Feasibility study of nano plating for the visualisation of hydrogen in steels

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ABSTRACT

Visualisation of hydrogen in metals is a very challenging topic as microscopic techniques are not yet able to visualise hydrogen atoms accurately. Several micrometre sized techniques were already developed to visualise hydrogen in a qualitative way and link it to the metal's microstructure. However, many disadvantages still limit these techniques. Two innovative approaches have been evaluated in the present work. Both are based on the nano plating principle where a redox reaction occurs between metal ions in an electrolyte and hydrogen atoms in the metal. Adapted silver nano plating appears to be a very promising technique while gold nano plating suffers from kinetic issues which remain to be dealt with.

Keywords

Hydrogen embrittlement, steel, visualisation, nano plating

INTRODUCTION

As society evolves and technology improves, new problems arise. A well discussed matter these days is the global warming and the need to lower CO_2 emissions. The transportation sector is one of the key players in this matter. Automotive industry has been an important driving force for the development of new high strength steels (HSS) motivated by the need to obtain lighter structures in vehicles. Along with the rise of these new alloys, the problem of hydrogen embrittlement (HE) became more important as an increased strength level increases the metal's susceptibility to HE.

Another important currently discussed issue is energy. Hydrogen (H) could fulfil the role of an energy carrier and likewise compete with fossil fuels. However, transportation and storage of hydrogen causes serious limitations to the potential of using hydrogen as renewable energy source as the containers are in direct contact with hydrogen gas. Structural components as well as current pipelines will not perform appropriately because they are prone to hydrogen embrittlement.

The phenomenon of hydrogen embrittlement is a problem encountered in many metallic materials and is characterised by a degradation of the mechanical properties caused solely by the presence of hydrogen inside the metal. The metal's ductility, i.e. its ability to accommodate plastic deformation, typically shows a significant drop. This can result in unexpected and therefore catastrophic failures.

When a metal comes into contact with a hydrogen rich environment, H adsorbs onto the metal surface followed by absorption into the metal. Subsequently, H diffuses via interstitial lattice sites through the metal. In order to diffuse from one site to another, hydrogen should possess a sufficient amount of energy to overcome the energy barrier for interstitial diffusion. Moreover, a metal lattice is far from perfect as it contains many defects e.g. dislocations, grain boundaries, second phase particles … These features in the microstructure typically provide a lower energy state for hydrogen which make them favourable to diffuse to. This interaction results in a temporary or more permanent stay of H at these positions. When two hydrogen atoms recombine at these locations, they will form hydrogen gas (H_2) with a significant pressure increase associated with this recombination. When this happens close to the metal's surface, hydrogen blisters are formed which are local elevations of the surface. Blisters are a clear visible proof of the presence of hydrogen inside a metal, but it would be useful to visualise hydrogen before permanent damage has occurred in order to predict accurately its presence and intervene preventively. Since hydrogen atoms are too small to be visualised by any currently developed microscopic technique, other, more qualitative micrometre sized methods need to be invented or optimised. In this way, the presence of hydrogen can be linked to certain features of metal microstructure. This paper aims to experimentally check the feasibility of two new methods to visualise hydrogen, i.e. gold nano plating and an adapted silver nano plating technique.

CURRENT HYDROGEN VISUALISATION TECHNIQUES

At the moment, several methods already exist to visualise hydrogen inside a metal. However, each of them has some disadvantages. In the following paragraphs, the most important methods and their disadvantages will be discussed.

A first technique is the Hydrogen Microprint Technique (HMT). Hydrogen diffuses from the sample interior to the surface where it reduces an applied silver bromide coating to metallic silver. Subsequent reaction with a fixing solution results in the localised presence of metallic silver on the metal surface, i.e. at locations where hydrogen has diffused out of the metal. The presence of silver can be visualised by microscopic techniques. Unfortunately, the amount of deposited silver atoms highly depends on the microstructure of the sample, despite an equal amount of hydrogen present in the material [1].

