RESEARCH ARTICLE

Post-testing measurement of freely movable and diffusible hydrogen in context of WEC formation at cylindrical roller thrust bearings from 100Cr6

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Abstract: Sub-surface crack networks in areas of altered microstructure are a common cause for bearing failures. Due to its appearance under light microscopy, the damage pattern is referred to as White Etching Cracks (WEC). The root causes leading to the formation of WEC are still under debate. Nevertheless, it has already been shown that atomic hydrogen can have an accelerating effect on the formation and propagation of WEC. In addition to hydrogen pre-charging, hydrogen can be released and absorbed during rolling/sliding due to the decomposing of the lubricant and water. The current work focuses on the analysis of the hydrogen content of cylindrical roller thrust bearings after testing in a FE8 type test rig using two different lubricants. Within the framework of this work, two different hydrogen analysis methods were used and assessed regarding their applicability. The results show that the so-called Hydrogen Collecting Analysis (HCA) is more suitable to investigate the correlation between lubricant chemistry and hydrogen content in the test bearings than the Local Hydrogen Analysis (LHA). The measurements with the HCA show a continuously increasing freely movable and diffusible hydrogen content under tribological conditions, which leads to the formation of WEC. Comparative tests with an oil without hydrogen showed that the tendency of the system to fail as a result of WEC can be reduced by using a lubricant without hydride compounds.

1 Introduction

The estimation of the service life of rolling bearings is usually carried out following DIN ISO 281 [1] and assumes a failure caused by subsurface initiated rolling contact fatigue (RCF). However, early failures due to cracks in regions of altered microstructures below the surface have occurred over the years in various applications, including wind turbines [2–4], motor vehicles [2, 4–6], washing machines [2, 7], paper machines [2, 5, 6], and cement mills [2, 5, 7]. The sub-surface damage pattern is characterized by regions of altered microstructure areas that appear white under the light microscope due to their etching resistance, hence the name White Etching Areas (WEA). In combination with cracks, the damage pattern is known as White Etching Cracks (WEC). The

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mechanisms that lead to WEC have been controversially described by various hypotheses. It is still unclear whether crack formation occurs first [6, 8] or the white etching areas precede the crack formation [9, 10]. However, there is a consensus that an increased hydrogen content in the bearing steel, e.g., by artificial pre-charging the test sample, promotes the formation of WEC [2, 4, 11, 12]. Furthermore, it has been previously discussed that hydrogen released from the lubricant can promote the formation of WEC [13–15]. Regarding the source of hydrogen, two main theories are described in the literature. According to Refs. [13, 14, 16–18], the main source of hydrogen is water in the lubricant. Iso et al. [18] propose that the source of hydrogen lies in the tribochemical reaction of water with the metal fresh surface. In contrast, the source of hydrogen is according to Refs. [13, 16, 19] the lubricant itself. Kohara et al. [19] report that certain basic components and additives in oil are responsible for the diffusion of hydrogen into steel. It should, however, be noted that the formation of WEC can also occur using hydrogen-free lubricants [20]. The driving effect of hydrogen on the formation and promotion of WEC is thus still unclear.

Nevertheless, the role of hydrogen on rolling contact fatigue has already been previously intensively investigated and described by two main hypotheses [21–25]: Hydrogen Enhanced Localized Plasticity (HELP) [21–23] and Hydrogen Enhanced Decohesion Embrittlement (HEDE) [21, 24, 25], which can be respectively assigned to the aforementioned possible formation mechanisms of WEC. The HELP theory describes the embrittlement of the material by local plastic failure. This is attributed to increased dislocation mobility due to hydrogen deposition [21–23]. The HELP theory would thus support the hypothesis that the microstructure alteration precedes the crack formation. In contrast to this, the HEDE theory describes a crack formation due to hydrogen accumulation and the resulting reduction of cohesion forces within the metal matrix and interfaces [21, 24, 25], which would

suggest that crack formation precedes structural alteration.

The correlation between the amount of diffusible hydrogen as a result of lubricant decomposition and the formation of WEC has so far only been studied in a few studies. Noteworthy is the work from Richardson et al. [13] and Kürten and Kailer [26] who measured an increase of hydrogen content in the rolling elements from cylindrical roller thrust bearings depending on the lubricant composition. Furthermore, Franke et al. [27] correlate through simulations the location of WEC with the location of the maximum hydrogen concentration below the surface due to friction loading. For this reason, further insights into the relationship between the amount of freely movable and diffusible hydrogen content that can be produced during operation and the formation of WEC are advantageous to better understand the influence of hydrogen on WEC formation. A further point is an in-situ measurement of hydrogen in the test rig is currently not possible and the hydrogen effuses immediately after the test again from the specimen; therefore a new analysis method the Local Hydrogen Analysis (LHA) is also the subject of this investigation.

