CORRELATION BETWEEN THE SURFACE CHEMISTRY OF ANNEALED IF STEELS AND THE GROWTH OF A GALVANNEAL COATING

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ABSTRACT: An attempt is made to establish possible relationships between the quantity of oxides and hydroxides of the alloying elements on the outer interstitial-free steel surface after the annealing process and the characteristics of the galvanneal coating formed. XPS measurements reflect a clear influence of the alloying element contents and the water vapour content or dew point (DP) of the atmosphere on the oxide and hydroxide coverage of the steel surface. In general, much less Fe-Zn intermetallic formation is seen on the Ti steel substrate than on the Ti-Nb steel. The reason for this may be related with the higher oxide/(Fe+Mn) atomic ratio on the external surface of the Ti steel substrate. With the Ti-Nb-P steel, an absence of Fe was observed in the coatings obtained on the surface of this steel annealed in atmospheres with a DP of -45 or -10ºC. A clear direct relationship has been found between the inhibition of growth of Fe-Zn intermetallic compounds and the fraction of the steel substrate surface covered by manganese oxides as a result of the annealing process. For the Ti-Nb-P steel the increase in the DP of the galvannealing atmosphere to 10ºC resulted in the incorporation of a significant Fe content in the coating. XPS analysis suggests a change in the surface film, and the formation of a phosphate enriched layer, instead of manganese oxide. A lower fraction of oxide coverage on the annealed steel substrate resulted in less of an impediment to the diffusion of iron atoms from the steel substrate to the zinc coating in the galvannealing process.

Key words: Galvanneal, IF steels, diffusion and oxidation, alloying elements, X-ray photoelectron spectroscopy (XPS).

1. INTRODUCTION

The growing importance of galvanneal coatings on automotive bodywork has led in recent years to studies on the mechanisms of their formation on interstitial-free (IF) steel substrates of high mechanical strength. These steels are widely used due to their excellent workability (practically free of carbide precipitates at the grain boundaries) and also for their mechanical properties resulting from the incorporation of alloying elements such as Mn, P or Si. In these steels the reaction kinetics between iron and zinc are slower than in a conventional steel, which means that their annealing requires a longer time and a higher temperature in order to develop an Fe-Zn intermetallic layer with an average composition of 10 wt% Fe [1].

The suspicion that very small concentrations of alloying elements present in steels may have an important effect on the growth of Fe-Zn intermetallic compounds has led to the publication of a series of studies in recent years [2]. According to Hisamatsu [3], the formation of Fe-Zn intermetallics depends inversely on the capacity of the alloying elements in the bulk steel to diffuse and segregate at the grain boundaries of the ferritic matrix. Thus, grain boundaries that are free of the presence of precipitates do not block the formation of Fe-Zn intermetallics, while the segregation of elements at the grain boundaries slows the rate of the process.

This study aims to analyse the effect of the alloying elements Ti, Nb, P and Mn in the steel substrate on the characteristics of the galvanneal coating that is formed. In the literature it is suggested that the presence of “excess” Ti in IF steels (i.e. that which is not forming insoluble compounds such as titanium carbide, sulphide, nitride or phosphide) prevents segregation at the grain boundary and favours the formation of carbide-free grain boundaries, allowing the rapid interdiffusion of iron and zinc atoms [4]. Jordan et al. [5] suggest that steels microalloyed with Ti and/or Nb present a similar reactivity to those alloyed only with Ti. Hisamatsu [3] notes that the presence of Nb decreases the formation of outbursts. On the other hand it is well known that the presence of P in the steel substrate inhibits the growth of the galvanneal coating [1-12]. The segregation of small P contents at the grain boundaries in rephosphorised IF steels seems to inhibit the phenomena of localised nucleation and growth of Fe-Zn intermetallic compounds [1,2,4-10]. Some researchers have suggested that the segregation of phosphorus takes place in a uniform way across the surface of these steels rather than being localised [11-13]. Other elements such as Mn have received less attention, as is pointed out by Mintz [14]. Whereas Sebisty et al. [15] suggest that the presence of 1-2 wt% Mn does not seem to modify the microstructure of a galvanneal coating, Hertveldt et al. [1] report that the presence of 1 wt% Mn inhibits the diffusion of phosphorus towards the grain boundaries, favouring the galvannealing reaction in atmospheres with a high dew point (DP). According to Marder [2], most studies refer to steel substrates with several alloying elements, for which reason some doubts exist about the individual behaviour mechanisms of each one.

With the assistance of X-ray photoelectron spectroscopy (XPS), this study compares the tendency of Mn and P to segregate or to be selectively oxidized at the surface of annealed IF-steels [16], and its relationships with the rate of growth and composition of the metallic coating resulting from the galvannealing process. An attempt is also made to establish the influence of the water vapour content (dew point) of the galvannealing atmosphere on the formation of Fe-Zn intermetallic compounds.

2. EXPERIMENTAL PROCEDURE

2.1. IF steels

The chemical composition of the steels is shown in Table 1 (weight percentages). The specimens were cut from IF steel sheets supplied by CORUS. The phosphorus contents are 0.070 wt% in the rephosphorised steel and less than 0.011 wt% in the rest of the steels. The manganese contents are between 0.10-0.41 wt%. Two steels were alloyed with Nb. Considering that the stoichiometric relationship corresponding to TiN is 3.4 [17], only the Ti steel presents an important “excess” Ti content (Table 1) [16].

2.2. Annealing cycle

The annealing process was performed at laboratory scale in a simulator (RHESCA) [16]. The atmosphere of the annealing furnace was constituted by a reducing mixture of gases with a composition of N_2-5%H_2. In accordance with industrial practice, the water vapour content in the annealing atmosphere was expressed as the DP value [18]. In this study, atmospheres with DP values of -45, -10 and 10ºC were used. With these steels the annealing cycle consisted of a linear heating ramp (15ºC s^{-1}) up to 850ºC, holding the specimens at this temperature for 40 s and then immediately cooling them at a rate of 5ºC s^{-1} to a temperature of 500ºC. The specimens were held at this temperature for 20 s and then rapidly cooled to the molten zinc bath entry temperature (460ºC) at a rate of 30ºC s^{-1} [16].

2.3. Galvannealing process

After the annealing process, the steels were galvanised in a molten zinc bath with an aluminium content of 0.135 wt%. The immersion time was 10 s and the bath temperature was 460ºC. The galvanised specimens were subsequently subjected to an annealing treatment at 500ºC for a time of between 4 and 12 s and immediately cooled at a rate of 12ºC s^{-1} to room temperature. The Ti and Ti-Nb steels were annealed for approximately 4 s, while the Ti-Nb-P steels were annealed for 12 s. This important difference in the annealing time is necessary in order to obtain a similar Fe-Zn intermetallic content in the galvanneal coating. The coating weight was, in most cases, 45 g/m^2 (equivalent to a thickness of between 8 and 10 µm).

2.4. Gravimetric determinations

Specimens of a size of 2x2 cm^2 were cut from the galvanneal coated sheets and cleaned with a suitable solvent. The specimens were weighed before and after dissolving the galvanneal coating in a hydrochloric acid solution with urotropin [19]. The specimens were submerged in the solution until the difference between two successive weighings was negligible. The Fe, Zn and Al contents in the solution were obtained by chemical analysis.

2.5. Observation by optical microscopy and scanning electron microscopy with energy dispersive analysis (SEM/EDX)

The morphology and composition of the different phases were characterised by optical microscopy, scanning electron microscopy (SEM) and EDX analysis. Metallographic observations were made for two planes: cross section and parallel to the surface of the steel sheet. Cross section observations were made on unattacked specimens and after their attack with 1% Nital. The equipment used for SEM/EDX observations was a JEOL JXA 840A unit operating with Rontec EDR288 software for EDX spectra acquisition and image digitalisation.

2.6. X-ray photoelectron spectroscopy (XPS)

The experimental set-up and the conditions used to obtain XPS spectra have been described in detail elsewhere [20]. The analyses were obtained in two different areas cut from the same annealed steel specimen. The total analysed area was 1mm^2[16].

