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Diffusion Analyses Using GDOES Technique of the 22MnB5 Press Hardened Steel with Al-Si and Zn-Ni Coatings

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Abstract. The hot stamping process consists to heat the steel blank, at total austenitization temperatures and to transfer it into the press tooling for forming and fast cooling to fully martensitic transformation. This transference from furnace to press stage promotes some steel oxidation. The application of metallic coatings avoids this phenomenon. The Al-Si coating, a patented process, has been the most applied on steel. Hence, alternative coatings like Zn-Ni are under development. It is known that this furnace heating causes chemical elements diffusion that results in intermetallics formation. This study had the objective of analyze the diffusion profiles of chemical elements present in the substrate, 22MnB5 steel, and coatings of Al-Si and Zn-Ni, using glow-discharge optical emission spectroscopy - GDOES and to correlate the results with those obtained with energy dispersive X-ray spectroscopy - EDS. The results showed that for the Zn-Ni sample, the Zn and Fe profiles at the interfacial zone, are predominant; which justify the high proportion of ZnFe phases as showed using scanning electron microscopy - SEM images. For the Al-Si sample at the interfacial zone, the profile of Al and Fe varies simultaneously; besides that, silicon diffusion in the substrate is more effectively than the nickel diffusion. For this reason, it was possible to identify AlFeSi phase near to the steel substrate.

Introduction

The application of hot stamped components in automotive industry is steadily increasing. It is a strategic product to help the automakers satisfying safety needs and fuel reduction requirements by means of the lightweight design concept, a current trend for new vehicles [1]. Press hardened steels (PHS) are boron-manganese steels classified as ultra high strength steel [2]. They are usually used in hot stamping process achieving at the end of the process tensile strength of up to 1500 MPa [3,4]. Moreover, the spring back effect is not seen as a consequence of steel chemical composition combined with high temperatures during the hot stamping [3]. The steel grade of PHS widely applied in the automotive industry is known as 22MnB5, which comprises basically 0.23 C, 1.50 Mn and 0.003 B in mass % [4]. The hot stamping consists in heating a blank at total austenitization temperatures, around 900 °C by 10 minutes, and transfer the blank into the press tooling for forming and fast cooling to fully martensitic transformation. At the beginning of the process the steel has around 600 MPa of tensile strength due to the microstructure, which comprises ferrite and perlite; at the end it increases up to 1500 MPa as consequence of martensitic transformation [2-6].

Due to the use of high temperatures in the hot stamping, it is unavoidable steel oxidation by the contact with the atmospheric air during the transfer step of the blank from the furnace into to the press tooling [4]. Moreover, the oxide layer shows high hardness, which results in a premature wear of the die tooling. In order to avoid the steel oxidation and insure corrosion resistance, metallic coatings are applied on the steel [6]. The Al-Si coating has been the most applied on PHS by hot dip. The bath consists in 10 % in mass of Si in Al, which ensures a good corrosion resistance [7]. During the austenitization, AlFe intermetallic formation takes place in the protective layer due to diffusion occurring at the coating / substrate interface. At low temperatures, the microstructure shows Al_5Fe_2 and $Al_{13}Fe_4$ phases, which promote the initiation of cracks in the coated layer due to their high brittleness. Increasing the austenitization temperature further, favors the diffusion of the Al in the substrate, resulting in the formation of ductile phases like $AlFe_3$ and AlFe, which decreases the onset of cracks. Silicon occupies the vacancies of the Al_5Fe_2 structures and thus avoids the growth of this phase, in relation to the phases $Al_{13}Fe_4$ and Al_8Fe_2Si the silicon hinders the formation of the first and promotes the growth of the second [6].

Alternative coatings, such as electroplated Zn-Ni, are here investigated to evaluate their potential for replacement of Al-Si coatings, besides to keep up with the high projected world demand for this type of steel [8]. Zinc based coatings are advantageous comparatively to Al-Si because they provide cathodic protection to the steel substrates. Zn-Ni is one of alternative to Al-Si; it is a Zn electroplated coating, which has around 15 % in mass of nickel. It is characterized by micro roughness, refined microstructure and thermal stability [5]. An oxide layer can be observed after the hot stamping which is beneficial as it prevents the reduction of the Zn by evaporation. In addition, the presence of intermetallic, such as γ-Ni5Zn21, uniformly distributed avoids the phenomenon of steel embrittlement during the forming process, which is very common in the Fe-Zn system at high temperatures [5,9]. It is known that the heating causes chemical elements diffusion that results in intermetallics formation amongst the elements presents in the coating and base metal [5]. This study has the objective of analyze the diffusion profiles of chemical elements present in the substrate and both coatings Al-Si and Zn-Ni using glow discharge optical emission spectroscopy technique - GDOES and scanning electron microscopy - SEM with energy dispersive spectroscopy - EDS.

