PCN2 – CYCLIC LOADING PULSATOR, FOR RESEARCH ON HYDROGEN EMBRITTLEMENT IN SURFACE TREATMENT TECHNOLOGY

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Abstract. The article deals with the process of hydrogenation and evaluation using an experimental measuring device – Cyclic Loading Pulsator, for destructive testing and identifying the dependencies involved in the effect the hydrogen generated in the processes of surface treatment has on machinery parts.

Introduction

Research on the influence of hydrogen on the properties of steel and subsequent applications of surface treatment is an issue which is currently the subject of much attention. When using contaminated input raw materials there is a risk of hydrogen embrittlement, or it begins to occur in materials that were long considered resistant to this type of degradation.

Higher hydrogen content in steels affects their mechanical properties, almost always negatively. It is known that hydrogen reduces ductility, breaking strength and yield strength. Atomic hydrogen dissolved in the steel easily diffuses in the iron grid α even at normal temperatures, and therefore it is easy to saturate the steel by hydrogen and to release it from the steel depending on the external conditions. When exceeding the critical concentration, hydrogen can cause cracking or escape from the material during heat treatment of the material and thus exert a negative effect on the finishes applied to such damaged materials.

Formation of hydrogen

Hydrogen is most frequently formed during pickling in mineral acids, during cathodic electrolytic degreasing, electroplating processes (e.g. zinc plating), also during oxidation (corrosion) of the material, welding and phosphating.

In most cases it involves cathodic reduction. For example, during pickling in mineral acids (NHO_3, H_2SO_4, HCl) the relevant anodic step – here the dissolution of metal – takes place at the same place as the formation of hydrogen, [1].

In contrast, during electrolytic degreasing and galvanizing the formation of hydrogen – and dissolution of metal, if any – takes place separately at the anode (1) and (2):

in acidic medium: $$2\ H_3O^+ + 2\ e^- \rightarrow H_2\uparrow + 2\ H_2O, \quad (1)$$

in alkaline medium: $$2\ H_2O + 2\ e^- \rightarrow H_2\uparrow + 2\ OH^-. \quad (2)$$

Subsequent reactions take place step by step. Hydroxyl ions decharge separately one by one, water molecules are broken down one after the other. In any case, atomic hydrogen is formed first (3).

$$H_3O^+ + e^- \rightarrow H + H_2O. \quad (3)$$

Atomic hydrogen necessarily needs to form a bond and is therefore reactive. When it meets another hydrogen atom, they form a bond. In this case we speak about adsorbed (atomic) hydrogen H_{ad}. Adsorbed atomic hydrogen can bind with another of its kind to form a molecule of H_2, which is eventually released in the form of gas bubbles and no longer poses any threat to the base material. However, adsorbed atomic hydrogen can also diffuse into the material and damage its structure (4).

Formation of gaseous H_2: $$2\ H_{ad} \rightarrow H_2\uparrow \text{ or } H_{ad} + H_3O^+ + e^- \rightarrow H_2\uparrow + H_2O, \quad (4)$$

diffusion into the material: $H_{ad} \rightarrow H_{mat}$.

There is no way to remove hydrogen recombined in hydrogen traps.

Experimental device

The experimental device PCN2 (see Fig. 1) is used for cyclic loading of components that have been exposed to the processes causing hydrogenation. PCN2 consists of three-phase asynchronous electric motor, frequency converter, which allows us to set the acceleration and braking times, to set the engine speed and to program frequency changes in relation to time. Compared to the first version, the new device has been fitted with an electronic circuit and sensors that allow us to stop the device if the tested component gets damaged and to record the time. It also employs an eccentric crank mechanism with a balancing feature, where one rod is placed in the slide housing and a second rod for pre-stressing is mechanically clamped in a clamping cage, [3].

The tested sample, in this case a retaining ring, is placed between the rods and the load is set according to the measuring parameters. The device alternately develops tension and compression at the end of the retaining ring which causes it to open and close. This movement is generated in the mechanical pulsator simulated by the testing device. Intensive simulation of the cyclic stress accelerates the spread of the crack caused by hydrogen present in the material, [2].

Thanks to this device we will be able to get an approximate idea of the number of cycles or the service life of a component that was exposed to the processes involving hydrogenation.

Fig. 1. Experimentaldevice – PCN2

Experimental part:

The measurement was carried out using the **DIN 471-AS 35 x 2.5** retaining rings.

Table 1.The chemical composition of the material of the rings in [%]

C	Mn	Si	P	S	Al	Cr	Ni	Mo
0.72	0.64	0.25	0.01	0.001	0.032	0.17	0.042	0.002

The retaining rings were supplied in the raw state without any surface treatment or heat treatment. All samples were degreased ultrasonically using 6 % sodium Pragold 68S, t_o = 2 min, T = 45 °C and then dried with hot air. In total, 8 sets of measurements were carried out for different types of pre-treatment, 5 pieces for each set. The result of the measurement is the number of cycles calculated based on the time needed to destruct individual rings.

