

Hydrogen Solubility Effects in Galvanized Advanced High Strength Steels

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ABSTRACT

Advanced high strength steels used in automotive body and structure applications are exposed to hydrogen during several steps of their processing. For galvanized sheet steel, one of these is the continuous galvanizing process, during which the sheet is prepared for coating in a H_2 - N_2 furnace. This paper shows the relationship between hydrogen uptake in DP600 and DP980 grades, together with an IF steel control composition, and galvanizing process conditions. Hydrogen uptake is strongly dependent on the furnace atmosphere and the amount of martensite in the steel but has little dependence on the soaking time, the humidity of the furnace atmosphere, or the temperature within the usual intercritical annealing range. Rapid outgassing was observed during overageing prior to the zinc dipping. Slow strain rate tests showed that there was no loss of ductility in galvanized samples that had been treated in a 5% H_2 atmosphere or that had been overaged before the galvanizing.

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INTRODUCTION

High strength steels can be sensitive to delayed fracture. This phenomenon can be described as unexpected fracture or ductility loss arising after a certain period of time. A critical combination of factors must be reached to induce the delayed fracture: the presence of diffusible hydrogen^{1,2} applied or residual stresses^{3,4} of a sufficient level (due to the assembling process for example) and metallurgical factors such as the crystallographic structure and the chemical composition or the microstructure^{5,6,7,8}. Little knowledge has been developed on hydrogen issues in galvanized high strength steels used in automotive applications. As the metallurgy and the stresses are usually driven by the manufacturing process, uncontrolled hydrogen charging must be avoided to obtain safe products, especially when a coating hinders hydrogen escaping from the steel^{9,10}. This paper describes results of a study of hydrogen charging during the hot dip galvanization process of two advanced high strength steels, dual phase grades DP600 and DP980 in comparison with interstitial-free steel used as a reference.

MATERIALS AND EXPERIMENTAL PROCEDURE

Three steels were studied: an interstitial-free (IF) grade as a reference, together with dual phase grades DP600 and DP980. All steels were provided by ArcelorMittal Europe in a full hard state with a thickness of about 1.5 mm. Chemical compositions are shown in [Table 1](#).

Experiments were performed in the CRM multidip simulator (MDS) presented schematically in [Figure 1](#). This simulator is equipped with two connected furnaces. The top furnace was used for the heating and soaking treatments while the bottom furnace was used for the overageing treatments. This arrangement permitted two separated atmospheres can be used without an intermediate prolonged gas purging step. After pretreatment, sheet steel samples can then be dipped in the zinc bath. A reference thermal cycle, simulating a hot dip galvanizing line running at 100m/min was used, as shown in [Figure 2](#), also shown is the response of a thermocouple attached to a 1.5mm sheet being processed with this cycle.

In order to freeze the diffusible hydrogen inside steel and to allow a precise characterization by thermal desorption spectroscopy (TDS) as developed at CRM, samples were quenched directly from different stages of the thermal cycle into liquid nitrogen within 1 minute after the removal from the MDS. The use of deuterated water (D_2O) for humidifying the annealing atmosphere allowed for defining the role of water vapor on hydrogen charging in the furnace in comparison with gaseous hydrogen. Hydrogen desorption during the cooling and the transfer to the hot dip galvanizing step was also evaluated. The TDS set-up consists of a heating chamber in which sheet samples are heated by an infrared furnace at $20^\circ C/min$ under a flow of pure N_2 up to $900^\circ C$ as shown in [Figure 3](#). The temperature is followed by a thermocouple spot welded on the sample. The released diffusible hydrogen is carried by N_2 and detected by a quadrupole mass spectrometer. The typical sheet sample dimensions are $25 * 80 mm^2$. Filters are included before analyzing in order to avoid the spectrometer contamination due to any coating release. A key parameter to realize

reliable measurements, is the calibration. In this study, calibration is performed by a certified gas mixture of 50 ppm (+/- 0.7 ppm) H_2 in N_2 . In order to avoid hydrogen desorption before the measurement, the samples are stored in liquid nitrogen until the measurement. After removal from the cryotank, samples are cleaned in acetone and dried. Desorption curves shown depict the desorption rate (mass ppm/min) as a function of the temperature ($^{\circ}C$). Diffusible hydrogen is quantified during the heating by integrating the signal from room temperature to a temperature ranging from 270 $^{\circ}C$ to 360 $^{\circ}C$ as a function of heating rate and the coating. Three TDS samples were studied for the first samples and results were found to be reliable, therefore only one TDS reading was taken on most samples.