There are two main objectives of this paper. The first objective is the assessment of the applicability of two different hydrogen analysis methods for measuring the freely movable hydrogen content in cylindrical roller thrust bearings after testing under operating conditions which leads to bearing failure due to WEC. The second objective is to examine whether a continuous increase in hydrogen content occurs during the formation and propagation of WEC and to correlate hydrogen content with the lubricant composition. In order to achieve this, tests will be conducted under operating conditions favouring the formation of WEC in alignment with previously conducted investigations [28, 29] and manually stopped after pre-defined test durations. Two lubricants are used, a fully formulated mineral oil and a perfluoralkylether (PFAE) which contains neither additives nor any hydrogen.

2 Materials and methods

2.1 Lubricants

Two lubricants are used in the tests on the roller bearing test rig. The first lubricant is a fully-formulated mineral oil from a group I base oil with a viscosity class ISO VG 100 and referred to as "mineral oil" in the following, which has already been used in previously published work [28–32]. Analysis results of the elemental analysis are shown in Table 1. The kinematic viscosity at 40 ℃ was measured to be 103.78 mm²/s. Noteworthy is the presence of the additive Ca alkylsulfonates, which is considered to increase the risk of WEC [14].

The second lubricant is a perfluoroalkylether with a viscosity class ISO VG 100 referred to as "PFAE" in the following and the sample was provided by the company Fuchs Lubritech. This PFAE contains neither additives nor any hydrogen in its molecular structure. Therefore, it is considered to significantly reduce the risk of WEC.

2.2 Test bearings

For the investigations, cylindrical roller thrust bearings of type 81212 according to Fig. 1(a) are used. Both the bearing washers and the rollers are made of martensitic through-hardened 100Cr6 steel (AISI 52100). In alignment with previously conducted investigations, a polyamide cage (PA66) with fifteen rollers was used [28–32]. Figure 1(b) shows exemplarily the FE8 test rig for cylindrical roller thrust bearings of the type 81212, comprehensive details of which can be seen in Refs. [31, 32].

2.3 Test conditions

The tests in this work were stopped manually after a pre-defined test duration under the operating conditions listed in Table 2 [28]. The contact

Table 1 Concentration of different elements in the mineral oil (%).

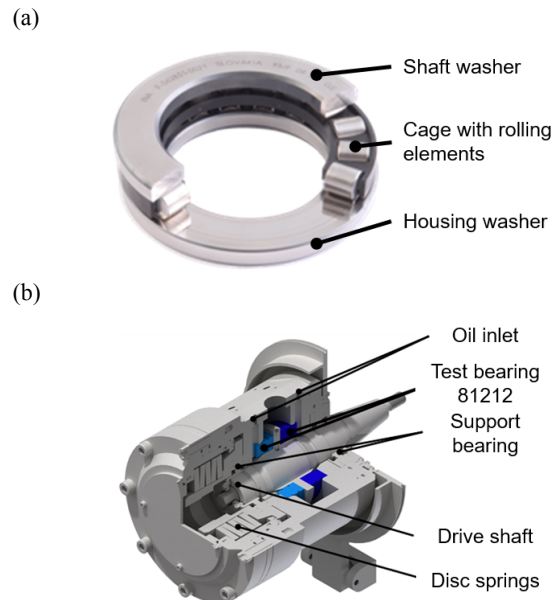| $w_{sulphur}$	$w_{phosphor}$	w_{zinc}	$w_{calcium}$	$w_{magnesium}$
0.8343	0.0512	0.0616	0.0039	0.1950

(a)

(b)

Fig. 1 (a) Sectional view of the used cylindrical thrust roller bearing and (b) FE8 test rig according to DIN 51819-3 [33].

Table 2 Operating conditions on the roller bearing test rig.

Test parameter	Value
Axial load	80 kN
Shaft speed	300 min^{-1}
Bearing mass temperature	100 °C
Oil volume flow	0.25 L·min^{-1}

pressure was calculated to be 1,888 N/mm² and the specific film thickness λ to be ~0.5. In this work, λ was calculated using the measured surface roughness $Ra_{1,2}$ and the lubrication film thickness h_{min} according to the Dowson and Higginson [34] equation.