A second technique is Scanning Kelvin Probe Force Microscopy (SKPFM). In this technique, hydrogen diffuses through the metal into a palladium coating. The presence of hydrogen in the palladium layer lowers the Volta potential. Measurements of this potential at the surface reveal where hydrogen has accumulated. The limitations of this technique are its calibration issues and its very local character. Moreover, SKPFM is not suitable as a high throughput screening since it takes around an hour before the results are visualised [2, 3].

Another hydrogen visualisation method is silver nano plating. The technique is based on a redox reaction. A

$KAg(CN)_2$ solution containing silver ions (Ag^+) is reduced by hydrogen atoms that diffuse out of the metal. The precipitated silver particles can be visualised by microscopy. The technique is very fast and enables global qualitative imaging of the hydrogen distribution in a material. A negative aspect is the use of toxic cyanides in the silver solution which implies that special care should be taken when the technique is applied [4].

GOLD NANO PLATING

In this section, a gold nano plating technique as alternative possibility to visualise hydrogen is discussed. The idea for this technique arose from the currently used silver nano plating technique [5, 6].

Principle

Hydrogen visualisation via gold nano plating is based on an electrochemical redox reaction. Gold ions in solution are reduced and hydrogen at the metal surface is oxidised [7]. The reactions are given in (1) and (2).

$$Au^{3+} + 3e^- \rightarrow Au \quad (1)$$

$$H \rightarrow H^+ + e^- \quad (2)$$

The hydrogen oxidation reaction is not the only possible oxidation reaction. Metal atoms from the used material can oxidise and participate as well. This reaction is given in (3).

$$M \rightarrow M^{n+} + ne^- \quad (3)$$

The biggest advantage of this technique is its driving force, namely the potential difference between reaction (1) and (2): +1.42 V [8] which makes it thermodynamically more favourable than the existing silver cyanide technique. The kinetics of this gold technique, on the other hand, are less beneficial since three hydrogen atoms are needed for the reduction reaction to occur (versus one for silver nano plating as will be discussed later).

Materials and methods

The material used in this paper has been dual phase (DP) steel consisting of a two phase microstructure of ductile ferrite and high strength martensite as indicated in Fig. 1. The production process firstly cools the austenitic steel sample to a temperature between its A_1 and A_3 temperature to introduce ferrite grains. Thereafter, the steel is quenched to transform the remaining austenite to martensite. Industrially, this DP HSS is extensively used in automotive body frames.

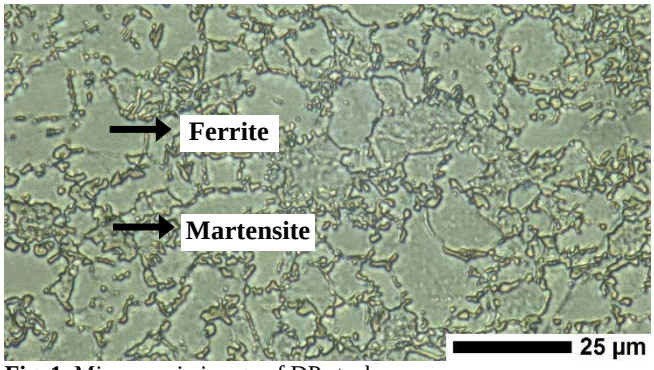

Fig. 1. Microscopic image of DP steel

Hydrogen charging was performed electrochemically in a 0.5 M H_2SO_4 electrolyte solution containing 1 g/l of thiourea (CSN_2H_4) at a current density of 0.8 mA/cm² during 30 minutes [9]. These conditions were chosen after a characterisation by optical microscopy to exclude the presence of damage by hydrogen. As stated in the introduction, this would be beyond the stage at which hydrogen visualisation is desired.

The gold ions have been obtained by dissolving solid $HAuCl_4$ in demineralised water until a solution with a certain concentration was reached. This solution has been placed in a temperature controlled water bath and the either uncharged or hydrogen charged metal was placed in the solution for a certain time. The gold atoms precipitated at the metal surface as a result of reaction (2), reaction (3) or a combination of both reactions. This metal surface was then characterised using scanning electron microscopy (SEM).