The relationship between diffusible hydrogen content and embrittlement behavior was measured using the stressed ring test as set forth in SEP 1970 of VDEh11.

RESULTS

Effect of Steel Composition

Hydrogen desorption behavior of the three grades after using the reference cycle (5% H_2 during annealing and cooling, annealing furnace dew point of -30 $^{\circ}C$ and nominal speed line of 100 m/min) is depicted in Figure 4. Most of the hydrogen is desorbed below 280 $^{\circ}C$. The first peak (probably diffusible hydrogen or traps with low activation energy) is highest for the DP980 grade (0.16 ppm) while it is only 0.01 ppm for the IF steel. To understand if the difference of hydrogen pick-up between the DP600 and the DP980 grades is linked to the microstructure, a series of quench dilatometer studies were performed with the DP980 steel using different annealing temperatures. Higher levels of martensite were found with the quench dilatometer because of the slower cooling of samples from the annealing section of the MDS. To compare the results, thermal cycles were run at 770, 800 and 830 $^{\circ}C$ with the DP980 steel. As expected, the fraction of martensite increased with increasing annealing temperature, as a comparison the martensite volume fraction of the DP600 is estimated between 10 and 15%. Figure 5 shows that at each annealing temperature, the fraction of martensite produced with MDS was lower than that produced with the dilatometer. Desorption curves for samples processed in the MDS are shown in Figure 6; the total amount of diffusible hydrogen, related to the area under each desorption curve, and percent martensite corresponding to each annealing temperature are shown. Because they are cooled from the soaking temperature, no overageing has been performed and in this experiment a 20% H_2 - N_2 atmosphere was used, leading to higher values than those of Figure 4. It is also worth noting that the dislocation content in the ferrite and in the martensite can influence the TDA curves because dislocations can serve as reversible traps and because the dislocation distribution in the DP600's ferrite is different from that in the DP980's ferrite.

Effect of Furnace Atmosphere - Hydrogen Content

A series of experiments has been performed in which 5 or 20% H_2 containing atmospheres was present for the annealing step, followed by jet cooling and overageing steps using a 5% H_2 gas inlet for all experiments. TDS curves for steels DP600 and IF are shown in

Figures 7a and 7b. For these two grades, a slight increase of the first peak, related to the amount of diffusible hydrogen, is observed for both microstructures in case of annealing in 20% H_2 .

On the contrary a larger signal increase of the first peak is seen in the results for DP980 as shown in Figure 8. In this case, the second peak dealing with hydrogen possessing higher trapping energy is also different. However, this peak is directly influenced by the decomposition of the water adsorbed on the sample holder and only the use of deuterium charging experiments can confirm steel-related behavior.

Effect of Furnace Atmosphere - Moisture Content

During the heating cycle, two hydrogen sources are present: first, the gaseous hydrogen present in the furnace atmosphere (H_2) and second the hydrogen coming from water molecule dissociation (H_2O , humidity in the furnace atmosphere). Humidity is directly related to the dew point. It has been demonstrated for example that the dew point clearly influences the hydrogen introduction in press hardened steels12. Figure 9a and 9b show the effect of dew point (0 $^{\circ}C$ instead of -30 $^{\circ}C$) on desorption curves for the DP600 and the IF grades. Although there is a difference in higher temperature desorption behavior of DP600, no difference in the amount of diffusible hydrogen, desorbed at lower temperatures, is observed. No effect of the dew point on the desorption behavior of DP980 shown in Figure 10, indicating that the diffusible hydrogen likely comes from the H_2 - N_2 atmosphere and, at most, only a negligible amount comes from humidity in this atmosphere.

Annealing Time

The effect of the annealing holding time on the diffusible hydrogen introduced in the DP980 grade was determined by first using the reference cycle with its 1 minute holding time and then increasing the holding time in 5% H_2 to 2, 5 and 10 minutes. As shown in Figure 11, the holding time does not affect the diffusible hydrogen content. One possible explanation could be that after 1 minute at 800 $^{\circ}C$, the microstructure is already saturated in hydrogen and an equilibrium is established between the incoming hydrogen and the hydrogen that escapes from the microstructure.

A similar set of experiments were carried out with a 20% H_2 atmosphere using the DP980 grade. The corresponding TDS curves are shown in Figure 12. As with the 5% H_2 atmosphere, the first peak is not affected significantly although the desorbed quantities are higher with the higher H_2 atmosphere.

