EFFECT OF HEATING TEMPERATURE ON Fe-Al-Si DIFUSION IN Al-Si COATING DURING THE AUSTENITIZATION STAGE IN HOT STAMPING PROCESS*

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Abstract

Currently, continuous implementation of safety and CO_2 emission standards in automotive vehicles has driven the search for weight reduction and safety enhancement solutions. In this context, the development of high mechanical strength in steels has been highlight as the most applicable. Those pieces have complex geometric and require greater mechanical strength, thus they are produced by hot stamping. The selected steels for this application have addition of boron, such as 22 MnB5. In parallel, researches related to the development of metallic coatings capable of withstanding mechanical stresses and heat treatment have been carried out. The Al-Si coating composed of Al-Si-Fe multiphases has been strongly used, because during the austenitization occurs to the formation of new phases by the inter-diffusion of Fe and solidification reactions defining the final microstructure. Samples of coated 22MnB5 steel (Al-Si) were treated between temperatures of 500°C to 900 ° C. Through the analysis of microscopy (SEM) and GDOES it was possible to identify the diffusion of Fe along the coating layer. Based on the ternary phase diagram and the simulations, it was possible to propose a way of understanding the transformation of the Al-Si coating by the diffusion of the iron.

Keywords: Al-Si Coating; Phase Transformation; Fe-Al-Si diffusion.

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1 INTRODUCTION

The hot stamping process has been optimized to enable the production of advanced high strength steels (AHSS) in automotive applications. This process allows dimensional control, avoiding the occurrence of strong elastic return (springback effect). Thus, hot stamping consists of heating the sheet metal to its total austenitization, promoting a joint deformation with accelerated (tempering) cooling to temperatures below the Mi (beginning of the martensitic transformation) temperature. This procedure aims to obtain parts composed of 100% martensitic microstructure, which implies high resistance and flow limits, and a significant reduction of the springback effect [1]. In general, the process can be divided into three main stages: heating, transferring Blank from the kiln to the press and stamping itself, as represented schematically in figure 1 [2].

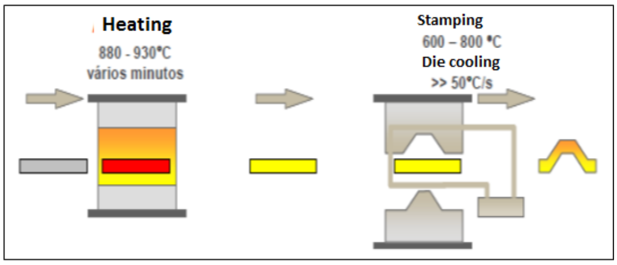

Figure 1: Schematic representation of the steps of the hot stamping process [2].

In summary, during heating the coated blanks (Al-Si) pass through an austenitizing furnace, where they are heated at temperatures ranging from 900 to 930 ° C, for 5 to 10 minutes. After the blanks are transferred from the furnace to the stamping tool, this step should be performed quickly, reducing the thermal exchange between the blank and the atmosphere. The final step consists of accelerated deformation and cooling, as indicated in figure 1.

The final microstructure of the Al-Si coating after hot dip is defined by the aluminizing reactions occurring during the continuous hot dip process, wherein the metal bath composition plays an important role. The initial composition of the bath is about 88% Al, 9% Si and 3% Fe and the bath is maintained at 650 ° C [3].

At this temperature there is the presence of the metal compound $Al_9Fe_2Si_2$ (Ʈ6) in equilibrium with the liquid bath [1, 3-5]. According to the ternary Al-Si-Fe diagram, the bath composition is close to the boundary between phases Ʈ6 and Ʈ5 ($Al_{12}Fe_3Si_2$). Thus, when the metal sheet is immersed in the bath, immediately diffusion of iron into the bath occurs, which produces a region, near the surface of the plate, rich in iron. The bath which was previously in equilibrium with the solid phase Ʈ 6 tends to rebalance with the Ʈ5 phase, due to the increase of the localized concentration of iron, thus forming other phases.

