METALLOGRAPHIC TECHNIQUES PROCEDURES FOR THE INTERMETALLIC LAYER MORPHOLOGY CHARACTERIZATION IN HOT DIP GALVANIZED STEELS – GI *

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Abstract

The automotive industry, when aiming to increase the resistance to corrosion, uses in the Body in White (BIW) concept the galvanized steels. The hot-dip galvanized steels that stand out most are known as GI steels. They are formed by the zinc element and by phases of intermetallic intermediate iron-aluminum-zinc compounds. The characteristic properties of the GI coating are directly related to the formation of the intermetallic layer, which is responsible for providing the connection between the metal substrate and the coating layer. In this context, two different types of steel (SAE1005 and TRIP780 steel) were used for laboratory characterization of their intermetallic layers through metallographic techniques. The results of the tests showed that the inclined section metallographic inlay technique allows obtaining a larger region of analysis of the intermetallic layer. For the surface analysis, it was observed that the chemical solution used in the preparation of the samples was effective, making possible an analysis more specific about the intermetallic layer formation, distribution and morphology.

Keywords: Gi Coating; Intermetallic Layer; Metalographic Characterization.

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1 INTRODUCTION

Zinc coated steel sheets and their possible alloys are widely used in the automotive sector because they have excellent corrosion resistance, combined with mechanical forming and weldability. The corrosion resistance property is acquired through the galvanizing process, where the coating layer protects the metal from contact with the corrosive environment.
Among the range of steels in the market, the most important are galvanized, called GI. The GI coating can be divided into two main layers, the first composed of intermetallic phases of iron, aluminum and zinc, called the “intermetallic layer”. Its formation and composition may vary according to the characteristics of the substrate used (steel grade and surface texture), the chemical composition of the zinc bath and the process parameters used during its production (temperature, time and etc). The second layer consists mainly of pure zinc [1].
The properties and characteristics of the GI coating are directly related to the formation of the intermetallic layer, which is responsible for providing a connection between the metal substrate and the zinc layer, thereby effecting anchoring between both.The intermetallic layer is formed by the elements Fe - Al - Zn ($Fe_2Al_5Zn_X$). It has a density of 4.5 g / m ^{3}, having a mean and continuous thickness of approximately 1 µm [2].
Thus, a characterization of this intermetallic layer becomes of paramount importance for evaluation of the characteristics of the GI coating.
The purpose of this study is to present differentiated metallographic techniques of preparation used to characterize intermetallic layers in samples of galvanized steel (GI) produced by hot dip. Samples were collected on coils produced in two industrial steels with different chemical compositions: Steel SAE1005 and TRIP780 (Transformation Induced Plasticity).
These materials were chosen based on the difference in their chemical compositions. TRIP steels present higher complexity chemistry due to the addition of high levels of alloying elements, such as Si, Al, Cr and Mn. The SAE1005 steel is characterized as carbon steel. In this way, it was possible to evaluate the influence of the substrate composition on the formation of the intermetallic layer.
The intermetallic layers were characterized for their morphology using hot - metallographic inlay techniques and surface analysis.
For the surface analysis, the immersion process was used in chemical solution for dissolution of zinc, ultrasonic cleaning and metallographic preparation.
For metallographic section analyzes, techniques based on positioning the sample with different angles of inclination were used, providing a greater amplitude of the field of view in the region of interest. The images were analyzed using a scanning electron microscope, and their chemical compositions were obtained by the coupled energy dispersive X-ray spectrometer (SEM / EDS).

2 MATERIAL AND METHODS

2.1 Material

The steels used in the present study were produced by ArcelorMittal Vega. The TRIP steel has the chemical composition: carbon (0.01-0.40%), manganese (1.00-2.60%), silicon (0.50-2.50%) and aluminum (Max 3.0%). Other elements such as molybdenum and nickel were also observed. For the SAE1005 steel the chemical composition has: carbon (≤ 0.050%), manganese (0.35 - 0.55%) and silicon (≤ 0.060).
The TRIP steel has low carbon content, however, with the addition of alloying elements such as aluminum and silicon, in other hand the SAE1005 steel is a conventional carbon steel without important additions of alloying elements.