3. RESULTS

3.1. XPS characterisation of steel surfaces after annealing and cooling to 500ºC in atmospheres with a DPs of –45, -10 and 10ºC

Figure 1 shows the variation in the O/(Fe+Mn) atomic ratios obtained by XPS on the surface of Ti, Ti-Nb and Ti-Nb-P steels as a function of the DP of the annealing atmosphere. Irrespective of the chemical composition of the bulk steel, a reduction is seen in the O/(Fe+Mn) ratio as the DP of the atmosphere decreases.

Figure 2 compares the Oxide/(Fe+Mn) and Hydroxide/(Fe+Mn) atomic ratios obtained by XPS on the surface of Ti, Ti-Nb and Ti-Nb-P steels annealed in the different atmospheres. On Ti-Nb steel, attention is drawn to the continuous decline in the Oxide/(Fe+Mn) ratio as the DP of the annealing atmosphere decreases (Figs. 2a). No similar tendency is seen with Ti steel at the highest DP (Fig. 2a). In general, a tendency is seen for Oxide/(Fe+Mn) ratios on Ti steel to be greater than those found on Ti-Nb and Ti-Nb-P steels (Fig. 2a). According to Figure 2b, the reduction in the DP of the annealing atmosphere is translated into a significant reduction in the Hydroxide/(Fe+Mn) ratios obtained on the Ti and Ti-Nb steels. It is interesting to note that while the Oxide/(Fe+Mn) atomic ratio observed on Ti steel increases as the DP decreases from 10 to –10ºC (Fig.2a), the hydroxide/(Fe+Mn) ratio drops very significantly (Fig. 2b) [16].

Table 2 shows the elemental compositions obtained by XPS on the surfaces of Ti, Ti-Nb and Ti-Nb-P steels after the annealing process prior to entering the molten zinc bath. Attention is drawn to the presence of significant amounts of manganese and phosphorus on the surface of the Ti-

Nb-P steel. The manganese contents observed on the surface of the Ti-Nb-P steel annealed in an atmosphere with a DP of 10ºC is lower than the contents obtained in atmospheres with lower DPs. It is noted that the phosphorus contents observed on the steel annealed in atmospheres with a DP of 10 or -10ºC are higher than those observed with a DP of -45ºC [16]. It is also notable that the resulting (Mn+P)/(Fe+Mn+P) atomic ratios are two times higher at the lower DPs (-45 and –10ºC) compared with the atmosphere with DP of 10ºC.

Figure 3 shows the $Mn2p_{3/2}$ and P2p high resolution XPS spectra obtained on the surface of Ti-Nb-P steel after the annealing process in the different atmospheres. The $Mn2p_{3/2}$ spectra contain one single component with a binding energy of 641.5 eV. This binding energy is typical of manganese in the form of MnO [18 and 21-23]. The P2p spectra contain one single component with a binding energy of 133.8 eV. This binding energy is typical of phosphorus as phosphate [24].

3.2. Characterisation of galvanneal coatings by optical microscopy in unetched condition

Cross-sectional light optical images in unetched condition are shown in Figure 4. The different phases through the galvanneal coating were identified by EDX analysis, as discussed in section 3.3.3. The Ti and Ti-Nb samples show a two layer structure containing delta phase near the substrate steel with a top layer of zeta phase (Figs 4a-4f). The coating on the Ti –Nb-P steel substrate is composed by a mixture of zeta and eta phases, with zeta phase identified as the major phase of the galvanneal coating on the Ti-Nb-P steel for a D.P. of 10ºC (Fig.4g).

3.3. Characterisation of galvanneal coatings by SEM/EDX

3.3.1. Coating surface morphology

Figure 5 compares the micrographs recorded on the surface of the metallic coatings obtained on the steel substrates in the studied atmospheres. In general, the superficial morphology of the galvanneal coating on Ti and Ti-Nb steels is very smooth, which may indicate that the outer surface of the coating is completely covered by metallic zinc or by Fe-Zn intermetallics with a low Fe content (Figs. 5a-5f). On the surface of the coating on the Ti steel substrate for a DP of -45ºC (Fig. 5c) a slight presence of Fe-Zn crystals is observed.

Figures 5g-5i show the evolution of the surface morphology of the coating on the Ti-Nb-P steel substrate with the DP of the annealing atmosphere. Unlike the other two steels, the outer surface of the coating obtained on Ti-Nb-P steel annealed in an atmosphere with a DP of 10ºC appears completely covered by Fe-Zn crystals (Fig. 5g), which suggests the presence of zeta phase. The major presence of zeta phase may be due to the fact that the galvannealing time for Ti-Nb-P steel is three times longer than with Ti and Ti-Nb steels. Attention is drawn to the absence of these crystals on the outer surface of the coating obtained on the same steel at lower DPs (-10 or -45ºC) (Figs. 5h and 5i).

3.3.2. Cross section morphology after chemical etching

Figure 6 compares the SEM micrographs obtained on the cross section of the metallic coatings after slight chemical attack with 1% nital. The major Fe-Zn phase in each layer was determined from the Fe concentration profiles obtained by EDX analysis (Fig 7).

The galvanneal coating formed on Ti steel substrate annealed in an atmosphere with a DP of 10ºC (Fig. 6a) contains predominantly zeta phase. On the other hand, the micrographs obtained on the galvanneal coating on Ti steel substrate annealed in atmospheres with DPs of –10 and –45ºC (Figs. 6b and 6c) reveal the presence of delta phase close to the steel substrate and that of zeta and possibly eta phase close to the outer surface. The thickness of the region containing the zeta and eta phases seems to be the same or even greater than that of the delta phase.

On the Ti-Nb steel an important increase is seen in the thickness of delta phase, which comes to occupy most of the cross section of the coating (Figs. 6d-6f). The zeta phase ceases to form a more or less uniform layer and tends to be localised in pores or cracks within the delta phase. A faster reaction rate between iron and zinc is observed on Ti-Nb steel (Figs. 6d-6f) than on Ti steel (Figs. 6a-6c) in all the tested galvannealing atmospheres.

On the galvanneal coating formed on Ti-Nb-P steel substrate annealed in an atmosphere with a DP of 10ºC (Fig. 6g), the zeta phase is the major phase. The galvanneal coatings obtained on Ti-Nb-P steel substrates annealed in atmospheres with DPs of -10 or -45ºC (Figs. 6h and 6i, respectively) differ from the others (Figs. 6a-6g) in that they apparently present one single layer containing predominantly eta phase and some zeta phase as well.

3.3.3. Concentration profiles through galvanneal coatings

Figure 7 shows the Fe concentration profiles obtained by EDX through the galvanneal coatings. According to Figures 7a-7c, referring to galvanneal coatings obtained on the substrate of Ti steel, the delta phase is the major phase throughout the coating obtained after annealing in atmospheres with a DP of -45 or -10ºC, while in an atmosphere with a DP of 10ºC it seems to be the zeta phase. For Ti-Nb steel, the delta phase seems to be the major phase irrespective of the galvannealing atmosphere (Figs 7d-7f). For Ti-Nb-P steel, attention is drawn to the absence of Fe in the galvanneal coatings obtained on the steel annealed in atmospheres with a DP of -45 or -10ºC (formation of eta phase, Figs 7h aand 7i), while in an atmosphere with a DP of 10ºC the zeta phase seems to be the major phase (Figs. 7g).

The graphic integration of the Fe concentration profile is directly related with the iron content that is incorporated in the metallic coating as a result of the galvannealing process [12]. Figure 8 shows the area (obtained by integration of the line profiles in Fig. 7) as a function of the DP of the annealing atmosphere and the studied steel substrates. Higher Fe contents have been obtained in the galvanneal coating with Ti-Nb steel than with Ti steel in all the three tested atmospheres. Attention is drawn to the absence of significant amounts of iron in the galvanneal coating obtained on Ti-Nb-P steel previously annealed in atmospheres with a DP of -45 or -10ºC. In contrast, considerable iron contents are observed in the coating obtained on this steel annealed in an atmosphere with a DP of 10ºC.