During the deposition of the Al-Si coating by the hot immersion process, diffusions of Fe and Al occur at the interface between the substrate and the coating, resulting in the formation of intermetallic phases Al_xFe_y [2,4,5]. The intermetallic compound Ʈ 5 is not in equilibrium with the ferrite. A thin layer of Fe_2Al_5 + $FeAl_3$ [4] is formed and tends to grow according to the thermodynamic equilibrium, along the entire interface between the steel and the Ʈ5 layer. At 575 ° C, the last liquid reaches the eutectic composition (87.02% Al, 12.2% Si and 0.78% Fe) solidifying as a tertiary Al + Si + Ʈ6, determining a microstructure composed of binary and ternary multiphases.

The Al-Si coating layer can be divided into two main zones [6,7]. The first one is formed by an aluminum matrix containing several phases resulting from the interaction Al-Si-Fe (zone 1). The second is formed by the interface region between the coating and the substrate (zone 2). This interface zone is composed of a ternary system Al, Si and Fe, denominated of Ʈ5 and an intermetallic layer formed mainly by Fe_2Al_5 + $FeAl_3$, as shown in figure 2.

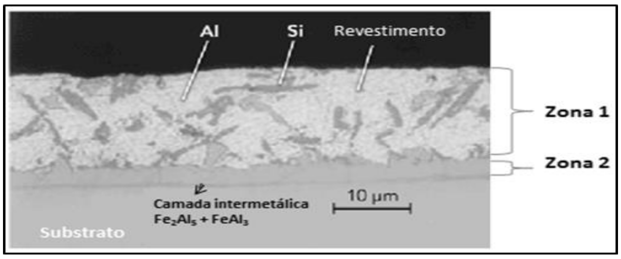

Figure 2: Al-Si coating in zones before the hot stamping process [7].

During the heating and austenitizing step in a hot stamping process the formation of Al_xFe_y intermetallic compounds is strongly influenced by the chemical composition, coating thickness, time of soaking and the temperature used. The present phases become ternary inter-metallic compounds of Al-Fe-Si or Fe-Al binary by inter-diffusion and solidification reactions being controlled mainly by the diffusion of Al and Fe at the substrate/coating interface. The Fe present in the intermetallic layer tends to diffuse towards the surface of the coating, contrary to Al diffusion path, thus forming different ternary phases along the thickness of the coating.

Thus the understanding of the phase transformations during blanks heating becomes important for the better definition of the time and temperature parameters to be used in the hot stamping process. This work aimed to study the effect of the heating temperature on the formation of the Al-Si coating microstructure by diffusion of Fe-Al-Si elements.

2 MATERIAL AND METHODS

Samples of the 22MnB5 steel obtained from industrial coils submitted to continuous annealing and Al-Si coated by hot dip were used in this work, being the chemical composition shown in table 1.

Table 1: Chemical composition of 22MnB5 steel used in this work (% by weight).

C	Mn	Ti	Al	B
0,24	1,8	0,038	0,05	0,005

The samples were cut into 100 x 100 mm specimens and heated in a muffle oven between 500 ° C and 900 ° C with variations of 50 ° C. The samples were identified with the letter N followed by the temperature at which they were treated, where N0 refers to the sample without heat treatment, called the standard sample, according to table 2. The immersion time used was 3 minutes, at the end of the time the samples were cooled in water to room temperature.

Table 2: Identification of samples and heat treatment temperatures studied.

SAMPLES	HEAT TEMP °C	AMOSTRAS	HEAT TEMP °C
N 0	Standard (25)	N 700	700
N 500	500	N 750	750
N 550	550	N 800	800
N 600	600	N 850	850
N 650	650	N 900	900

After heat treatment, the coating was removed and subjected to wet chemical analysis. In this analysis, the spectrometer Plasma - ICP (Inductile Coupled Plasma) was used. The coating was removed through a stripper solution composed of hydrochloric acid and inhibitor (avoid chemical etching to the substrate iron) at a temperature of 50 ° C. The resulting solution was heated until its volume was reduced to 50 ml, then 2 ml of hydrofluoric acid and 6 ml of nitric acid were added for complete solubilization of the sample. After these steps, 2.0 grams of boric acid was added to complex the residual hydrofluoric acid. Demineralized water was added to make up a final volume of 200 ml solution, the final solution being subjected to the analysis itself. Thus, it was possible to quantify the total content of Al, Si and Fe present in the coating layer in the studied samples. The analyzes were performed in triplicate and only the calculated mean value was presented in this study.