These steels were selected for the accomplishment of this study based in their distinct chemistries, thus allowing the evaluation of the efficiency of the chemical attack techniques tested. The cold rolling process was performed aiming reductions between 60 and 70% with the final sheet thickness of 1.50mm in the coil before the annealing process (Full Hard). In the galvanizing line the materials were processed obtaining zinc coating weights between 50 and 60 g / m ^{2}. The Al concentration present in the zinc bath had levels of 0.15 to 0.30%.

2.2- Experimental procedures

2.2.1 Metallographic Sections Analysis:

The metallographic analyses were performed using Scanning Electron Microscope (JEOL of Model JSM 6360). The samples were cut in the roll direction, embedded, prepared using sandpapers with different mesh granulometry (120, 320, 800 and 1200) and polished with diamond pastes as JP4(3-6μm) and JP $^{1/4}$(0-½μm).
The samples were positioned in different angles during the embedded with the help of metallic wedges. The metallic wedges were used for promote better support and protection for the samples during the preparation steps, as showed in the figure1. In this way it is possible to have a more comprehensive view of the intermetallic layer.

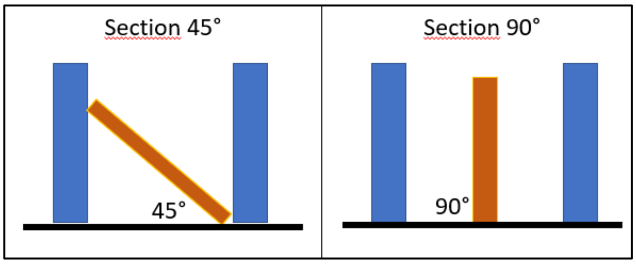

Figure 1: Hot-inlay preparation for metallographic section analysis.

Subsequently, these samples were attacked with nitric acid solution (Nital 4%) for submersion approximately 7 seconds, followed by alcohol washing and drying.
It is important to emphasize that the excess of nitric acid inside the reagent solution Nital can directly influence in the visual control of the chemical attack. Because the solutions rich in nitric acid promote an accelerated and non-uniform corrosion in the samples surface (super attack), making the microstructural analysis impossible.
Figures 2 and 3 represents the difference section picture obtained to SAE1005 steel through the two preparations methods (embedding) used for the section analyzes. Figure 2 shows the conventional method, 90 ° in relation to the base of the metallographic inlay machine (reference plane). Figure 3 shows the angle method used, in which case the sample is positioned at 45 ° to the reference plane, in this way it is possible to have a more comprehensive view of the intermetallic layer,
Note that the angles method presents greater area for analysis of intermetallic layers, allowing more details about its formation and constitution.

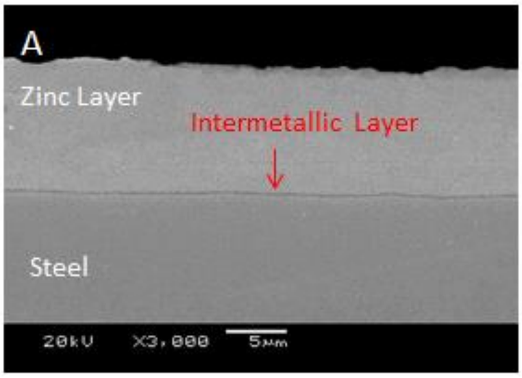

Figure2: Section prepared at 90 ° from the reference plane - Nital Attack 4% - Magnification 3000x - SAE1005

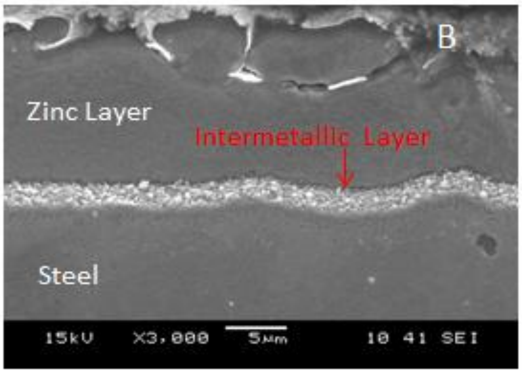

Figure3: Section prepared at 45° from the reference plane - Nital Attack 4% - Magnification 3000x - SAE1005

2.2.2 Metallographic Surface Analyze

One of the most used techniques for the characterization of the intermetallic layer region in galvanized steels is the metallographic surface analysis. Due to larger regions of analysis, thus obtaining a better view on the morphology and distribution of the sample analyzed.
The zinc layer was removed by chemical attack using a 4: 1 solution of acetic acid (Glacial) and hydrogen peroxide, this solution removes the zinc layer, preserving the Fe-Al phase [3]. The sample preparation was performed by immersing the 15x15mm specimens in the Glacial solution at room temperature for three different times, 5, 10 and 15 minutes.
The same procedure was performed for the SAE1005 and TRIP780 samples.