3.4. Iron contents in galvanneal coatings determined by chemical analysis

Figure 9 shows the iron contents determined by chemical analysis of the solution resulting from the dissolution of the galvanneal coating. In general, a higher iron content is found in the coating obtained on Ti-Nb steel than on the other two steels. As in the line profiles (Fig. 7), attention is drawn to the absence of iron in the galvanneal coating on Ti-Nb-P steel annealed in atmospheres with a DP of -10 or -45ºC, in contrast to the same steel annealed with a DP of

10ºC. Although the galvannealing time is three times longer for Ti-Nb-P steel, no marked differences are seen in the iron content in the galvanneal coating obtained on the steel annealed in an atmosphere with a DP of 10ºC (Fig. 9) compared with the other two steels.

4. DISCUSSION

It is of fundamental interest to know what transformations experienced by the outer surface of the steel substrate during the annealing process determines either the inhibition or the rapid growth of intermetallic compounds during the galvannealing process. In a previous study involving optical microscopy and SEM/EDX [16], no appreciable changes were observed on the steel surface that could explain the effect of the water content in the annealing atmosphere, or the chemical composition of the bulk steel on the thickness and the morphology of the different Fe-Zn intermetallic layers. In contrast, XPS measurements have been of great utility for the analysis of thin films like those of the alloying element oxides and hydroxides formed on steel in contact with the annealing atmosphere (thicknesses between 2-5 nm). The significant changes in the chemical composition of the surface of the material revealed by XPS have provided valuable information for the discussion below on the possible mechanisms of the inhibition of growth of Fe-Zn intermetallic compounds, as well as a quantitative means of comparing the effect on this growth of the steel composition and water content in the annealing atmosphere.

4.1. Effect of steel substrate chemical composition on galvanneal coatings

4.1.1. Presence of titanium

The iron contents determined by graphic integration of the line profiles (Fig. 8) and by chemical analysis (Fig. 9) are greater in the galvanneal coating on Ti-Nb steel than on Ti steel. In general, this suggests a greater reaction rate between iron and zinc on the Ti-Nb steel than on Ti steel.

Figure 1 compares the O/(Fe+Mn) atomic ratios observed by XPS on the surface of annealed Ti, Ti-Nb and Ti-Nb-P steels. A tendency is seen for this ratio to be greater in Ti steel than in the other two steels annealed in the DP atmospheres of 10ºC and –10ºC. The reasons for the greater O/(Fe+Mn) atomic ratios observed on the surface of the Ti steel substrates are not clear. Probably, due to the small number and size of the Ti compounds and also due the strong tendency of the Ti particles to be covered by oxides in the outer surface area analysed, the XPS spectra do not present significant signals of Ti. For this reason, it can be speculated that a fraction of the “excess” titanium content in Ti steel could precipitate in the form of titanium oxide on the outer surface during the manufacturing process of these steels. The lower thickness of the delta phase region observed in the galvanneal coating on the Ti steel compared with Ti-Nb steel could be in agreement with the additional presence of titanium oxide and a possible inhibiting effect of this oxide on the growth of Fe-Zn intermetallic compounds.

4.1.2. Presence of manganese and phosphorus

Figure 7 compares the iron line profiles obtained by EDX through the galvanneal coating on the three tested steels, showing the absence of iron on the Ti-Nb-P steel which had been annealed at low DPs (-45 and -10ºC). At the highest DP (10ºC) the formation of a major content of zeta phase is observed. Despite the fact that the galvannealing time has been three times longer in the case of the Ti-Nb-P steel substrate than for the Ti-Nb steel, chemical analysis reveals similar iron contents on both steels when annealed in the atmosphere with a DP of 10ºC (Fig. 9). Assuming an approximately linear progress of the reaction between Fe and Zn, such a result suggests a lower reaction rate on the Ti-Nb-P steel substrate than on Ti-Nb steel. As in the line profiles obtained by EDX, attention is drawn to the absence of iron in the metallic coatings obtained on Ti-Nb-P steel annealed in the atmospheres with the lowest DPs (-10 and -45ºC). In general, this data suggests that the reaction between iron and zinc on the Ti-Nb-P steel substrate is either completely impeded in atmospheres with a low DP (-45 or -10ºC) or is slower than on Ti-Nb and Ti-Nb-P steels at the highest DP (10ºC).

It will be observed from Table 2 that, as a result of the annealing process, significant amounts of alloying elements (Mn and P) have been detected on the surface of Ti-Nb-P steel, mainly as MnO and phosphates, which were not observed on the Ti and Ti-Nb steels. The binding energy of the high resolution spectra in Figure 3 is typical of manganese in the form of MnO. XPS results do not give information about the details of the oxide distribution. According to literature, it seems rather usual to find a continuous and thin oxide film of iron oxide over the steel surface, while the manganese oxides may be distributed in the form of islands [23]. Unlike the cases of elements C, O and Fe, important variations in the Mn contents have not been detected in a previous work [25] as the thickness of the steel was reduced by AIB (Argon Ion Bombardment) (Fig. 9 in ref. 25). This was interpreted as a proof that the oxides of these elements do not form a continuous film on the surface but instead form well-defined islands. Despite the low P (0.070 wt%) bulk steel content and the high tendency of P to segregate at the grain boundary in the temperature interval of 450-550ºC [26], our XPS data show that P has also a strong tendency to segregate to the surface. Assuming an island model and that the nodules of manganese and phosphorous oxides are thick enough to avoid iron signal to come through, the fraction of the steel surface covered by them would be represented approximately by the (Mn+P)/(Fe+Mn+P) atomic ratio. According to Table 2, this ratio reaches values between 0.25 and 0.5, which seems to indicate that a high percentage of the steel surface is covered by manganese and phosphorus oxides.

The absence of Fe-Zn intermetallic compounds in the coating formed on the Ti-Nb-P steel substrate after annealing in atmospheres with a DP of –45 or –10ºC, and its low Fe content after annealing at a DP of 10ºC (Figs. 7 and 8), may be attributed to growth inhibition of these compounds by the high coverage of the outer steel surface with MnO and phosphates.

4.2. Effect of water content in the annealing atmosphere

4.2.1.Ti and Ti-Nb steel substrates

No marked differences have been observed in the content of Fe-Zn intermetallics growing on the Ti-Nb steel substrate in the three studied galvannealing atmospheres (Figs. 4-9) In contrast to the behaviour found for Ti-Nb steel, the galvanneal coating obtained on Ti steel after annealing in atmospheres with a low DP (-45 or -10ºC) seems to show a higher delta phase content (Figs.4, 6 and 7) than that observed at the highest DP (10ºC).

XPS surface analysis of Ti steel shows a greater increase in the Hydroxide/Fe ratio as the DP of the annealing atmosphere changes from -10 to 10ºC (Fig. 2b) than is observed with Ti-Nb steel (Fig. 2b). Thus, the reduction in the Fe-Zn intermetallics content seen on the coating obtained on Ti steel in the annealing atmosphere with the highest DP (10ºC) compared with the lower

DPs (-45 and –10ºC) (Figs. 8 and 9), could be related with the inhibiting effect resulting from the hydroxide enrichment during the annealing process.

4.2.2.Ti-Nb-P steel substrate

According to Figures 4-9, referring to the Ti-Nb-P steel substrate, the degree of Fe incorporation in the galvanneal coating is much higher after the annealing of the steel in the atmosphere with a DP of 10ºC than with lower DPs (-10 or -45ºC). This increase in the reaction rate between iron and zinc as the DP of the annealing atmosphere rises was also observed by Hertveldt et al. [1]. In our research, attention is drawn to the almost complete absence of iron in the coatings obtained after annealing in atmospheres with a DP of -10 or -45ºC (Figs. 7-9), This phenomenon may be related with the strong tendency for Mn surface segregation, and oxidation during annealing of the steel. The low oxygen content in the annealing atmosphere and the greater affinity of Mn for oxygen compared with P give rise to the preferential diffusion of Mn towards the outer surface in order to precipitate in the form of MnO [16]. The (Mn+P)/(Fe+Mn+P) atomic ratios values obtained for the lower DP atmospheres (-10 and –45ºC) are nearly 0.5 (Table 2), suggesting that nearly half of the annealed steel surface is covered by oxides of the alloying elements, mainly manganese oxide.

