07 wt.% aluminium. Galvanisation lasted 4 minutes in order to break the silicon oxide layer on TRIP steel. Zinc in excess was drained by gravity and cooling proceeded naturally in air.

Electrochemical etching were performed in (NaCl, $ZnSO_4$: 3.4 M, 0.32 M) with acidity fixed at pH = 4 by addition of sulphuric acid. A platinum counter electrode has been used. Anodic dissolution were performed at constant current density, at room temperature with no steering. Potentials measured versus time during galvanic dissolution (chronopotentiometric data) are referred to a saturated calomel electrode (SCE potentials). Standard potentials can be obtained by adding 241 mV.

Chronopotentiometric data have been quantitatively analysed by integrating current over time in order to correlate charge transfer to the amount of matter etched from the surface. We assumed a double charge both on iron and zinc ions. Values were converted in thickness without hypothesis on the nature and composition of each phase, considering average mass and density for zinc, iron and intermetallic compounds. Averaging causes a $\pm$ 10 % error because densities of iron, zinc and compounds are very close.

3 RESULTS

Cross section and chemical etching with nital (2%) reveal intermetallic phases (figure 1). Overall thickness' of coatings on both steels are close. A, B, C labels on figure 1 refer respectively to ξ (pure zinc), $\Sigma$and ι phases [1]. Proportion and tridimensional distribution into the coating depends on the substrate. Quantitative measurements are collected in table 2. Peak to peak variations are reported too.

Figure 2 shows variations of sample potential during etching. Corrosion potential A, B and C are fingerprints of ξ, $\Sigma$and ι phases. Potential of iron is the highest. (E). Potentials compare with similar data from the literature [3]. Quantitative analysis of chronopotentiometric data are reported in table 1. In order to get quantitative agreement between thickness' measured by microscopy and dissolution, the galvanic yield is assumed to be between 0.66 and 0.75 when erosions are performed at ~15 mA/cm^2. Both kind of data are complementary since microscopy measures mean thickness ; and electrochemical etching, weight composition. Finally, since electrochemical potentials are sufficiently different, selective etching of zinc and iron-zinc compounds is possible. Micrographs

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obtained by electron scanning microscopy and taken at time pointed by the arrows on figure 1 are presented on figure 3 to 6.

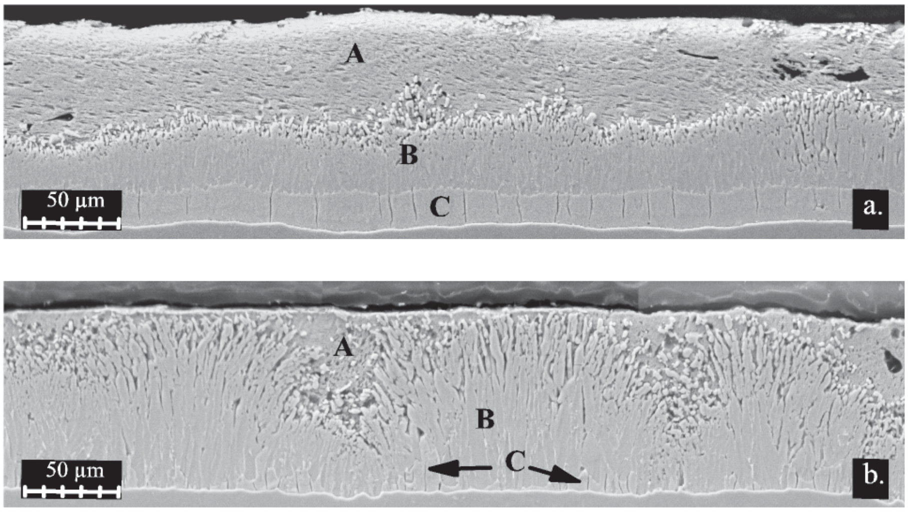

Figure 1. Cross cuts of coatings on standard (a.) and TRIP (b.) steels.

Table 1. Thicknesses (in microns) of (sub)layers evaluated from micrographs and dissolution.