3 RESULTS AND DISCUSSION

In this item will be presented and discussed the main results of the techniques used to characterize the intermetallic layer in the selected steels.

3.1 Metallographic section

The metallographic section analysis of SAE1005 and TRIP780 samples are shown in figures 4 and 5 respectively.
For each steel, two imagens were represented, (A) with magnification of 3000X and magnification of 10000X to present more details about the intermetallic layer.

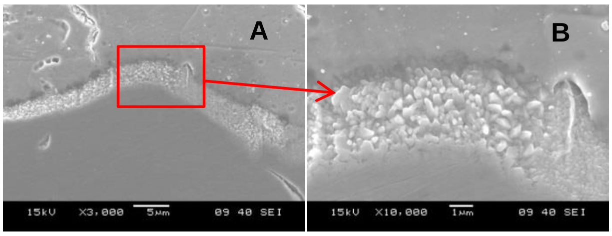

Figure4: SAE1005 Steel, Inclined section. Nital Attack 4%. (A) Magnification 3000x and (B) Magnification 10000X.

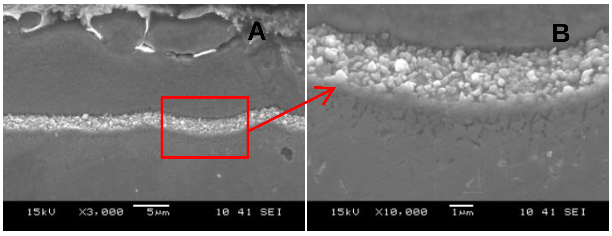

Figure5: TRIP780 Steel, Inclined section. Nital Attack 4%. (A) Magnification 3000x and (B) Magnification 10000X.

The same samples were analyzed by X-ray spectroscopy by energy dispersion (EDS), with the objective of qualifying and semi-quantifying the concentrations of the elements Fe-Al-Zn presents in the intermetallic layer. The tables 1 and 2 show the semiquantitative results by EDS for SAE1005 and TRIP780 samples respectively.
The values present in the tables refer to the mean values obtained after analysis in different fields. The figures 6 and 7 show the result of spectroscopy (semi-quantitative value) in the SAE1005 and TRIP780 steel sample respectively.
SAE1005 samples present the typical elements for an intermetallic layer in low alloy steel (zinc, iron and aluminum).
The intermetallic layer analyzed for the SAE1005 samples shown high Zn concentration than the TRIP780. However, analyzes on the TRIP 780 layer evidenced the presence of other elements than the basic Fe-Al composition (Al, Si, Mn).
However, TRIP steel, due the presence of alloying elements in its chemistry, tends to segregate the steel surface after annealing in intercritical temperature, between AC1

and AC3. This phenomenon can cause the segregation of the elements, producing interference in the formation of the intermetallic layer [4].

Table1: The semiquantitative results by EDS analysis for SAE1005 samples.

EDS Analysis – SAE 1005 Results (% mass) semiquantitative			
Element	Fe	Al	Zn
%	~2,0	~12,0	~86,0

Table2: The semiquantitative results by EDS analysis for TRIP780 samples.

EDS Analysis – TRIP780 Results (% mass) semiquantitative					
Element	Fe	Al	Mn	Zn	Si
%	~3,0	~10,0	~5,0	~81,0	~1,0

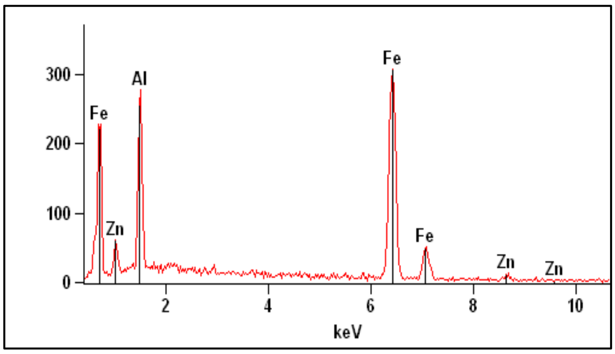

Figure6: EDS curve obtained for the SAE1005 steel.