The XPS analyses of the annealed steel surface (Table 2 and Fig. 3) show a considerable reduction of the MnO content in the atmosphere with a DP of 10ºC compared with the atmospheres of lower DPs (-10 or -45ºC). This reduction is in agreement with a change of the oxidation mode of the manganese from external to internal oxidation with the increase of DP. As a result of annealing with a DP of 10ºC, the area of the steel surface covered by the alloying elements may be approximately two times less than that observed with lower DPs (-10 and –45ºC). Thus the external surface of the steel annealed with a DP of 10ºC is less restrictive for the diffusion of iron atoms from the steel substrate to the zinc coating in the galvannealing process.

5. CONCLUSIONS

1) XPS surface analysis of the steel substrate resulting from the annealing process has proven to be a useful tool to study the factors affecting the evolution of the different Fe-Zn phases that grow in the subsequent galvannealing process.
2) In general, the strong tendency of the alloying elements such as P and Mn to segregate to the surface and to precipitate in oxide form on the annealed steel surface has resulted in a significant reduction in Fe-Zn intermetallic compounds in the coating.
3) With the Ti steel, the XPS results suggest a negative contribution of the oxide particles present on the outer surface on the growth of Fe-Zn intermetallics. With this steel, the intermetallics content in the coating obtained after annealing in an atmosphere with a DP of 10ºC is seen to be less than that obtained with lower DPs (-10 or -45ºC).
4) With the Ti-Nb steel, the absence of alloying element oxides on the outer surface of the annealed steel leads to a greater formation of the delta phase in the galvanneal coating than with the other studied steels.
5) With the Ti-Nb-P steel, attention is drawn to the absence of Fe in the metallic coatings obtained after annealing in atmospheres with a DP of -45 or -10ºC. A clear direct relationship has been found between the inhibition of growth of Fe-Zn intermetallic compounds and the fraction of the steel substrate surface covered by manganese and phosphorous oxides (predominantly MnO at low dew points), as a result of the annealing process.
6) With the Ti-Nb-P steel, the increase in the DP of the annealing atmosphere to 10ºC resulted in the incorporation of a significant Fe content in the coating. XPS analysis suggests the formation of a phosphate enriched layer, instead of manganese oxide, with a lower fraction of the annealed steel substrate covered, resulting in less of an impediment to the diffusion of iron atoms from the steel substrate to the zinc coating in the galvannealing process.

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FIGURE CAPTIONS

Figure 1. Variation in O/(Fe+Mn) atomic ratios obtained by XPS on the surface of the three steels annealed in atmospheres with different DPs (-45, -10 and 10ºC).

Figure 2. Variation in Oxide/(Fe+Mn) (a) and Hydroxide/(Fe+Mn) (b) atomic ratios obtained by XPS on the surface of the three steels annealed in atmospheres with different DPs (-45, -10 and 10ºC).

Figure 3. Mn $2p_{3/2}$ and P2p high resolution XPS spectra obtained on the surface of Ti-Nb-P steel annealed in atmospheres with different DPs (-45, -10 and 10ºC).

Figure 4. Cross-sectional light optical images in unetched condition of the coatings obtained on the substrates of Ti, Ti-Nb and Ti-Nb-P steels annealed in atmospheres with DPs of -45, -10 and 10ºC.

Figure 5. Micrographs of the surface morphology of coatings obtained on the substrates of Ti, Ti-Nb and Ti-Nb-P steels annealed in atmospheres with DPs of -45, -10 and 10ºC.

Figure 6. Micrographs of the cross section after chemical attack with 1% Nital of metallic coatings obtained on the substrates of Ti, Ti-Nb and Ti-Nb-P steels annealed in atmospheres with DPs of -45, -10 and 10ºC.

Figure 7. Fe concentration profiles obtained by EDX through galvanneal coatings obtained on the substrates of Ti, Ti-Nb and Ti-Nb-P steels annealed in atmospheres with DPs of -45, -10 and 10ºC.

Figure 8. Area (obtained by integration of the line profiles in Fig.7) as a function of the DP of the galvannealing atmosphere and the steel substrate.

Figure 9. Iron contents obtained by chemical analysis of the galvanneal coating as a function of the DP of the annealing atmosphere and the steel substrate.

Table 1. Chemical composition of the IF steels (weight percentage x10^{-3}).

Type	C	N	Ti	Nb	Mn	P	B	S	Si	Cr	Ni	Al	Cu	Excess Ti
Ti	1	2	43	1	150	8	0	5	7	17	22	31	8	36
Ti-Nb	2	2.3	13	18	109	6	0	6	5	14	22	22	7	5
Ti-Nb-P	2	1.7	14	19	410	70	0.5	7	7	23	24	34	14	8

Excess Ti = Total Ti - 3.42 * N

Table 2. Atomic percentages observed by XPS on the outer surface of steels Ti, Ti-Nb and Ti-Nb-P steels after the annealing process in atmospheres with DPs of -45, -10 and 10ºC.

STEEL	DEW POINT	%C	%O	%Fe	%Mn	%P	(Mn+P)/(Fe+Mn+P)
Ti	10ºC	59	33	8	0	0	0
	-10ºC	52	37	11	0	0	0
	-45ºC	50	38	12	0	0	0
Ti-Nb	10ºC	57	34	9	0	0	0
	-10ºC	57	33	10	0	0	0
	-45ºC	60	30	10	0	0	0
Ti-Nb-P	10ºC	54	34	9	1	2	0.25
	-10ºC	57	31	6	4	2	0.5
	-45ºC	62	28	5	4	1	0.5

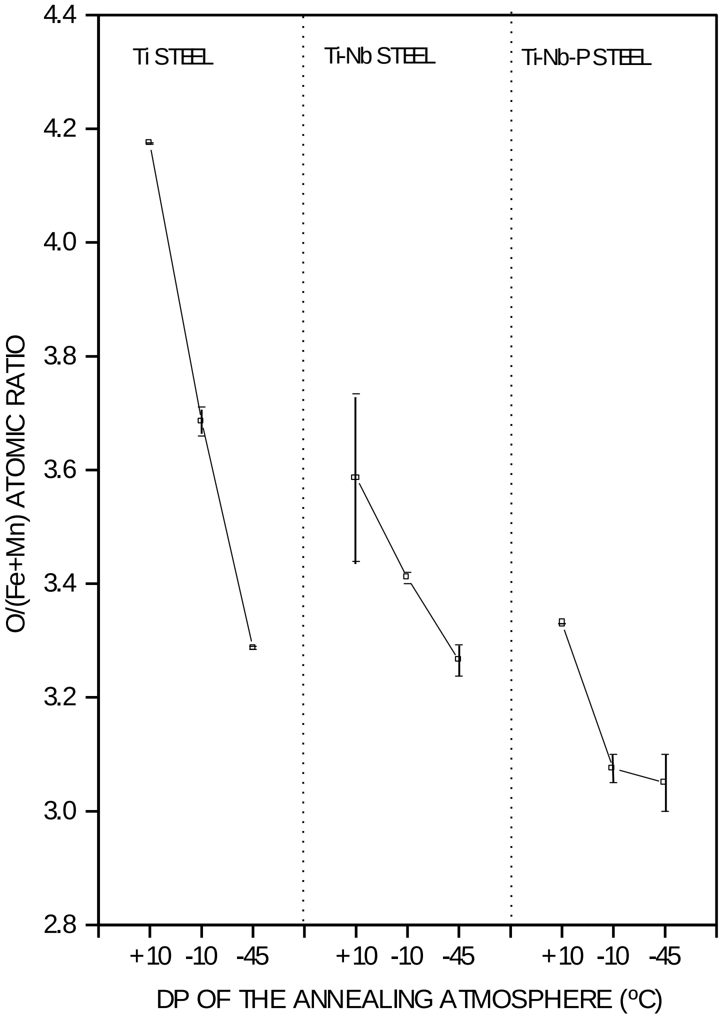

Ti STEEL
Ti-Nb STEEL
Ti-Nb-P STEEL
O/(Fe+Mn) ATOMIC RATIO
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
+10 -10 -45
+10 -10 -45
+10 -10 -45
DP OF THE ANNEALING ATMOSPHERE (ºC)

FIGURE 1.