To evaluate the effect of temperature on the diffusion of the Fe-Al-Si elements and the growth of the intermetallic layer, metallographic analyzes were performed according to ASTM B487.

The cross section of the coating was analyzed in five different fields on the same sample, considering the average of the results. A Zeiss optical microscope model Imager A was used. The samples were polished (diamond paste granulometry 1 and 0.3µm) and attacked with 4% Nital in a time of 6 seconds of immersion. The images were acquired and treated through the Axion Vision SE64 system that is directly coupled to the optical microscope.

In addition, scanning electron microscopy (SEM) and EDS (Energy Dispersive X-ray Spectrocospy) spectroscopy mapping were used to determine the qualitative and semiquantitative chemical composition of the samples.

In parallel to the EDS mapping, the samples were subjected to an ultrasonic surface cleaning in acetone PA with purity of 99.8% and analyzed by GDOES (Glow Discharge Optical Emission Spectrometry) determining the distribution of the elements along the coating layer for the different temperatures studied.

3 RESULTS AND DISCUSSION

Table 3 and Figure 3 show the variation of Al-Fe-Si contents of the coating as a function of the heat treatment temperature, obtained by ICP.

Table 3: Chemical analysis of the Al-Si coating for thermally treated samples.

SAMPLE	Al %	Si %	Fe %	SAMPLE	Al %	Si %	Fe %
N 0	81,3	9,18	9,52	N 700	80,49	8,45	11,07
N 500	81,59	9,22	9,19	N 750	80,02	7,1	12,87
N 550	81,77	9,08	9,15	N 800	68,95	7,68	23,36
N 600	81,64	9,71	9,65	N 850	63,98	7,22	28,8
N 650	82,06	8,81	9,48	N 900	54,32	8,47	37,21

Among the heat treatment temperatures of 500 ° C to 650 ° C, no significant changes were observed in the total contents of Al, Si and Fe in the coating layer. From the temperature of 750 ° C, variations in the contents of the analyzed elements were noticed with greater intensity, thus presenting temperature dependence.

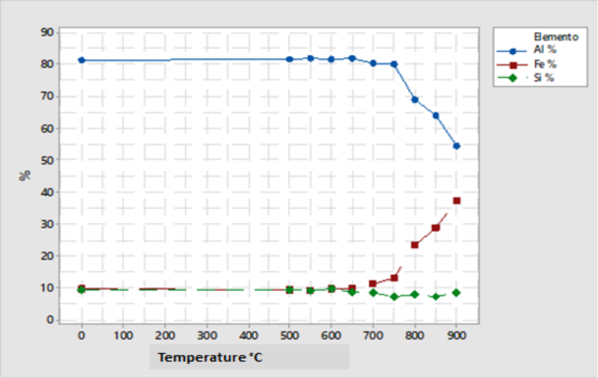

Figure 3: Variation of the percentage of iron, silicon and aluminum in the Al-Si coating layer as a function of the heating temperature. Chemical analysis by ICP.

As the heating temperature increases the percentage of total Fe present in the coating layer increases, on the other hand the Al percentage has a reduction. This effect is the result of the formation of several Fe_yAl_x binary phases that occur due to diffusion of the Fe from the substrate to the Al - rich coating layer. The formation of ternary phases, $Al_xFe_YSi_Z$ are also present during heating, but to a lesser extent [8 - 10]. The silicon exerts a strong influence on the formation of iron and aluminum rich phases inhibiting the growth of the Fe_2 Al_5 phase [11].