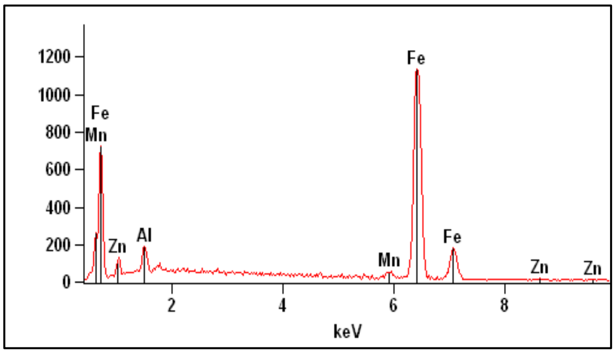

Figure7: EDS curve obtained for the TRIP780 steel.

3.2 Metallographic surface Analysis

The technique used to submerge acetic acid (glacial) and hydrogen peroxide showed through the surface characterization images to be a favorable methodology. Figure 8 shows the surface analysis performed on the SAE1005 steel for three different immersion time, 5, 10 and 15 minutes respectively. For the samples with immersion time of 5 minutes was observed that the intermetallic layer had homogeneously distributed along the entire surface of the analyzed region. For the immersions times of 10 and 15 minutes the intermetallic layer was consumed by the reaction between the reagent and the elements present.

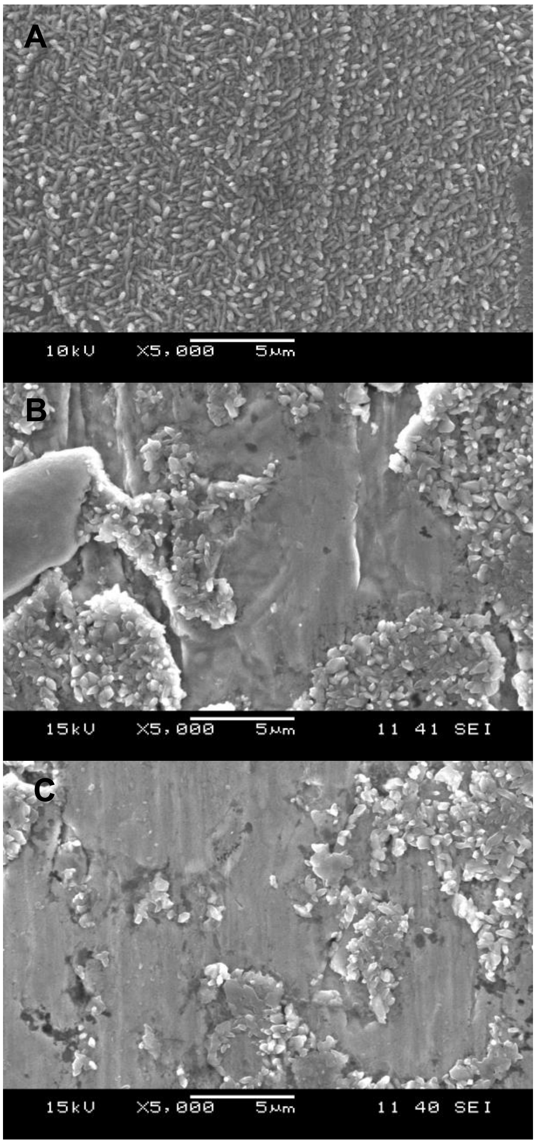

Figure8: Surface Analyze for SAE1005 samples - Magnification 5000x - Acetic acid (glacial) and hydrogen peroxide – (A) 5 minutes, (B) 10 minutes, (C) 15 minutes.

Figures 9 and 10 illustrate the results found for the TRIP780 samples after application of the same technique described above, using the similar immersion times, 5, 10 and 15 minutes. For the samples after 5 minutes in immersion (Figure 9A) the removal of the upper zinc layer to the intermetallic layer occurred partially, thus not allowing an analysis of the intermetallic layer in its fullness. Increasing the immersion time to 10 minutes (Figure 9B), resulted in the complete removal of the zinc, providing the perfect visualization of the intermetallic layer. For a longer time of 15 minutes (Figure 10), the zinc was completely removed from the surface, however, the intermetallic layer was also affected by the excess time and was partially removed. In this case, it observed the occurrence of regions where the zinc and intermetallic layers were removal completely, exposing the base steel surface.