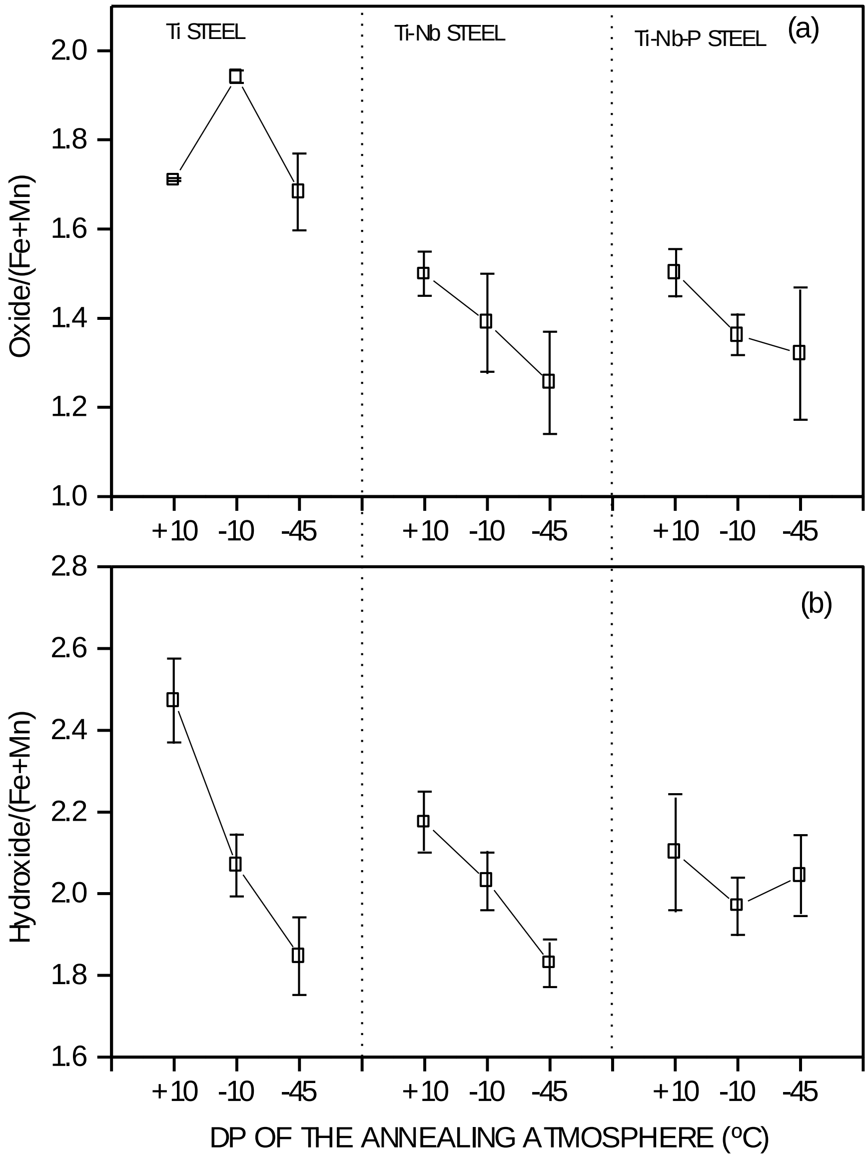

Ti STEEL
Ti-Nb STEEL
Ti-Nb-P STEEL
(a)
Oxide/(Fe+Mn)
2.0
1.8
1.6
1.4
1.2
1.0
+10 -10 -45 +10 -10 -45 +10 -10 -45
2.8
(b)
2.6
2.4
2.2
2.0
1.8
1.6
Hydroxide/(Fe+Mn)
+10 -10 -45 +10 -10 -45 +10 -10 -45
DP OF THE ANNEALING ATMOSPHERE (ºC)

FIGURE 2.

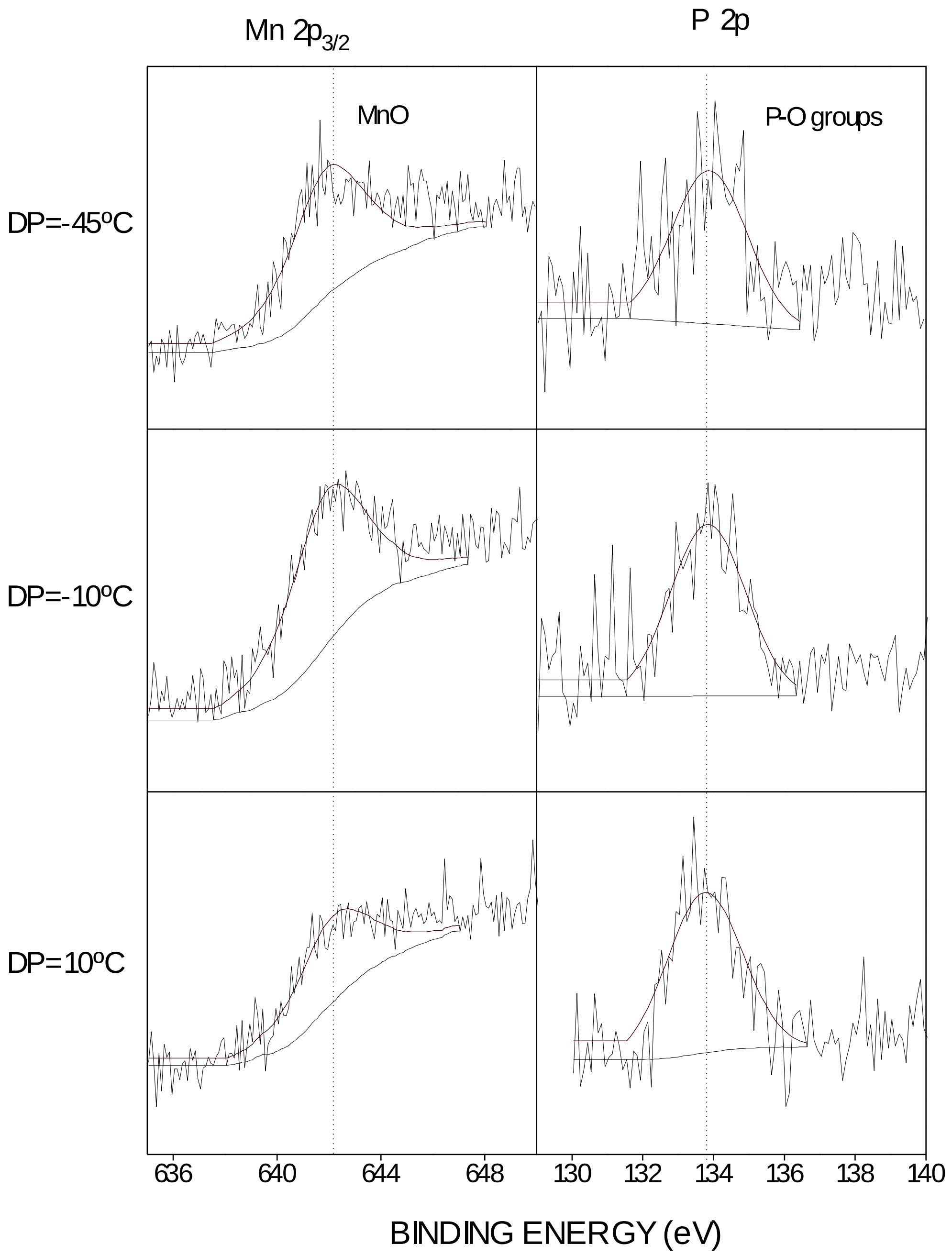

Mn 2p3/2
P 2p
MnO
P-O groups
DP=-45ºC
DP=-10ºC
DP=10ºC
636
640
644
648
130
132
134
136
138
140
BINDING ENERGY (eV)