	TRIP steel		Standard low carbon steel	
	Cross section	Dissolution	Cross section	Dissolution
Total	95 ± 10	90	85 ± 7	84
ξ#	40 ± 25	30	33 ± 11	18
Σ#	50 ± 20	50	40 ± 9	43
ι#	?	11	17 ± 6	24

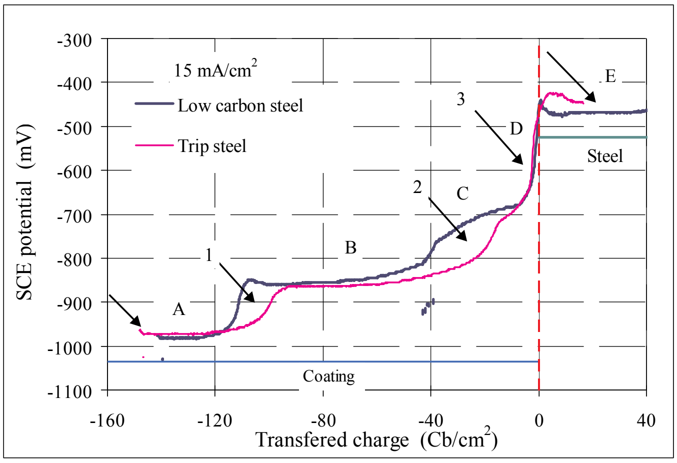

Figure 2. Chronopotentiometric data recorded during dissolution at constant current = 15 mA/cm^2.

Coating on TRIP steel exhibit extended surface defects (figure 3). Pits entering deeply into the bulk degrade corrosion resistance. They are caused by emergence of dense underlying intermetallic structure and local dewetting of zinc. Smooth surface are obtained on standard steel.

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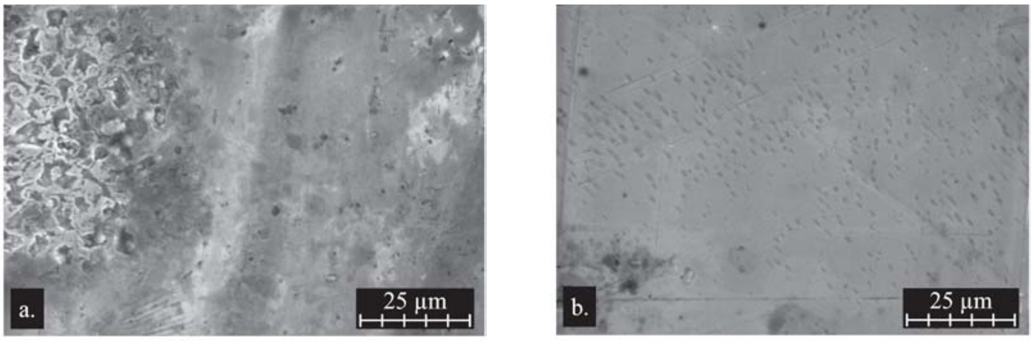

Figure 3. Surfaces of galvanised TRIP (a.) and standard (b.) steels.

Figure 4 shows that phase Σ forms bunches of filaments on TRIP steel which are not observed on standard steel. Spatial dispersion and porosity of Σ on TRIP probably favours retention of ξ phase (pure zinc) by capillarity during drain off. Dewetting when dense entanglements of Σ filaments reach the surface corroborates his hypothesis.

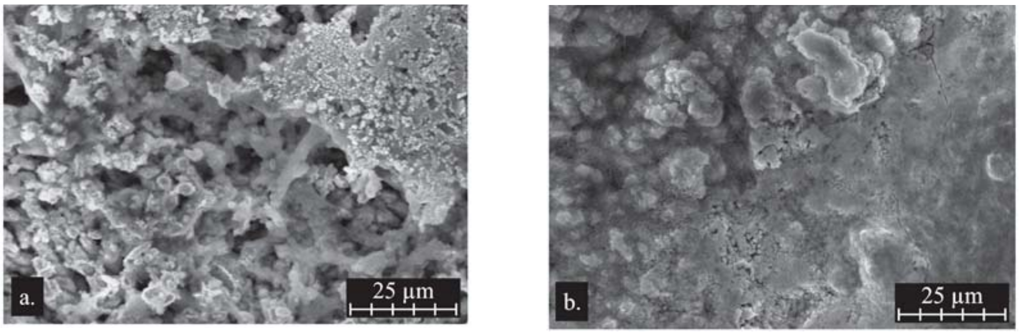

Figure 4. Micrographs of the Σ phase on TRIP (a.) and standard (b.) steels.