Experimental

The samples were removed from the B type inner pillar from both, a commercial and an experimental part made of the 22Mn5B 1.2 mm thick steel plate. Two types of samples were taken: Zn-Ni coated and Al-Si coated (20x20 mm^2). Due to the shape of the part, it was not possible to obtain totally flat samples. The press hardening conditions were not supplied due to confidentiality of the industrial process.

The study of diffusion profiles of chemical elements present in the substrate and in the coatings was done using glow discharge optical emission spectroscopy (GDOES) technique [10]. Through a plasma discharge, the sample is cathodic sputtered from the surface. The removed atoms are excited by the collisions with argon atoms. When the excited atoms return to ground state, they emit light. A holographic diffraction grating separates and focuses the wavelengths and each element has one. The composition profile is given by the correlation between the amounts of removed material in function of time, and then, they are converted in depth profile: mass percent (%) versus depth (μm) [10-12].

The microstructural characterization of the samples cross section was carried out using scanning electronic microscope in back scattering electron mode (EBS) and the semi quantitative chemical composition of the different observed phases was given by energy dispersive spectroscopy - EDS. The samples were mounted with phenolic resin; grinded using 100, 320, 800 and 1000 grit emery paper; and finally, polished with diamond paste of 1 μm and 3 μm. After each step the samples were cleaned in ultrasonic bath. The samples were not etched.

Results and Discussion

Fig. 1 shows the GDOES depth profile resulted for the 22MnB5 steel PHS sample coated with Zn-Ni. Comparing the depth profile with SEM images of the 22MnB5 steel PHS sample coated with Zn-Ni, see Fig. 2, it is possible infer the formation of oxide at the surface layer, formed by Zn (light green line) and O (yellow line). At the surface layer is seen a high concentration of Zn (around 75 %) and O (around 15%). The concentration of O and Zn decreases towards to steel substrate. On the other hand, the concentration of Fe (blue line) increases from the surface to the substrate. That is justified by diffusional effect, which is activated by heating during the hot stamping process. The literature shows that the Fe enrichment in the interfacial region pushes Ni (red line) toward the surface [5]. Ni diffuses from the surface to the substrate; however its content is low, less than 10 % at the interfacial zone. At the interfacial zone is predominant the gradients of Zn and Fe, which justify the formation of phases composed by ZnFe in the coating.

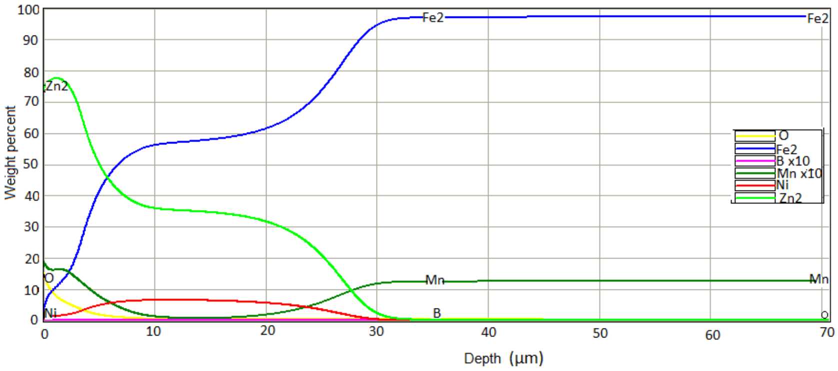

Fig. 1. GDOES depth profile of O, Fe, B, Mn, Ni and Zn for 22MnB5 steel PHS sample coated with Zn-Ni.

Fig. 2 is a secondary electrons micrograph of the transverse cross section of the sample coated with Zn without etching. Four distinct regions were identified in Fig. 2, moreover, cracks were found in the coating layer, but they did not reach the substrate. With EDS it was possible to identify that the region 1 and 2 are composed by Zn and O, the region 3 comprises Zn and Fe. The region 4 is the 22MnB5 steel substrate. The EDS results are given in Figs. 3 and 4.