FIGURE 3

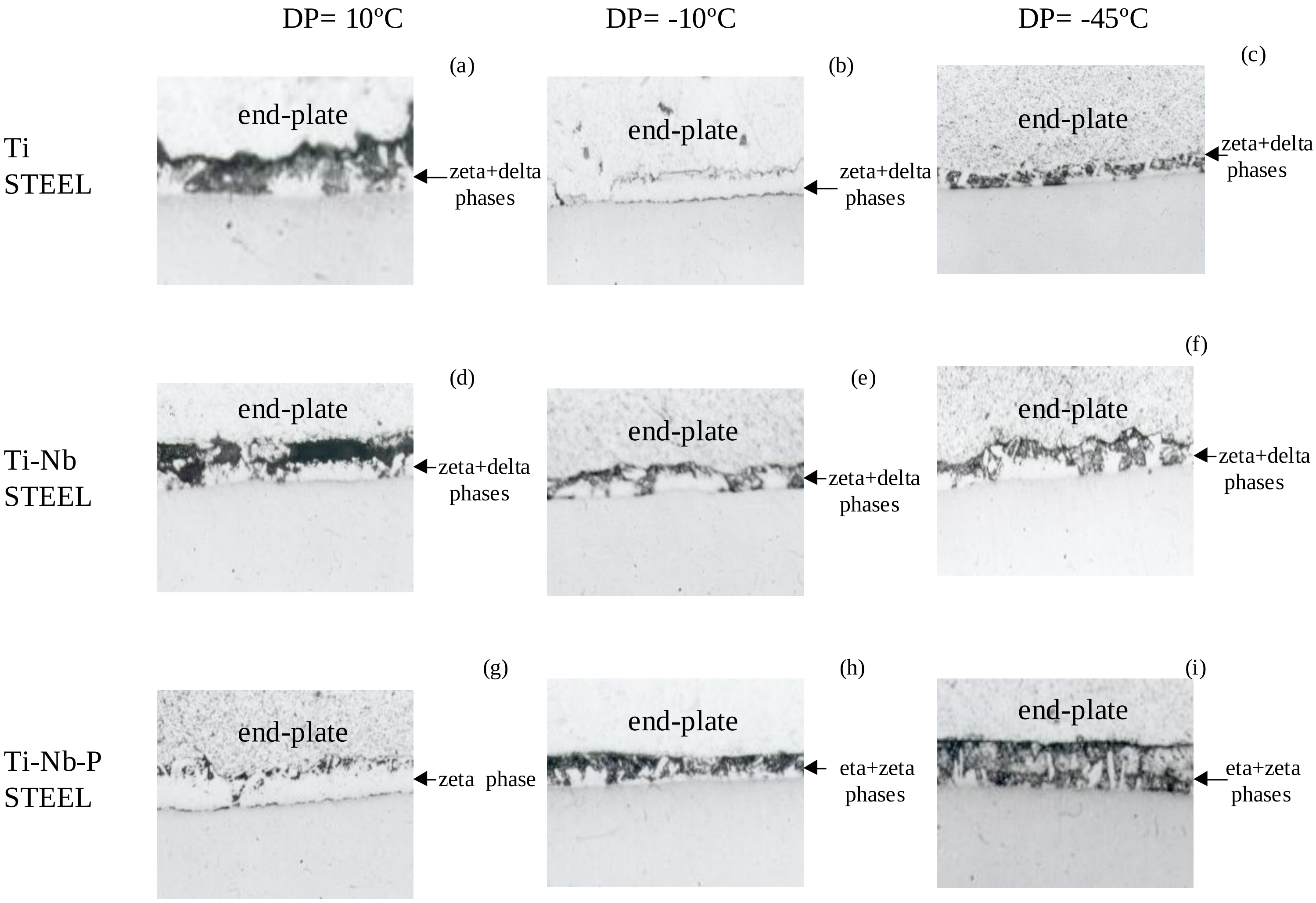

DP= 10ºC
DP= -10ºC
DP= -45ºC
Ti
STEEL
(a)
end-plate
zeta+delta
phases
(b)
end-plate
zeta+delta
phases
(c)
end-plate
zeta+delta
phases
Ti-Nb
STEEL
(d)
end-plate
zeta+delta
phases
(e)
end-plate
zeta+delta
phases
(f)
end-plate
zeta+delta
phases
Ti-Nb-P
STEEL
(g)
end-plate
zeta phase
(h)
end-plate
eta+zeta
phases
(i)
end-plate
eta+zeta
phases

FIGURE 4.

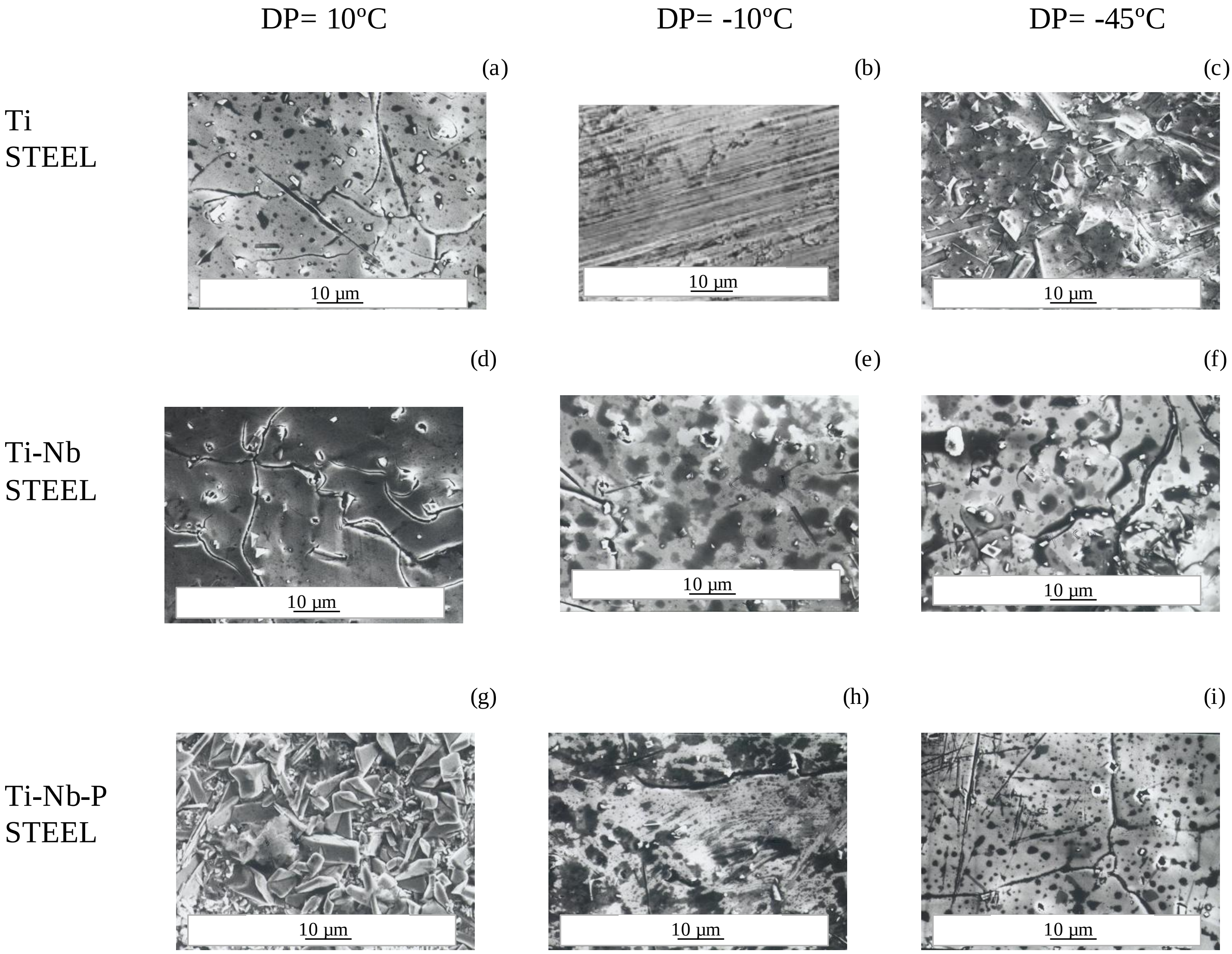

DP= 10ºC
DP= -10ºC
DP= -45ºC
Ti
STEEL
Ti-Nb
STEEL
Ti-Nb-P
STEEL
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
10 µm