The formation of ternary or binary phases in combination with Fe and or Al occurs mostly at higher temperatures. This observation is in agreement with studies carried out in several studies [12-14], which state that the solubility of Si in the intermetallic phase of Fe_2Al_5 is strongly influenced by temperature. As the temperature increases, the diffusion of iron along the coating layer is favored by the fusion of the already existing thermally activated phases and the allotropic change in the structure of the free iron, which diffuses from the substrate.

Analysis by EDS qualitatively determined the iron content along the coating layer at the temperatures studied. Three points were determined along the thickness of the coating layer, Point 1 (blue line) concentrated in the Ʈ 5 phase, which phase is initially iron rich.

Point 2 (red line) located in a central region of the coating, Al-rich region. The Point 3 (green line) at the end of the coating. The results of the three analyzed points are represented in figure 4, where the diffusion path of the iron is represented by an arrow, indicating the direction of diffusion of the substrate to the outermost layer of the coating.

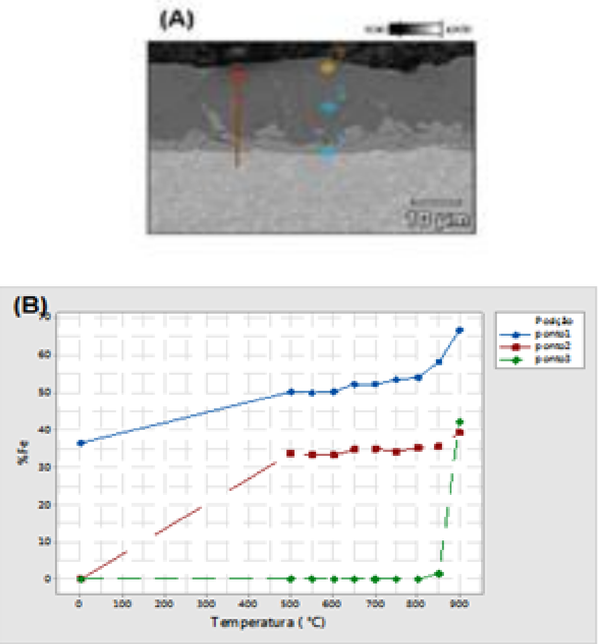

Figure 4: Determination of the variation of the iron content in the Al-Si coating layer as a function of the heating temperature. A- Analysis via MEV-EDS performed at three different positions along the thickness of the coating layer. B- Values of the iron content found in the three analyzed.

The results show that the iron content in the intermetallic layers and Ʈ5 (point 1) increases gradually with temperature, presenting a uniform growth between the temperatures of 500 ° C to 800 ° C, being accelerated to temperatures of 850 and 900 ° C. In the central region of the Al-Si coating layer (point 2), the iron content did not show significant changes between the temperature range analyzed:

- Between 25 ° C and 500 ° C: The concentration of Fe increases from less than 1% to approximately 35%.
- Between 500 ° C and 850 ° C: The Fe concentration is practically maintained at close to 35%.
- At 900 ° C: A slight increase in Fe concentration occurs, the value found is approximately 40%.

When analyzing the surface 3 of the coating, it was observed that only at the temperature of 900 ° C it was possible to evidence the presence of Fe.

The enrichment of iron along the coating layer by increasing the temperature can be explained by the diffusion of the iron from the substrate towards the surface of the coating [15-16].

Where the Fe_yAl_x-type phases formed, especially in the intermetallic layer due to the interface with the substrate, diffuse towards the Ʈ5 layer advancing towards the surface of the coating. The iron-rich Fe_yAl_x phases are formed from the tertiary phase $Al_2Fe_3Si_3$ present in the center of the coating layer thus running the decrease of the silicon content, which diffuses towards the surface of the coating forming silicon-rich oxides.

By means of metallographic analyzes it was observed that the increase of the heating temperature promoted the gradual growth of the intermetallic layer and Ʈ5 (zone2), as well as the growth of the total coating layer (zone 1 + zone2).

The growth of zone 2 (phase Ʈ5 and intermetallic) characterized by an iron rich region occurs only significantly at temperatures above 750 ° C. The growth of the total layer (zone 1 and zone 2) occurs to a lesser extent than the growth of zone 2, but its variation starts to be noticed from lower temperatures, 650 ° C.