Measurement parameters:

The amplitude of opening the retaining ring is 4 mm. The preload of the ring l_p=5 mm, n_s=2800 rev/min^{-1}. The rings were exposed to the pickling solution of **$HCl + FeCl_2 + H_2O$** (HCl content: 96.0 g/l $FeCl_2$ content: 119.0 g/l), then they were rinsed in demineralised water T_o = 23 °C and dried with hot air T_s = 20 s. Then, according to various parameters for individual sets, the rings were exposed to cyclic loading using the experimental device PCN2.

Parameters of individual sets:

Set 1: Retaining rings in the raw state exposed to variable loads.

Set 2: Retaining rings exposed to a temperature of 250 °C for 4 hours, let to cool to room temperature on a metal plate and exposed to variable loads.

Set 3: Retaining rings exposed to pickling solution for 2 hours, rinsed in water, dried and with the maximum delay of 10 minutes after pickling exposed to variable loads.

Set 4: Retaining rings exposed to pickling solution for 2 hours, rinsed in water, dried, exposed to a temperature of 200 °C for 1 hour and then exposed to variable loads.

Set 5: Retaining rings exposed to pickling solution for 2 hours, rinsed in water, dried, exposed to a temperature of 250 °C for 4 hour and then exposed to variable loads.

Set 6: Retaining rings exposed to pickling solution for 16 hours, rinsed in water, dried and with the maximum delay of 10 minutes after pickling exposed to variable loads.

Set 7: Retaining rings exposed to pickling solution for 16 hours, rinsed in water, dried, exposed to a temperature of 200 °C for 1 hour and then exposed to variable loads.

Set 8: Retaining rings exposed to pickling solution for 16 hours, rinsed in water, dried, exposed to a temperature of 250 °C for 4 hour and then exposed to variable loads.

Results

Table 2. Values measured by the experimental device of PCN2

	Set 1		**Set 2**		**Set 3**		**Set 4**	
Sample No.	Time **t [min.]**	No. of cycles **N [-]**	Time **t [min.]**	No. of cycles **N [-]**	Time **t [min.]**	No. of cycles **N [-]**	Time **t [min.]**	No. of cycles **N [-]**
1	57	79800	45	63000	32	44800	45	63000
2	72	100800	44	61600	38	53200	33	46200
3	66	92400	45	63000	30	42000	23	32200
4	56	78400	47	65800	29	40600	39	54600
5	66	92400	42	58800	33	46200	35	49000
Average value	**63.4**	**88760**	**44.6**	**62440**	**32.4**	**45360**	**35**	**49000**

	Set 5		**Set 6**		**Set 7**		**Set 8**	
Sample No.	Time **t [min.]**	No. of cycles **N [-]**	Time **t [min.]**	No. of cycles **N [-]**	Time **t [min.]**	No. of cycles **N [-]**	Time **t [min.]**	No. of cycles **N [-]**
1	31	43400	29	40600	37	51800	30	42000
2	36	50400	30	42000	34	47600	31	43400
3	37	51800	32	44800	27	37800	27	37800
4	35	49000	31	43400	32	44800	38	53200
5	30	42000	24	33600	36	50400	36	50400
Average value	**33.8**	**47320**	**29.2**	**40880**	**33.2**	**46480**	**32.4**	**45360**

Samples after destruction in each set:

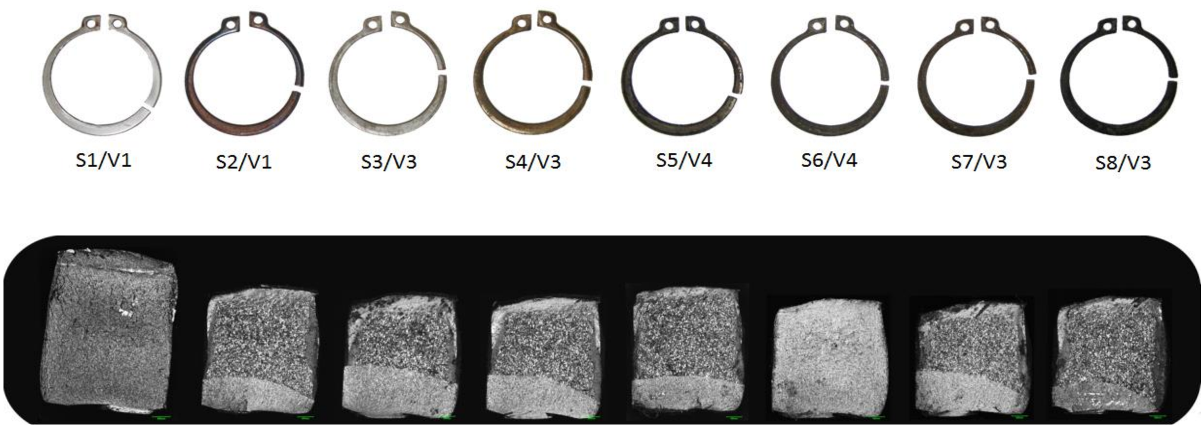

Fig. 2 Detailsoftheretainingrings and fracturesrecorded by a laser confocalmicroscope
Olympus LEXT OSL 3000 – magnification 120x