FIGURE 5

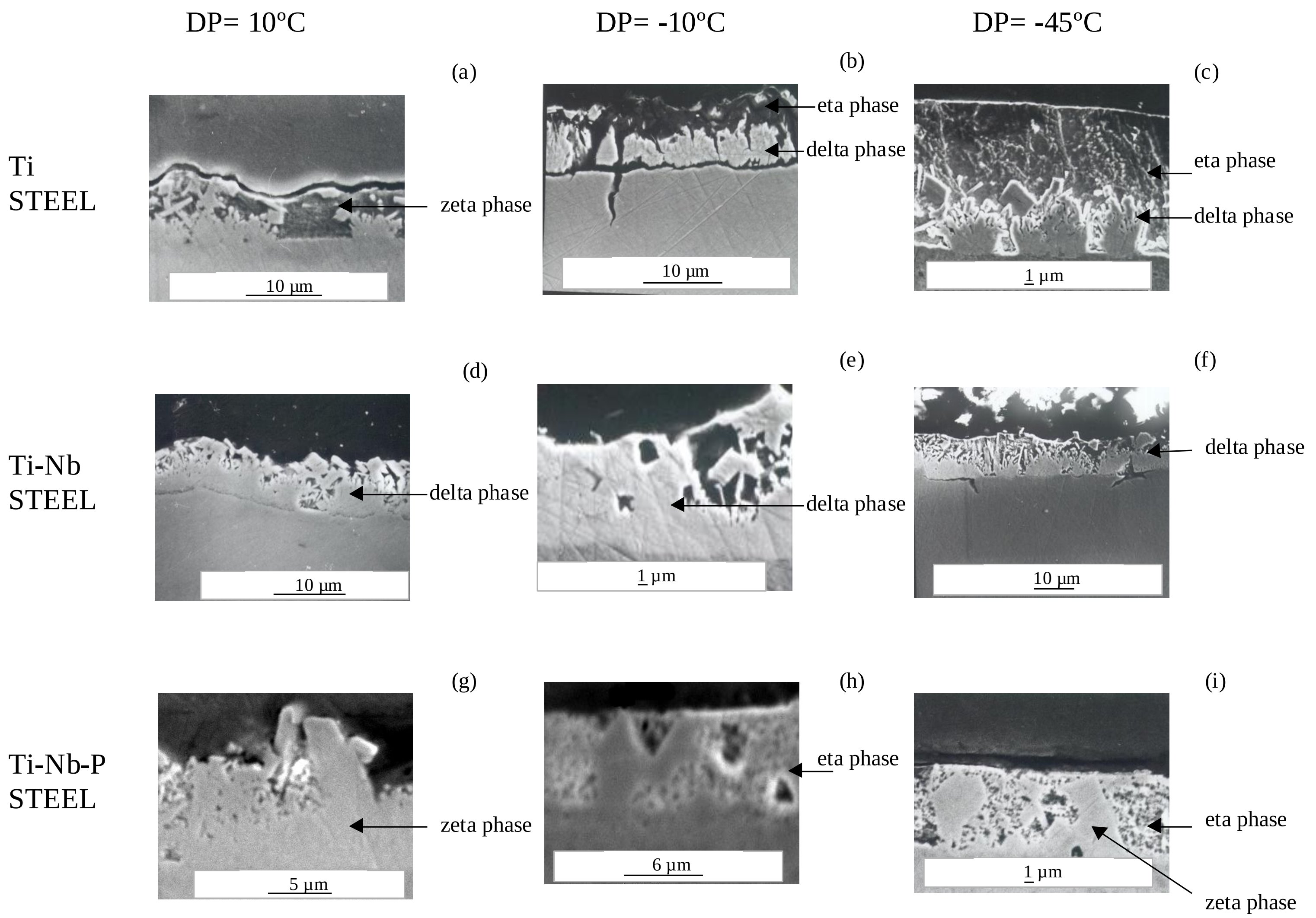

DP= 10ºC
DP= -10ºC
DP= -45ºC
Ti
STEEL
Ti-Nb
STEEL
Ti-Nb-P
STEEL
(a)
zeta phase
10 µm
(b)
eta phase
delta phase
10 µm
(c)
eta phase
delta phase
1 µm
(d)
delta phase
10 µm
(e)
delta phase
1 µm
(f)
delta phase
10 µm
(g)
zeta phase
5 µm
(h)
eta phase
6 µm
(i)
eta phase
zeta phase
1 µm

FIGURE 6

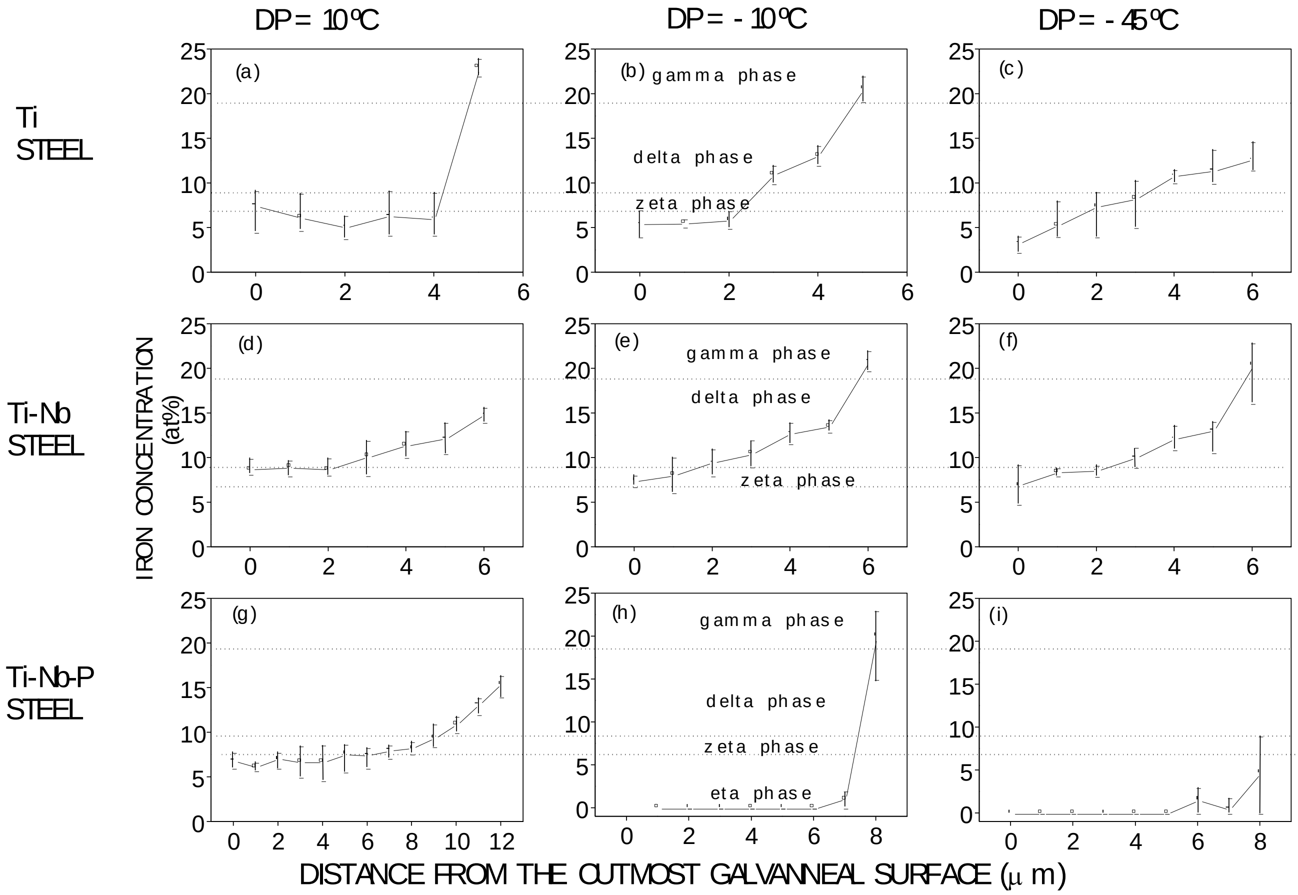
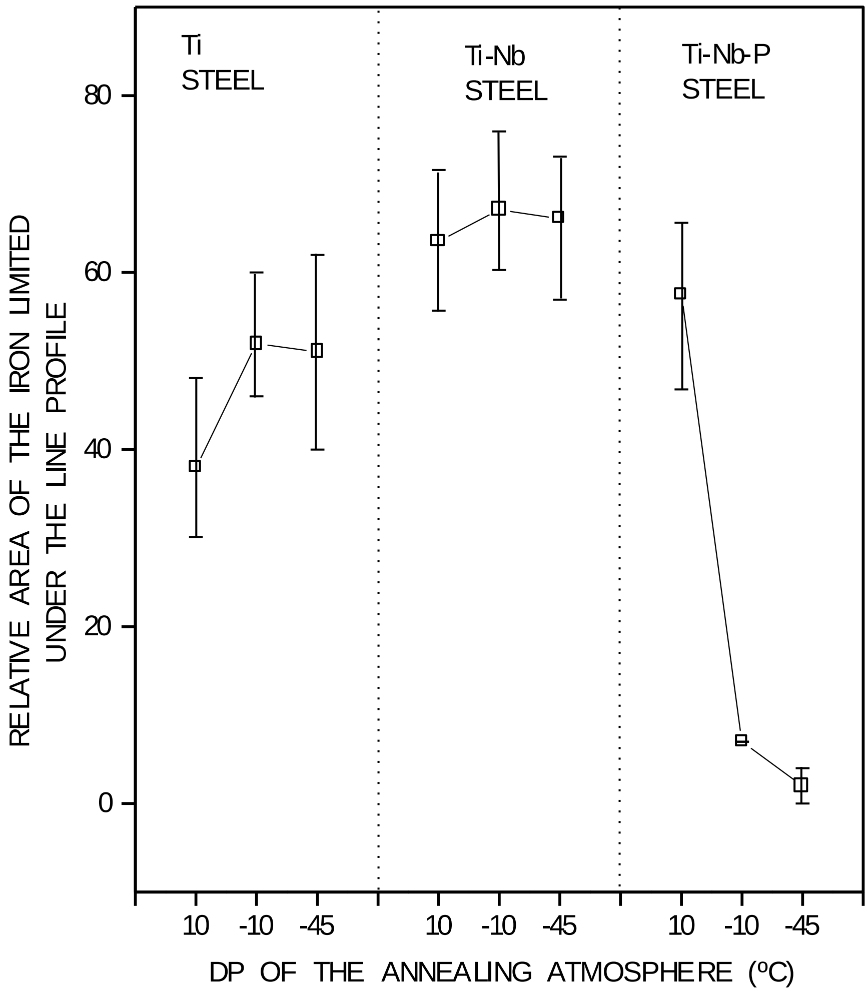