Results and discussion

In order to find the required conditions that provide a well performing hydrogen visualisation technique, several parameters were varied. The uncharged DP steel should contain no gold deposition or the precipitated gold should be scattered uniformly. The hydrogen charged DP steel on the other hand should show gold deposition at places where hydrogen will favourably diffuse to [10]. In the following paragraph, the influence of various parameters on the gold reduction are discussed. Subsequently, the optimal conditions are evaluated with respect to the hydrogen visualisation capability.

Increasing the concentration of the gold solution causes a higher and faster gold deposition. One should keep in mind that when the concentration gets too high, the accuracy will decrease since variations were found to appear in the order of seconds. A concentration of 10 mM has eventually been used. Increasing the time in the gold solution evidently results in more gold deposition on the sample. However, if the sample stays too long in the solution, its acidic nature damages the sample surface by introducing pitting corrosion. The metal surface layer also starts peeling off. A time of 60 seconds was chosen. A higher temperature of the water bath leads to the same result as a longer plating time. Room temperature (25°C) was adequate.

A hydrogen charged and uncharged DP steel have then been compared to evaluate the feasibility of gold nano plating as a hydrogen visualisation technique. The difference between uncharged and charged sampled steel was not clearly noticeable, as can be seen in Fig. 2 and Fig. 3. The amount of gold atoms deposited on the metal surface was slightly smaller for the hydrogen charged steel when compared to the uncharged steel.

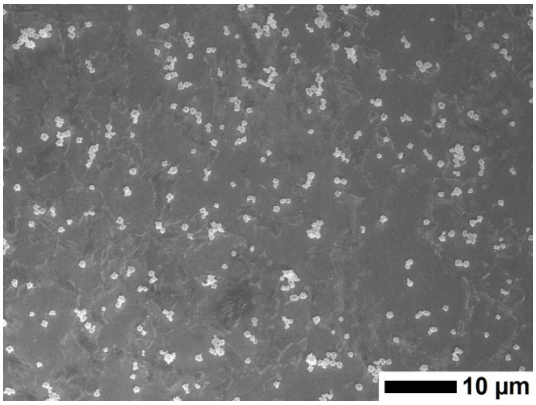

Fig. 2. SEM image of gold deposition after 60s 10mM $HAuCl_4$

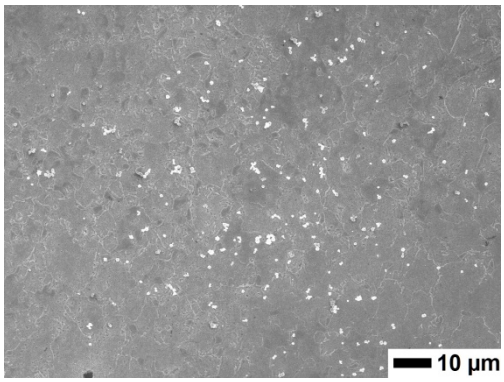

Fig. 3. SEM image of gold deposition after 30 min electrochemical H charging and 60s in 10mM $HAuCl_4$

This reduced deposition can be explained by the kinetics. As mentioned before, three hydrogen atoms are necessary for the reduction of gold ions (Au^{3+}) to metallic gold (Au). Hydrogen atoms at the surface will however rather combine to hydrogen gas (H_2) instead of reducing the gold ions. The gold on the surface mainly originates from the reaction of gold ions with iron atoms. This underlying mechanism is summarized in Fig. 4. The presence of hydrogen atoms does not lead to a higher or more specific precipitation of gold as most hydrogen atoms will recombine to H_2. Consequently, gold nano plating is not suitable as a technique to visualise hydrogen, although this technique could work if there is a possibility to avoid the hydrogen recombination reaction.