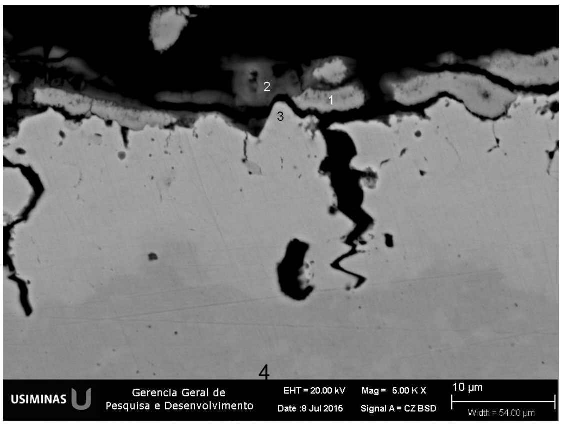

Fig. 2. Secondary electrons micrograph of the 22MnB5 steel PHS sample coated with Zn-Ni in the transverse cross section showing the 22MnB5 steel substrate (medium gray phase, region 4) and the coating phases (region 1-3). Not etched.

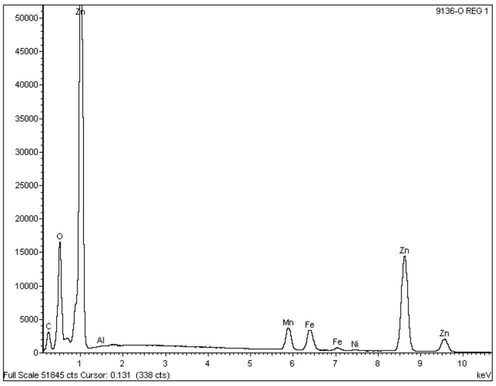

Fig. 3. The resulting typical EDS spectrum results reveal that Zn and O are the main elements present with Zn being the most abundant in the selected field in regions 1 and 2 of the 22MnB5 steel PHS sample coated with Zn-Ni.

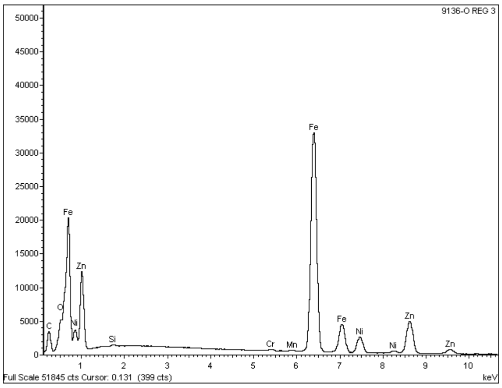

Fig. 4. The resulting typical EDS spectrum results reveal that Zn and Fe are the main elements present with Fe being the most abundant in the selected field in region 3 of the 22MnB5 steel PHS sample coated with Zn-Ni.

Fig. 5 shows the GDOES depth profile resulted for the 22MnB5 steel PHS sample coated with Al-Si. An oxide layer is also seen on the Al-Si coating, however it is formed by aluminum oxide due to the high concentration of Al (light green line) and oxygen (yellow line) at the surface layer. As seen in sample coated with Zn-Ni, the concentration of oxygen decreases toward the substrate zone and the Fe enrichment takes place. At the interfacial zone is shown that the element concentration profile of Fe and Al varies simultaneously, which indicates that the Al-Si coating is formed by layers composed of AlFe phases, as confirmed by literature [6]. Besides that, in a qualitative analysis, Si (red line) diffuses toward the substrate more effectively than Ni. The Al-Si coating is also characterized by a rich layer of Si close to the steel substrate.

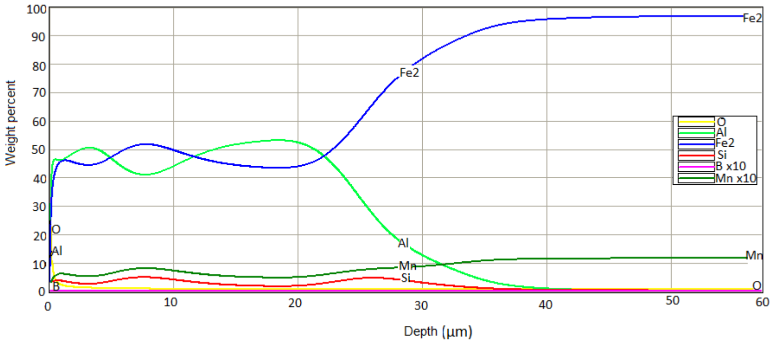

Fig. 5. GDOES depth profile of O, Al, Fe, Si, B and Mn for the 22MnB5 steel PHS sample coated with Al-Si.