Figure 5 shows the EDS mapping of the reference sample, highlighting the presence of Fe, Al and Si elements. A- separation of the coating layer in two zones, B- EDS mapping of the element Fe, C- EDS mapping of Fe, Al and Si elements.

The figures 6 and 7 show the analyzes performed by EDS and GDOS for samples treated at 0 ° C, 500 ° C and 750 ° C and samples treated at 800 ° C, 850 ° C and 900 ° C respectively. The GDOES analyzes show the increase of the iron content through the coating layers to the regions closest to the surface, as well as the decrease of the aluminum concentration.

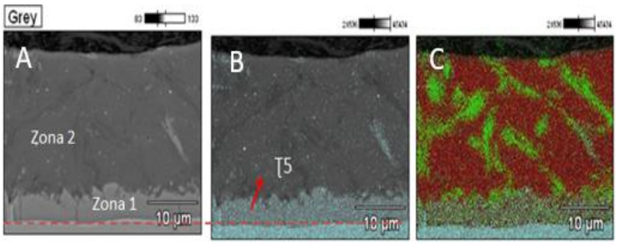

Figure 5: Mapping of the Al-Si coating layer by EDS for sample without heat treatment, reference.

The elements Al, Si and Fe are represented by the curves in orange, green and red respectively. In the reference sample (without heat treatment), the highest concentration of iron is observed in the region close to the substrate bounded by dashed lines in red and orange. The dashed lines in red correspond to the separation between the substrate and the Al-Si coating layer and the orange lines correspond to the separation between the iron-rich zone 2 and the Al-rich zone 1.

As the temperature rises it is possible to note spacing between the dashed lines, thus representing the diffusion of the iron between the layers of the Al-Si coating. As discussed earlier, diffusion of iron is most noticeably observed at temperatures above 800 ° C. At 900 ° C the iron is observed in almost the entire coating layer, as well as on its surface.

The growth of Fe_YAl_X layer has a strong dependence on the chemical potential of aluminum and silicon present in the coatings, as well as on the diffusion coefficients of these elements in the phases already transformed close to the substrate / coating interface [15, 16]. Thus Fe_2Al_5 transformations can be accelerated by decreasing the iron diffusion pathways.

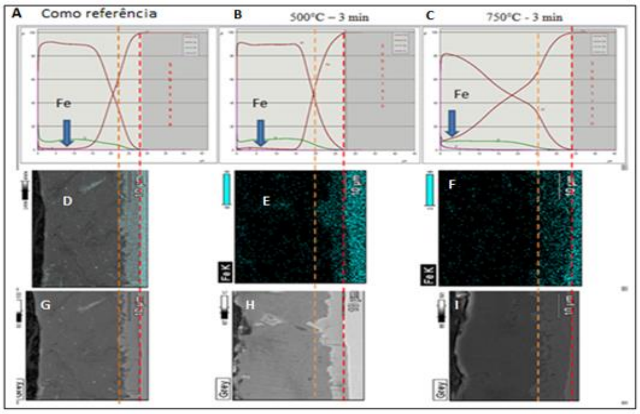

Figure 6: Mapping by GDOES (A-B-C), Fe element EDS (D-E- F) and metallographic analysis by MEV (G-H-I) of reference samples and heat treated at temperatures of 500 and 750 ° C.

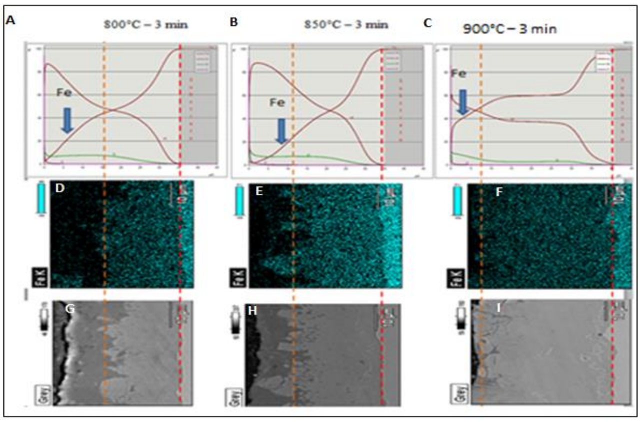

Figure 7: Mapping by GDOES (A-B-C), Fe element EDS (D-E- F) and metallographic analysis by MEV (G-H-I) of reference samples and heat treated at temperatures of 800 and 950 ° C.