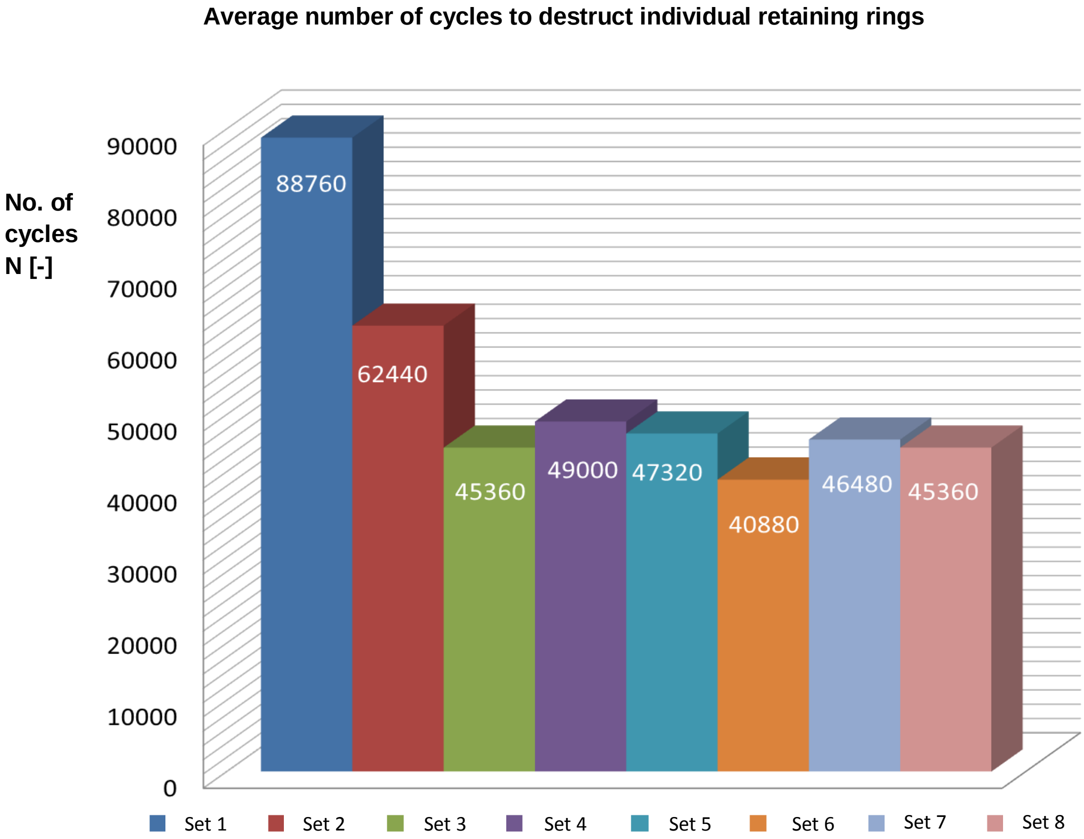

Fig. 2 Chart showing the average number of cycles to destruct individual retaining rings

Conclusion

The results of the measurements (Fig. 2) carried out using the experimental device PCN2 confirm the hypothesis saying which initial conditions of exposure of the material to pre-treatment processes susceptible to hydrogen embrittlement lead to its destruction. When comparing Set 1 and Set 3, we can see that the pickling time of 2 hours shortened the service life of the component by 43.400 cycles compared to Set 1 without pickling. The difference between Set 3 and Set 6 shows the reduction in the number of cycles by 4.480 caused a longer duration of pickling. Set 2, which was exposed to the temperature of 250 °C for 4 hours, shows 26.320 fewer cycles compared to Set 1. Efficient dehydrogenation can be seen in Set 4, where the number of cycles increased by 3,640 compared to Set 3. Longer dehydrogenation of 4 hours at 250 °C in Set 5 and Set 8 shows no difference in the degree of dehydrogenation in comparison with Set 4 and 7, and thus is economically wasteful. The device is currently being used for further detailed experimental tests. The evaluation of fractures in the samples exposed to surface treatments that involve intensive formation of hydrogen and its diffusion into the base metal has also been conducted.

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