In Fig. 6 it is observed a crack in the coating layer, but it did not reach the steel substrate, besides its tip been very close to it, similarly observed in Fig. 2 for the Zn-Ni coated sample. Moreover, the cross section morphology shows that the Al-Si coating layer is composed by different phases, as suggested by GDOES result and literature [6]. It was possible to observe 5 different regions, which were characterized by EDS and the results are shown in Figs. 7 and 8.

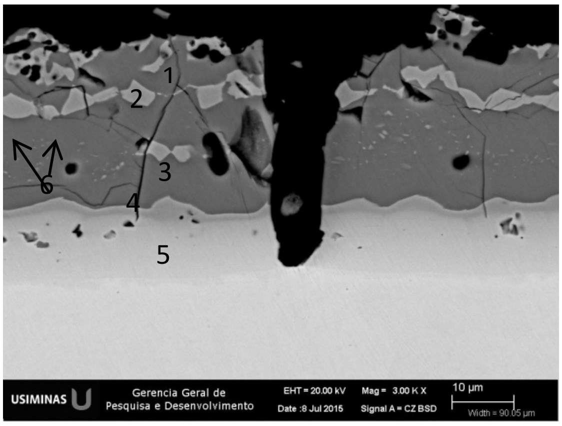

Fig. 6. Secondary electrons micrograph of the for the 22MnB5 steel PHS Al-Si coated sample in the transverse cross section showing the steel substrate (light gray major phase at the bottom of the image), the coating phases (1-5) and a deep crack almost reaching the phase 5. Not etched.

The EDS results for the 22MnB5 steel PHS sample coated with Al-Si shows that the 5 observed regions are not so different among then in terms of chemical composition, some of them are repeated. For instance, the regions 1, 3 and 4 have similar chemical composition, mainly a high in Al and Fe content. Whereas, regions 2 and 4 are very similar, comprising Al, Fe and Si. The region 5, closer to the steel substrate has a high Fe content, besides Al and Si were observed in lower concentration.

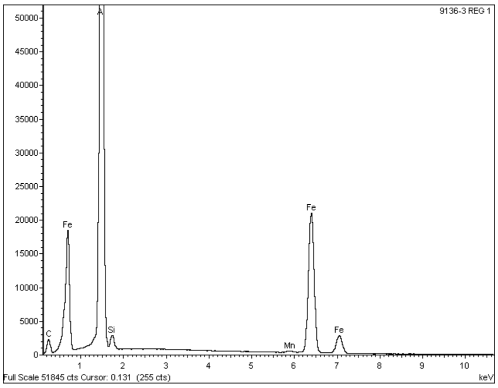

Fig. 7. The resulting typical EDS spectrum results reveal that Al and Fe are the main elements present in the selected field in regions 1, 3 and 4 of the 22MnB5 steel PHS sample coated with Al-Si.

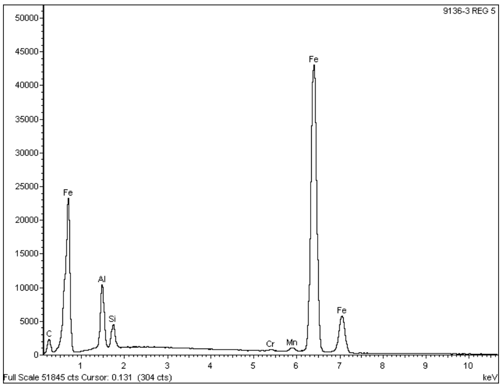

Fig 8. The resulting typical EDS spectrum results reveal that Al and Fe are the main elements present with Fe being the most abundant in the selected field in regions 2 and 5 of the 22MnB5 steel PHS sample coated with Al-Si.

Conclusion

The heating step during the hot stamping process promotes the chemical elements diffusion, which results in the formation of phases and intermetallics, which composes the coating, as shown by SEM results.

The gradients of Zn and Fe are predominates at the interfacial zone. Besides that, Ni showed low diffusion capability in the substrate. These facts justify the predominance of binaries phases composed by ZnFe, and the absence of ternaries phases, such as ZnFeNi.

In respect to Al-Si coating, at the interfacial zone is predominant the gradients of Al and Fe. The diffusion of Si in the substrate is more effectively in comparison with Ni diffusion. For these reason it was possible to identify different phases composed by AlFe and AlFeSi.

The GDOES is a useful technique to diffusion analyses, once it gives data input to follow the diffusional process in hot stamped steel.

Acknowledgments

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