RESISTANCE AGAINST HYDROGEN EMBRITTLEMENT OF ADVANCED MATERIALS FOR AUTOMOTIVE INDUSTRY

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Abstract

The paper is devoted to evaluation of resistance against hydrogen embrittlement of two advanced types of material for automotive industry. It concerns high manganese TRIPLEX alloy (Fe24Mn1.2C) hot rolled to 3 mm strip in thickness with hardness of 432HV30 and afterwards cold rolled to 2 mm strip with 461HV30 on average. Further, the attention is focused on two variants of the TRIP 800 steel with yield strength approx. 450MPa and tensile strength approx. 850 MPa (sheets of 1.5 mm in thickness). One investigated TRIP 800 steel variant had standard chemical composition (approx. 0.2C-1.5Mn-1.5Si in wt. %). In case of the second variant Si was partially substituted by Al. After hydrogen sulphide exposition the evaluation of resistance against hydrogen embrittlement was carried out using the hydrogen induced cracking (HIC) tests – in case of the TRIPLEX alloy and HIC and the sulphide stress cracking (SSC) tests – in case of the TRIP 800 steels. All investigated materials showed favourable resistance against hydrogen embrittlement. No cracks were detected by standard HIC testing in any of studied materials. The TRIPLEX microstructure showed very fine grain size, partially recrystallized, premature micro-size k-carbides precipitation during the deformation processes and fine Al oxides. All the mentioned cases represent numerous hydrogen traps. That fact can be understood as the reason of the favourable hydrogen response. In SSC tests of TRIP 800 steels (4-point bending) some defects were observed in both TRIP 800 steel variants only for stresses higher than 90% of the yield strength. The observed cracks corresponded to the HIC mechanism being formed under applied stress participation. The cracks were more frequent in steel variant with Al and they were predominantly initiated on stringers of non-metallic inclusions.

Keywords: TRIPLEX alloy, TRIP steel, hydrogen embrittlement, hydrogen induced cracking, sulphide stress cracking

1. INTRODUCTION

In the automotive industry a significant progress has been achieved concerning the safety and fuel economy. The high manganese TRIPLEX alloys and the new TRIP steels are perspective ductile high-strength materials able to comply with the goals given above [1, 2]. Beside the favourable mechanical properties and specific energy absorption the TRIPLEX alloys show a density decrease in consequence of higher manganese and aluminium contents. TRIPLEX alloys can be also used in cryogenic technique, for materials of rotating elements and/or of vessels for liquid gases transport [3], thus can be applied in sour environments. The low alloy TRIP steels show high strength values in combination with an excellent
deformability, making these steels the material of choice for impact-absorbing structural parts of car bodies. An enhanced ductility obtained thanks to the transformation induced plasticity is the result of the complex microstructure of the steel grades because low alloy TRIP steels consist of three main phases: ferrite, carbide free bainite and meta-stable retained austenite, which transforms to martensite during deformation. Here the austenite is gradually replaced by the much harder martensite phase and an increase in volume can be noticed. Both effects enhance the plastic hardening and lead to a delay in the onset of macroscopic necking [4, 5]. Chemical composition of conventional TRIP steel is usually based on C-Mn-Si, Si being in some grades partially replaced by Al. Aluminium changes transformation kinetics but it also has favourable effect on hot-dip galvanizing of TRIP steels [6]. Concerning hydrogen embrittlement, it can occur as a result of some technological operations, e.g. hot-dip galvanizing.

Extensive studies have been conducted to determine the conventional mechanical engineering characteristics [1, 2, 7], however the attention has not been paid to corrosion response in the sour environments being the aim of the presented work.

2. EXPERIMENTAL MATERIALS AND TECHNIQUES

For corrosion investigation one high manganese TRIPLEX alloy (Fe24Mn1.2C12Al) and two different variants of TRIP steels were used. As to TRIPLEX alloy, material of high purity was chosen for laboratory heat production. Vacuum melting under Ar atmosphere and casting into little ingot mould of dimensions 20x30x170 mm was realized. During casting and cooling process an intensive ultrasound was applied. Raw surfaces of the casting were milled and subsequently divided into samples of dimensions 30x50 mm with thickness of 18.6 mm. Those were finally rolled using the laboratory rolling mill Q110 at the Faculty of Metallurgy and Materials Engineering (FMME) of VŠB-TU Ostrava. Final thickness of the hot rolled TRIPLEX strip was 3 mm after 8 reductions. The material was afterwards cold rolled to the thickness of 2 mm using the laboratory rolling mill K350 of the four-high type situated at the VŠB-TU Ostrava. More details are given in [8]. After both rolling processes the hardness (HV30) and grain size (using conventional linear method) were determined. Volume fraction of ferrite was determined using the OLYMPUS X70 microscope equipped with the IMAGE-program and microanalysis of inclusions was carried out by use of the SEM JEOL JSM-6490 LV equipped with energy dispersion analyser (EDA) OXFORD INCA Energy 350. The observed carbide particles were evaluated as well. For the hydrogen induced cracking (HIC) dimensions of strips corresponded to 33x20x3 and/or 2 mm. The HIC exposition was realized in test solution of 5 % NaCl, 0.5 % CH₃COOH in distilled water. After purging of air from the testing vessel the test solution was bubbled by hydrogen sulphide. Duration of exposition was 96 hours. The procedure of the experiments was in agreement with the NACE Standard TM0284-2003, Item No. 21215 for the HIC resistance [9]. After exposition all the strips were transversely cut into four equal samples and in agreement with the concept of the work [9] the HIC susceptibility was metallographically probed. Samples were etched in glycerine, hydrofluoric-, nitric- and hydrochloric acid.