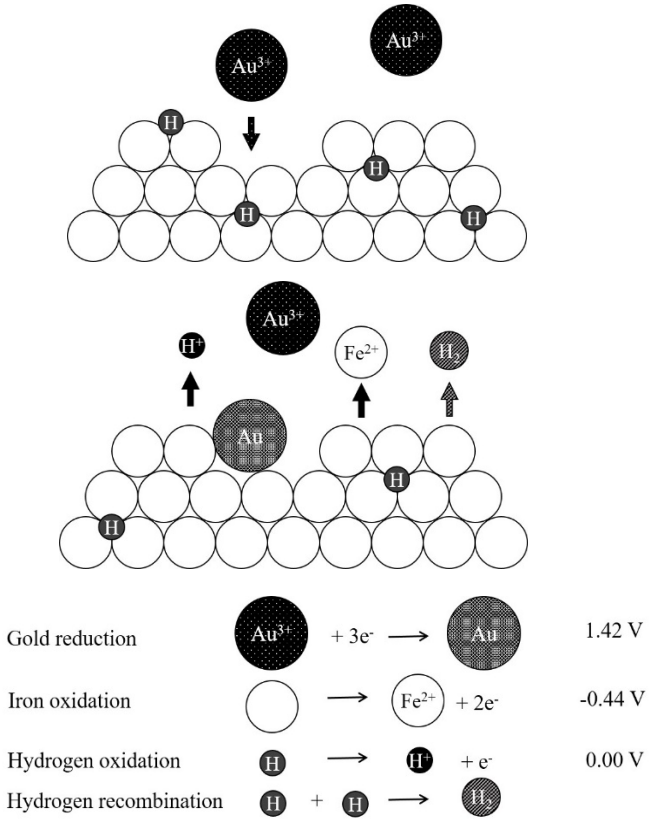

Fig. 4. Reaction mechanism of gold nano plating

(ADAPTED) SILVER NANO PLATING

As the gold nano plating technique was not capable of visualising hydrogen due to kinetic considerations, the silver nano plating technique has been adapted in order to avoid toxic cyanides. In this section, this technique is further discussed.

Principle

The principle of hydrogen visualisation via silver nano plating is very similar to gold nano plating. The reduction reaction is given by silver ions in solution, as shown in (4).

$$Ag^+ + e^- \rightarrow Ag \qquad (4)$$

The potential difference for the redox reaction with hydrogen ((2) and (4)) is 0.80 V [8]. Thermodynamically, this reaction is favourable, but to a lesser extent than the gold nano plating redox reaction. Kinetically, the reaction with silver is more favourable than the reaction with gold as only one hydrogen atom is needed for the redox reaction.

Materials and methods

The material, DP steel, as well as the hydrogen charging method remained the same for the adapted silver nano technique compared to gold nano plating. Only the nano plating solution was altered. The silver ions have been obtained in this case by dissolving silver nitrate ($AgNO_3$) in demineralized water. In contrast, the traditional silver method firstly converts silver nitrate to more reactive, but toxic, silver cyanide [3]. However, $AgNO_3$ provides sufficient silver ions for the reaction without being nocuous.

Results and discussion

As only one hydrogen atom is needed for the redox reaction, hydrogen recombination becomes less likely than in the case of gold plating. The mechanism is indicated in Fig. 5.