Findings from previously conducted works have shown that under these conditions a failure due to WEC can be expected in a time frame of 80–120 h [30, 31]. Therefore, the hydrogen content was measured in this work after a test duration of 30 h (1×), 50 h (4×), and 70 h (2×) with the mineral oil. An unused bearing (0 h) was also examined and used as a material reference. It is also assumed that the measured content of the reference is representative of the material batch and represents the hydrogen content absorbed during manufacturing. Subsequently, two tests were carried out with PFAE and stopped after 70 h to confirm a hydrogen release from the mineral oil.

After manually switching off the test rig, the test bearings were dismounted from the test rig. Subsequently, all bearing parts were cooled with liquid nitrogen and then stored in a cryo container at −196 ℃. Dismounting and cooling will take place within 20 min. The cooling and storage of the bearing parts are designed to prevent the mobility of the hydrogen in the steel so that neither a significant diffusion nor a significant effusion takes place after the rolling test. Thus, the hydrogen content of the bearing component remains nearly unchanged until the measurement so that the measured value corresponds approximately to the hydrogen content during the operation.

2.4 Hydrogen solubility in steel

Hydrogen is the lightest and smallest element in the periodic table and can easily diffuse into the lattice structure of steel due to its small atomic size of approx. 25×10^{-12} m (0.25 Å) [35]. The diffusion process can occur due to the interaction of the steel surface with the surrounding medium as well as during the steel manufacturing process and the rolling bearing manufacturing [36, 37].

The solubility of hydrogen in a metallic material is largely determined by its lattice structure. In an ideal pure iron crystal lattice, the hydrogen would be homogeneously distributed over the lattice. In reality, however, there are defects or lattice disturbances due to atomic and microstructural imperfections. These include, for example, grain boundary defects as well as inclusions or cracks. These lattice irregularities or disturbances are also known as hydrogen traps because they can capture and bind significant amounts of hydrogen [35, 38–40].

The hydrogen is thus not only interstitially dissolved in the lattice but also accumulates to a large extent locally in the traps. To classify the solubility of hydrogen in metallic materials, Hitzigrath [35] defines four categories (Table 3): freely movable hydrogen (I), hydrogen in reversible flat traps (II), hydrogen in irreversible deep traps (III), and hydrogen contained in

Table 3 Classification of the four categories of hydrogen solubility regarding its binding energy and mobility [35].

Category	Hydrogen type	Binding energy	Mobility
(I)	Freely movable	8 kJ/mol	Via interstitial spaces possible
(II)	In reversible flat traps	< 30 kJ/mol	Through lattice still possible, hydrogen bound to dislocations or widened interstitial spaces
(III)	In irreversible deep traps	> 50 kJ/mol	Through lattice not possible, hydrogen bound to precipitates or inclusions
(IV)	In hydride compounds	> 100 kJ/mol	Through lattice not possible, hydrogen bond in the chemical compound

metallic hydride (a compound containing hydrogen-bonded to metals or metalloid) (IV). Characteristics of these four categories are different binding energies and the consequences resulting in degrees of the mobility of the hydrogen atoms in the material.

The freely movable hydrogen (I) in the lattice has the lowest binding energy and is dissolved interstitially in the lattice. The hydrogen in reversible flat traps (II) is weakly bound with a binding energy < 30 kJ/mol and is located in dislocations or widened interstitial spaces. Due to the relatively low binding energy, hydrogen atoms in flat traps are reversible and can, therefore, diffuse and effuse from the material as a result of low energy input. The hydrogen atoms in the irreversible deep traps (III) are strongly bound with binding energy > 50 kJ/mol and need, therefore, a higher energy input, than the hydrogen in reversible traps, to diffuse or effuse. These hydrogen atoms are located on precipitates or inclusions. The hydrogen in hydride compounds (IV), on the other hand, is present as a chemical compound with another element and has the highest binding energy of > 100 kJ/mol.

Based on this definition, the total hydrogen content of a material sample consists of hydrogen from all four categories (freely movable, reversible flat, irreversible deep traps, and hydride compounds). In this work, it is assumed that the

usually called diffusible hydrogen represents the summation of the freely movable hydrogen (I) and the hydrogen in reversible flat traps (II) (Fig. 2) according to Hitzigrath [35].