The growth of the coating layer is mainly attributed to diffusion of the iron in the substrate - coating direction while the diffusion of aluminum towards the substrate occurs. The formation of binary or ternary alloys rich in Fe or Al in combination with silicon promotes the increase in the volume of the coating layer.

The phase transformations in the coating during the heating process can take two distinct reaction paths in an Al-Si-Fe ternary phase diagram [12]:

- In areas with low Si content, the present phases are represented essentially by binary Fe-Al-type compounds. The enrichment of iron through the diffusion induces the increase of the melting point of these phases.

Thus, the volumetric growth of these phases occurs mainly by the formation of Fe-Al compounds rich in Fe. Reaction path represented by the blue line dotted in figure 8.

- Areas composed of Si-rich phases initially grow by diffusion in the liquid state. The existence of these ternary phases initially rich in Si melts at temperatures below the heating temperature (tertiary eutectic, T5) thus allowing local enrichment by Fe. Enrichment by Fe in these phases will occur continuously at temperatures where the ternary phases Ʈ 5, Ʈ 2 and Ʈ1 are in equilibrium with binary phases $FeAl_3$ and Fe_2Al_5, thus being able to occur continuously in the solid state. Reaction path represented by solid blue line in figure 8.

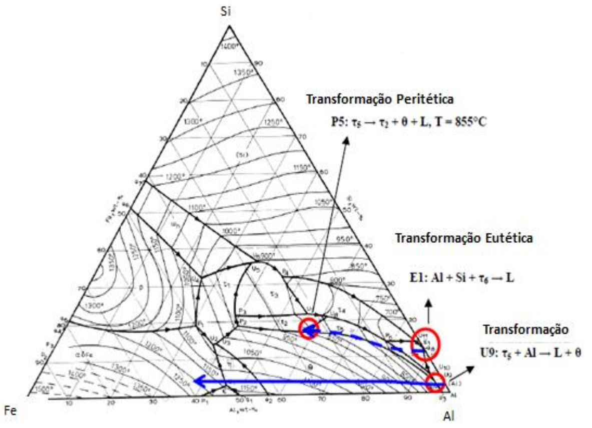

Figure 8: Representation of Al-Si reaction paths in an Al-Fe-Si ternary diagram as a function of temperature increase (GRIGORIEVA, 2011).

4 CONCLUSION

The approach suggested in this work was directed at evaluating the influence of the heating temperature on the diffusion of Fe, Al and Si elements along the total Al-Si coating layer.

Through the Fe diffusion path from the intermetallic and Ʈ5 layers, it was possible to evidence the formation of iron rich phases along the entire coating layer. Thus, for heating temperatures below 750 ° C the analyzes via ICP and EDS showed that the diffusion of the iron between the intermetallic layers and Ʈ5 occur less significantly.

The increase in the heating temperatures led to the modification and growth of the layers closest to the substrate, thus leading to the diffusion of iron to the surface layer of the coating. At the temperature of 900 ° C the presence of Fe was detected on the surface of the coating.

Through the EDS and GDOES analysis the iron enrichment in the Al-Si coating layer was observed as a function of the increase in temperature, as well as the decrease in weight of the Al and Si elements along the total coating layer.

These results are confirmed by chemical analysis carried out via ICP after removal of the metallic coating from the heat treated samples. The diffusion of the elements Al, Si and Fe at the heating temperatures tested produced in the coating the formation of a substructure formed by the uneven distribution of the concentration of these elements, causing an increase of the thickness of the coating. Effect explained by the formation of ternary phases as a function of the presence of iron, through diffusion, in regions previously rich in Si and Al.

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