DP= 10°C
DP= - 10°C
DP= - 45°C
Ti
STEEL
Ti-Nb
STEEL
Ti-Nb-P
STEEL
IRON CONCENTRATION
(at%)
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
gamma phase
delta phase
zeta phase
eta phase
DISTANCE FROM THE OUTMOST GALVANNEAL SURFACE (μ m)

FIGURE 7.



Ti
STEEL
Ti-Nb
STEEL
Ti-Nb-P
STEEL
80
60
40
20
0
RELATIVE AREA OF THE IRON LIMITED
UNDER THE LINE PROFILE
10
-10
-45
10
-10
-45
10
-10
-45
DP OF THE ANNEALING ATMOSPHERE (ºC)

FIGURE 8

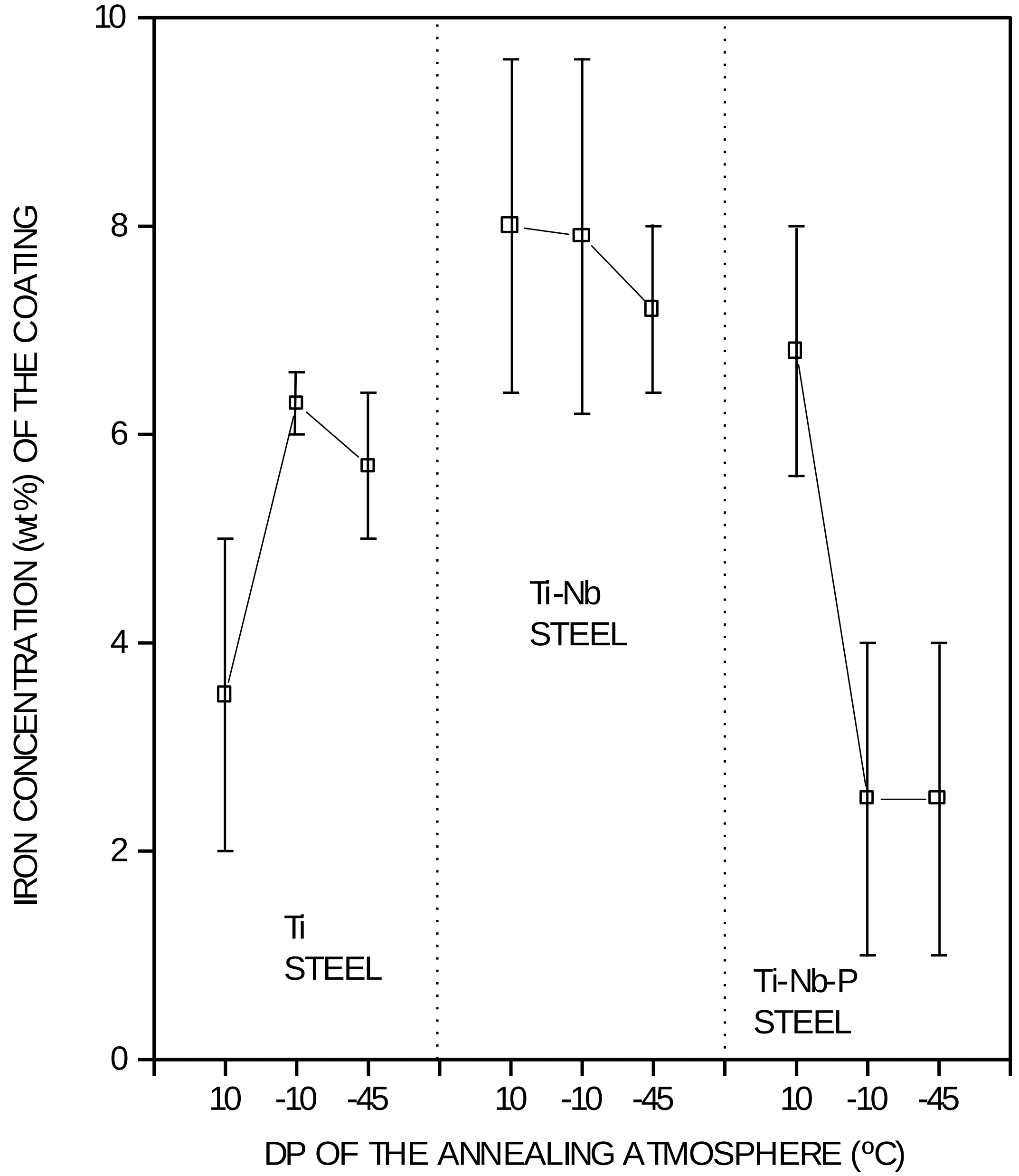

10
8
6
4
2
0
IRON CONCENTRATION (wt%) OF THE COATING
Ti-Nb
STEEL
Ti
STEEL
Ti-Nb-P
STEEL
10 -10 -45 10 -10 -45 10 -10 -45
DP OF THE ANNEALING ATMOSPHERE (ºC)

FIGURE 9.