Concerning the TRIP steels, two variants were prepared in laboratory conditions. The first of them represented the “classical” C-Mn-Si steel with 0.2% of C, and approx. 1.5% of Mn and Si. In the second variant of the TRIP steel Si was partially replaced by Al, which is beneficial from the point of view of hot-dip galvanizing. This variant of the TRIP steel contained 1% of Si and 0.5% of Al. Both TRIP steels were hot and cold rolled to the sheets with the thickness of 1.5 mm using the laboratory rolling mill at FMME VŠB – TUO. After rolling both TRIP steels were submitted to the two step annealing including intercritical annealing at 810°C followed by rapid cooling (cooling rate was faster than 10°C·s⁻¹). The second step represented
annealing at the temperature of the bainite formation. More details concerning the chemical composition and the heat treatment of the TRIP steels can be found in [10]. Firstly, mechanical properties of the TRIP steels were determined. After that, two kinds of tests were used to evaluate the resistance of the TRIP steels to the hydrogen embrittlement. The first of them represented HIC test performed in the same manner as for the TRIPLEX alloy. Not only 96 hour tests were performed but also prolonged tests, duration of which was 720 hours (one month). After the testing exposure, metallographic analysis was carried out in order to reveal eventual cracking. The second kind of test was sulphide stress cracking (SSC) test, which was conducted in accordance with the NACE TM 0177-2005 Standard [11]. The testing solution was the same as in the case of the HIC testing and the test duration was 720 hours. Testing specimens with dimensions 120 x 30 x 1.5 mm were loaded at four-point bending using special holders. The procedure was carried out in accordance with the ASTM G39 Standard. The applied stresses corresponded approximately to the 80%, 90% and 100% of the TRIP steel yield strength. After 720 hours of exposure in the testing solution, exactly the same as in the case of the HIC testing, the testing specimens were submitted to the visual observation and detailed metallographic analysis.

3. RESULTS AND ANALYSIS

Before the hydrogen sulphide exposition some chosen metallographic and mechanical properties of the TRIPLEX material were determined. Figure 1a shows micrograph of the cast TRIPLEX alloy. Track of dendrites can be observed with slight primary structure-boundary contrast. The columnar structure and the presence of micro-porosity require suitable rolling parameters to break the primary structure and revealed the tiny pits. Thanks to the used rolling parameters the microstructure did not show inhomogeneities and any characteristic central segregation unlike the matrix without used ultrasound and leading to crack propagation during deformation process. After hot and cold rolling the microstructures are demonstrated in Fig. 1b and 1c.

![Fig. 1. Micrographs of the investigated microstructure a) in as-cast state, b) after hot rolling, c) after cold rolling](image)

After hot rolling, the basis FCC microstructure is partially recrystallized with the grain size within the extent of 1-13 μm. This one corresponds to 5 μm on average. After the following cold rolling the medium grain size was 2.9 μm. Extent of the observed grain sizes was 0.5-7 μm. Further, 7.5 % of δ-ferrite was detected after hot deformation, while the cold deformation process was associated with 4.5 % of the δ-ferrite being in
agreement with the desired level [1, 3]. At higher magnification globular particles were sporadically observed at the austenite-austenite interface. Their maximal size corresponded to 1 μm in diameter representing boundary of detectability. Using the SEM equipped with EDAX the carbides of the (FeMn)₃Al type were revealed. Similar globular particles or pits of the same diameter were already found at the austenite-δ-ferrite interface after hot rolling. It can be assumed that detected pits represent former carbide positions. The carbides probably fell out during metallographic sample preparation. The finishing rolling temperature was approximately 950°C which is the ideal temperature for carbide precipitation [12]. In the investigated material fine oxygen-aluminium inclusions were also detected not forming any strings thanks to the used ultrasound during the casting and cooling of the TRIPLEX alloy. Due to the shortage of experimental material the hardness HV30 was only found. After hot rolling the HV30 was within the extent of 425-441, the average level showed 432 HV30. In case of the cold-rolled alloy the results corresponded to 457-465 HV30 and to 461 HV30 on the average. Differences between the sub-surface and central areas were not higher than 8 HV30. The maximal width of the rolled strip was 40 mm.