Overageing Time

In all the tests carried out up to now, an overageing time of 30 seconds has been applied. To determine the effect of overageing, a set of samples was annealed for the same times as indicated in Figure 12 and then quenched after annealing. As in Figure 12, the annealing atmosphere was 20% H_2 to enhance the effects. The amount of desorbed hydrogen for 0s and 30s of overageing is summarized in Figure 13. The results confirm the effect of annealing time, but also show that after 30s overageing, more than half of the hydrogen present in the steel after annealing is released. To learn more about

the effect of overageing, samples were then annealed in 20% H_2 at 800°C for 2 min and then overaged for 2 minutes in 20% H_2 or 2 minutes in 0% H_2 (100% N_2) or quenched without overageing. Results are shown in Figure 14. With the 0% H_2 overageing, much degassing must occur during the overageing step; less occurs with 20% H_2 overageing. With no overageing there is little chance to degas during processing and therefore high amounts of bulk diffusible hydrogen are found. The observation that about half of the diffusible hydrogen degasses during the 30s of overageing is expected to be very important for development of steel grades presenting low risk of hydrogen embrittlement.

Slow Strain Rate Tests

Defect-free galvanizing of the DP980 grade required annealing in a 5% H_2 atmosphere with a -45°C dewpoint. The TDS test result for the galvanized sample was consistent with the results of Figure 4; 0.19 ppm of desorption was measured and this also confirmed there was no effect of annealing atmosphere dewpoint. The hot dip galvanized tensile bar samples were prepared with tensile bars held in place so that complete sample coating could be achieved, as shown in Figure 15. To check the outgassing of hydrogen from galvanized samples, they were held at room temperature. TDS results after 1 week showed 0.22ppm desorbed hydrogen compared with the 0.19ppm figure above. This confirmed that the diffusion of hydrogen through solid zinc is much slower than through the steel substrate.

To evaluate the risk of hydrogen embrittlement, punched hole tests following SEP 197011 have been performed on galvanized samples of DP980. Four samples have been tested for each charging condition. The sample geometry is shown in Figure 16 and the test configuration in Figure 17. Two conditions of annealing have been tested as for the slow strain tests: 5% or 20% of H_2 in the heating, annealing and cooling sections using otherwise the reference thermal cycle. The samples are stressed at 100% of the yield strength limit during 96 hours. If no break arises after this time, the samples are safe from delayed fracture. To determine the yield strength, a tensile sample was extracted from the Multidip plate and measured. In this case, the delayed fracture test was discriminatory: all the samples annealed under 5% of H_2 did not exhibit fracture at the end of the 96 hours, while all the samples annealed under 20% H_2 fractured.

CONCLUSIONS

1. Thermal desorption tests using a reference galvanizing cycle showed that the amount of diffusible hydrogen increased from 0.01ppm in IF steel to 0.04ppm in DP600 to 0.16ppm in DP980. Differences in martensite volume fraction are postulated to be the reason for this difference, however, a chemistry effect cannot be excluded. The relationship between desorbed hydrogen and quantity of martensite in the DP980 grade was shown.
2. The effects of annealing parameters during pretreatment for galvanizing on the amount of diffusible hydrogen in DP980 have been studied. Increasing the quantity of H_2 in the annealing atmosphere increases the amount of diffusible hydrogen. Annealing time has a negligible influence on the diffusible hydrogen content after a few seconds. Most of the hydrogen is introduced during the heating and the first seconds of the

annealing. As well, negligible effect of furnace atmosphere dew point was found.

3. The overageing step has a large influence on the final diffusible hydrogen content. Without overageing and in case of annealing with 20% H_2 , all the samples of DP980 were fractured during punched hole tests, indicating the potential risk of delayed fracture in case of uncontrolled charging. This overageing step is then the crucial stage to control the final diffusible hydrogen content, the time must be around 30 seconds and the hydrogen content of the overageing atmosphere as low as possible, for the studied steel grade and conditions.

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Table 1. Composition of studied steels, wt%.

	IF	DP600	DP980
C	< 0.003	0.08	0.07
Si	< 0.010	0.26	0.27
Mn	0.12	1.83	2.54
Cr	0.02	0.19	0.30
Mo	/	/	0.11
Al	0.06	0.03	0.16
Nb	/	/	0.03
Ti	0.06	/	0.02
Thickness (mm)	1.5	1.5	1.6