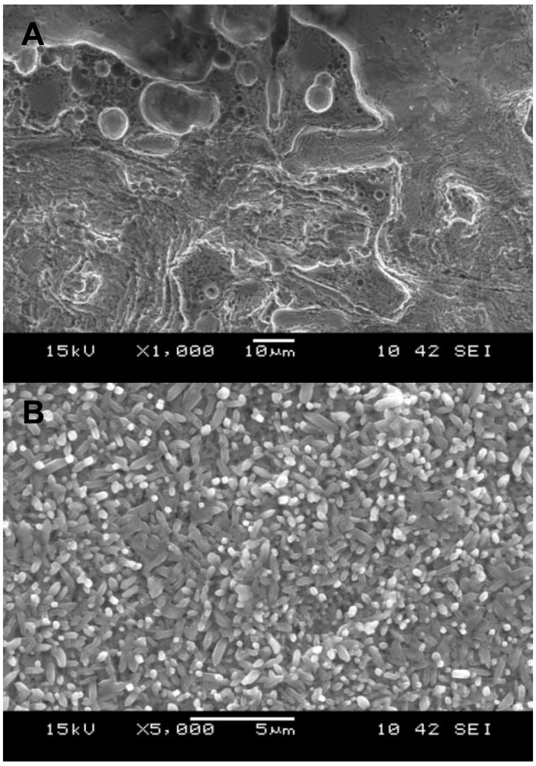

Figure9: Surface Analyze for TRIP780 samples - Magnification 5000x - Acetic acid (glacial) and hydrogen peroxide – (A) 5 minutes, (B) 10 minutes.

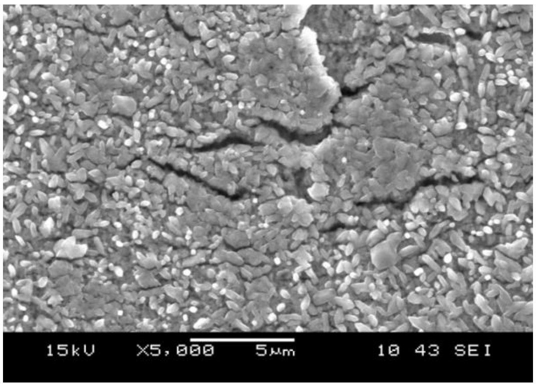

Figure10: Surface Analyze for TRIP780 samples - Magnification 5000x - Acetic acid (glacial) and hydrogen peroxide – 15 minutes.

4 CONCLUSION

The inclined metallographic inlay technique, 45 ° to the base, provided a greater visualization of intermetallic layer area in relation to the conventional technique (90° with the base), allowing a more detailed characterization of the intermetallic layer in relation to its formation.

For the metallographic surface analysis, the chemical solution used in the preparation of the samples was effective. It was observed that the preparation time of 5 minutes was the one that presented better images for the analysis, for SAE1005 steel. The immersion time higher than 5 minutes showed very aggressive for SAE1005 steel, the intermetallic layer was partially attacked by the solution, exposing the base steel.

On the other hand, this time was insufficient when used for TRIP780 steel. In this case, it was observed that the immersion time of 10 minutes provided better results as the zinc layer removal and intermetallic layer exposure for the TRIP780 steel.

However, for an immersion time of 15 minutes, excessive removal of the zinc layer occurred as well as partial removal of the intermetallic layer.

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REFERENCES

1 CHENG, W.J.; WANG, C.J. Growth of intermetallic layer in the aluminide mild steel during hot-dipping. Surface & Coatings Technology, v. 1, n.204, p.824-828, 2009.
2 CARVALHO, J.E.R. Tecnologia de Zincagem por Imersão a quente. Rio de Janeiro: Galvasud S.A., p.31, 1997.
3 SAGL, R.; JAROSIK, A.; STIFTER, D.; ANGELI, G. The role of surface oxides on annealed high-strength steels in hot-dip galvanizing. Corrosion Science, p. 268–275, 2013.
4 SONG, G. M. et al. Interface Microstructure and Adhesion of Zinc Coatings on TRIP Steels. Materials Science Forum, p. 1104-1109, 2007.