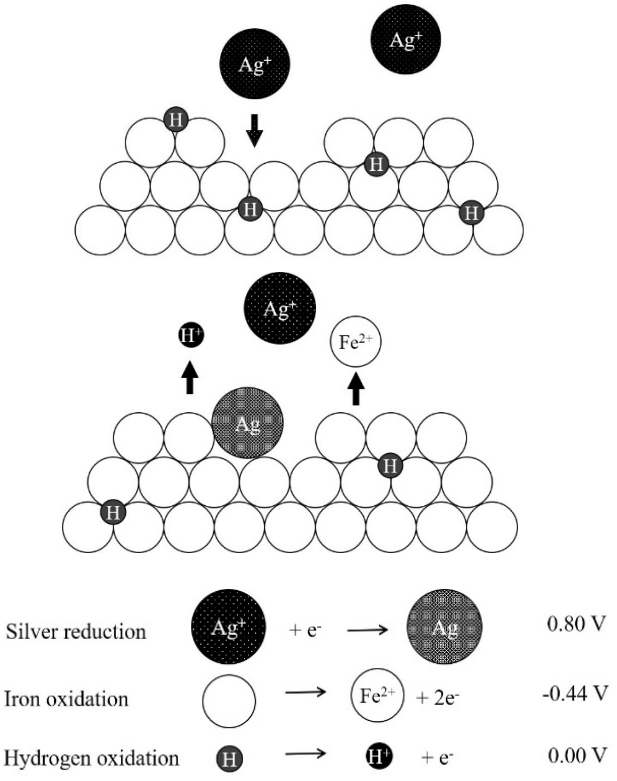

Fig. 5. Reaction mechanism of adapted silver nano plating

The difference between an uncharged and charged sample is evident in Fig. 6 and Fig. 7, respectively. As expected, silver deposits more easily in the presence of hydrogen because the latter provides the electron necessary for reduction, which makes initiation more favourable. Subsequently, more silver attaches on top of the deposited silver forming a network.

This is a promising method for hydrogen visualisation. The parameter screening has the same principles as gold nano plating. Optimised conditions are necessary as e.g. an overlong stay in the solution results in desquamation of the clustered deposited atoms that erases original preferential locations.

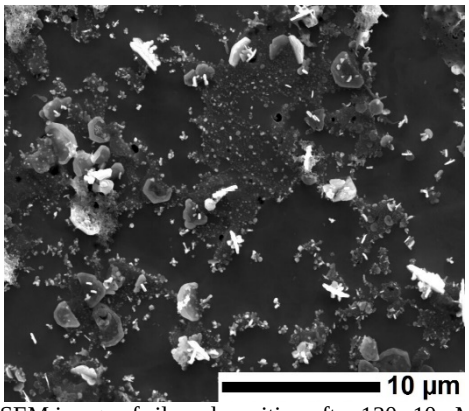

Fig. 6. SEM image of silver deposition after 120s 10mM $AgNO_3$

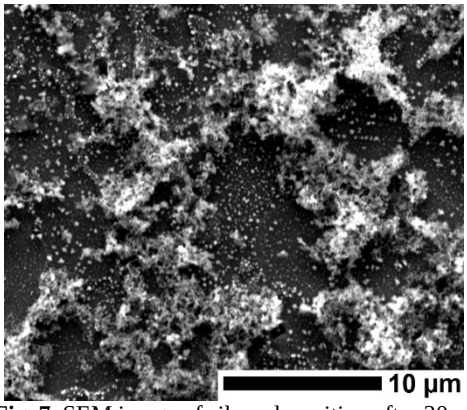

Fig. 7. SEM image of silver deposition after 30 min electrochemical H charging and 120s 10mM $AgNO_3$

At first sight, the adapted silver method has a more randomly deposition compared to the traditional silver nano plating, where silver lies more obviously on preferential hydrogen locations, although the type of steel used there was different [4].

Future work should prove why silver ions land on these specific spots and improve the parameters for an optimal contrast in samples with and without hydrogen. Possibly, the nitrate reduction (0.80 V) competes with the silver reduction reaction (0.80 V) because of their similar potentials [8].

CONCLUSION

Two possible new hydrogen visualisation techniques have been evaluated, i.e. gold nano plating using a chloroauric acid solution and adapted silver nano plating using a silver nitrate solution instead of the currently used toxic silver cyanide solution. Thermodynamically, gold nano plating was very promising. However, due to kinetic reasons involving the hydrogen recombination reaction, gold nano plating is not very suitable for hydrogen visualisation. A possible solution would be to limit the appearing hydrogen recombination reaction. Silver nano plating is promising both in terms of thermodynamics and kinetics. Further optimization of the experimental conditions to obtain a clear hydrogen visualisation is still needed. This would allow to use the adapted silver nano plating technique in various applications to visualise hydrogen in a metal in a non-destructive way.

ROLE OF THE STUDENTS

The three authors were bachelor students at Ghent University working as a group under the supervision of promotor prof. dr. ir. Kim Verbeken and daily supervisors ir. Lisa Claeys and ir. Tim De Seranno. The original idea about the topic of this bachelor thesis was proposed by the promotor. The design of new set-ups, the execution of the experiments, the interpretation of the results, the development of the alternative silver-based technique and the writing of the paper have all been done by the students.

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