Figure 5 shows that phase ι takes a typical microstructure made of submicron sheets [3]. Sheets are differently oriented on both substrates : - hexagonal in shape and laid on the surface on TRIP steel, - perpendicular to the interface on standard steel (dovetailing hinders lateral extension). Coverage seems more continuous on standard steel. On TRIP steel, piles of sheets are separated by large holes. Orientations are probably inherited from the parent Σ phase.

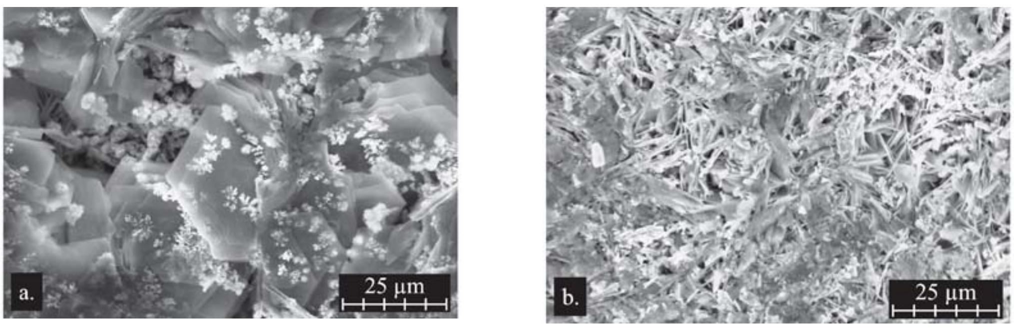

Figure 5. Micrographs of the ι phase on TRIP (a.) and standard (b.) steels.

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Figure 6 shows that phase B_1 appears as a cracked smooth film on TRIP steel. XRD signals from the substrate reveal that the thickness of this layer is ~1 µm. Shiny spots on the picture could be insulating materials like SiO_2. The micrograph of the standard steel discloses nodules. XRD indicates that the thickness of this layer is larger than 5 µm. Nodules are then probably extremities of a columnar structure not distinguished on figure 1.

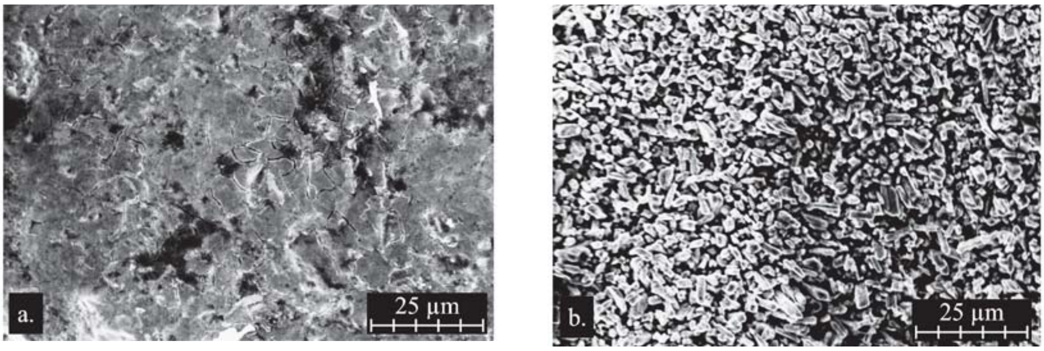

Figure 6. Micrographs of the B_1 phase on TRIP (a.) and standard low carbon (b.) steels.

4 DISCUSSION AND CONCLUSION

Selective electrochemical etching of galvanised standard low carbon and TRIP grade steels has been exploited in order to get a tridimensionnal and quantitative information about the microstructure of outbursts. These complex microstructures contrast with the layered one observed on galvannealed coatings. Differences of microstructures of intermetallic phases observed account for the variation of mechanical and anticorrosion properties of coatings on both steels.
Variations of proportions, morphology and texture of intermetallic phases indicate that composition of steel and interface structure plays an important role on reaction, nucleation, growth and transformation of Fe-Zn phases. As a matter of fact, the parent phase Σ is directly produced from the liquidus. Reactions are local on TRIP due to surface screening by the SiO_2 layer. Filaments probably evidences nucleation and fast growth of the Σ phase from the surface as soon as iron saturates the alloy. Limited transformation of Σ phase to secondary ι and B_8 phases on TRIP evidences that the SiO_2 layer hinders later iron diffusion.
Additional studies on samples galvanised with increasing duration will provide information about kinetics of growth and phase transformation, as well as on the nature of the reaction starting points.

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