The hydrogen susceptibility evaluation was without crack detection. It is true that the samples for the HIC exposition should be more bulky (100x20xthickness mm), according to [9], however hereby the corrosion conditions were much stricter. In smaller material volume more hydrogen atoms could be caught in traps during the exposition. Thanks to the deformation the rolling process can be also associated with higher dislocation density, especially after cold rolling, representing one type of hydrogen traps [13]. The higher dislocation density can be also taken as a compensatory factor of higher matrix strengthening after the cold rolling being rather dangerous for the hydrogen susceptibility. Moreover, the rolled alloy showed fine grain size. The numerous grain boundary surfaces also act as potential positions for hydrogen trapping [13]. The hydrogen resistance is strongly dependent on equally distributed potential hydrogen traps above all.

The TRIP steel mechanical properties corresponded to the requirements of the TRIP 800 steel grade. Both studied TRIP steels showed yield strength higher than 400 MPa and tensile strength higher than 800 MPa. Elongation at fracture reached 29.5% for both studied TRIP steels. More details can be found in [10]. The microstructure of the TRIP steels consisted of ferrite, free carbide bainite, some portion of martensite and retained austenite (RA). The amount of the RA was determined by means of X-ray analysis. The C-Mn-Si TRIP steel contained 11% of the RA whereas in the C-Mn-Si-Al TRIP steel 13% of the RA was found. An example of the C-Mn-Si TRIP steel microstructure is given in Fig. 2.

Metallographic analysis performed on the samples after HIC testing did not reveal any cracks in the studied TRIP steels even for the prolonged testing conditions (720 hours). In this way, the presumed high resistance of the TRIP steels to the hydrogen embrittlement was confirmed in the absence of mechanical loading [14]. This high resistance can be attributed mainly to the high amount of the retained austenite the regions of which act as very deep beneficial hydrogen traps [13]. It is supposed that the decisive parameters of the RA are the size of the RA regions and the ratio between their length and diameter [2].
The results of SSC testing of the TRIP steels were not so unambiguous. Fig. 3a represents an example of the specimen fixed in the holder after the performed SSC testing. In Fig. 3b a general appearance of the tensile specimen side is shown for the stress corresponding to the 90 % of the yield strength (C-Mn-Si steel). Some blister like regions can be observed there. Nevertheless, metallographic analysis revealed no blisters for any of the applied stresses in the studied TRIP steels. In addition, no cracks were detected for the specimens loaded to the 80 % of the yield strength.

Fig. 3a. Specimen in the holder after SSC testing

Fig. 3b. Tensile side of the C-Mn-Si TRIP steel after SSC testing

On the contrary, cracking was observed in the specimens loaded to 90 and 100% of the yield strength. However, the detected cracks did not correspond to the typical SSC cracks, which are predominantly parallel to the specimen surface. In the studied case, the cracks corresponded rather to the hydrogen induced cracking. Figures 4a, b show some typical examples of the observed cracks. In some cases, stepwise cracks were found (Fig. 4b).

Fig. 4a. Cracks after SSC testing (C-Mn-Si TRIP steel)

Fig. 4b. Stepwise cracks after SSC testing (C-Mn-Si-Al TRIP steel)

The cracks were always closer to the tensile side of the specimens but sometimes they progressed even to the centre of the thickness. The cracks were more numerous in the C-Mn-Si-Al TRIP steel very probably due to the higher non-metallic inclusion content and the presence of stringers of non-metallic inclusions in this steel. Taking into account the presented results it can be supposed that resistance to hydrogen embrittlement of the TRIP steels is rather worse in the presence of applied stress. The beneficial role of the residual austenite is probably exceeded by the negative influence of non-metallic inclusions (and segregations) in the presence of higher applied stresses. Despite of this, the resistance to hydrogen embrittlement of the studied TRIP steels can be considered as quite satisfactory as the testing conditions of SSC tests are extremely severe.
4. CONCLUSIONS

The following results were obtained from evaluating the hydrogen response of TRIPLEX alloy and C-Mn-Si and C-Mn-Si-Al TRIP steels using HIC and SSC testing:

- All studied materials show a favourable resistance to hydrogen embrittlement;
- No cracking was observed in the studied materials after 96 hour HIC tests, or prolonged 720 hour HIC tests;
- No cracking was detected in TRIP steels after SSC testing for applied stresses of 80 % of the yield strength. Some cracks were only observed for applied stresses corresponding to 90 - 100 % of the yield strength. The observed cracks were typical for the HIC. They were more numerous in C-Mn-Si-Al TRIP steel probably due to the higher local content of non-metallic inclusions, presented even in the form of stringers.

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REFERENCES