If the binding energy is exceeded through activation energy, e.g., thermal energy, all hydrogen atoms can move in the interstitial lattice. The activation energy forces the hydrogen atoms to leave its stable equilibrium and diffuse through the lattice. The amount of activation energy required depends on the amount of binding energy according to the aforementioned categories. Therefore, the activation energy can be classified depending on the depth of the traps. For instance, lower energy is necessary for releasing hydrogen atoms from flat traps than from deep traps [36, 39]. This activation energy which is necessary to overcome the binding energy is usually provided in the form of thermal energy. In the case of the freely moving hydrogen (I) a temperature above 0 K suffices. This means, in other words, that the movement of the freely moving hydrogen can only be repressed at absolute zero. Furthermore, the effusion rate can be increased by increasing the temperature up to 210 ℃. On the other hand, the necessary activation energy to overcome the binding energy of the hydrogen at reversible flat traps (II) is provided at a temperature between 210 and 400 ℃, depending on the type of the flat trap [41]. The necessary activation energy to overcome the binding energy of the hydrogen at the irreversible deep traps (III) is provided in the temperature range between 400 and 900 ℃. Subsequently, the hydrogen in the irreversible deep traps (III) effuses at temperatures above 900 ℃. In order to release the hydrogen of the hydride compounds (IV), it is necessary to increase the temperature above the steel melting point.
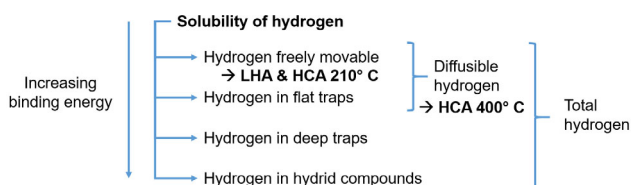

Fig. 2 Hydrogen bonding types in steel.

This work focuses on the detection of diffusible hydrogen. Therefore, measurements are carried out at room temperature and both 210 and 400 ℃. These temperatures are chosen to decrease the measuring time and for comparison with measurements carried out in Ref. [26].

2.5 Hydrogen analysis methods

As mentioned before, two different hydrogen analysis methods are used in this work. The electrochemical measuring method Local Hydrogen Analysis (LHA) makes it possible to determine the freely movable hydrogen content (I) locally concerning the surface of the sample (surface area ~1 mm²) [42] and is carried out at room temperature. The Hydrogen Collecting Analysis (HCA) makes it possible to determine the hydrogen content globally concerning the entire volume of the sample (volume ~750 mm³) [43] and is conducted at 210 ℃ as well as at 400 ℃. Like the LHA, the HCA at 210 ℃ detects the freely movable hydrogen (I). The HCA at 400 ℃ detects the diffusible hydrogen (I and II), which is composed of the freely movable hydrogen (I) and the hydrogen in the flat traps (II); this connection can be seen in Fig. 2. The amount of hydrogen in the reversible flat traps (II) is determined indirectly by considering the difference between the HCA at 400 and 210 ℃. According to Takai and Watanuki [44] and Hitzigrath [35], hydrogen in irreversible deep traps (III) should not have a negative influence on the material properties of high-strength steels and is believed to not accumulate in defects such as crack tips. For this reason, a measurement of the hydrogen in the irreversible deep traps (III) will not be performed in this work. The functional principles of the LHA and the HCA are described in more detail below.

2.5.1 Local Hydrogen Analysis (LHA)

The LHA takes place at room temperature since the necessary activation energy for the effusion of hydrogen is already provided at this temperature. The determination of the local freely movable hydrogen content (I) is carried out by applying an

electrochemical potential between the sample (segment from a test specimen) and a reference electrode [42]. This leads to oxidation of the hydrogen escaping from the surface. The hereby released electrons lead to a current flow which increases the oxidation current as a result of the anodic polarization of the sample surface. The higher the hydrogen content in the sample, the higher the measured oxidation current. The hydrogen concentration c_0 in the sample is then calculated from the diffusion coefficient D (depending on the material state), the oxidation current density J at the time t, and the Faraday constant F.

For comparison purposes, it is necessary to determine the oxidation current of an unused sample as a reference. Only in this way can the result of the measurement of a used sample be evaluated. The difference between the two currents corresponds to the free hydrogen content in the material, which in this case is additionally available due to the rolling/sliding [42].

The measuring system corresponds to a three-electrode design with the material surface as a working electrode, an Ag/AgCl reference electrode, and a platinum wire as a counter electrode (Fig. 3). A 0.2 molar NaOH solution is used as the electrolyte.

2.5.2 *Hydrogen Collecting Analysis (HCA)*

In contrast to the LHA, measurement methods such as carrier gas melt extraction can only determine the global total hydrogen content ((I), (II), (III), and (IV)) of a sample. The reason for this is that the temperature in the sample chamber is increased up to the melting point and thus so much activation energy is introduced that all hydrogen bonding energies are exceeded. HCA and Thermal Desorption Analysis (TDA), on the other hand, make it possible to distinguish indirectly between freely movable hydrogen (I) and hydrogen in reversible and irreversible traps. The differentiation between the different hydrogen types is possible because the HCA and TDA can be carried out at any temperature and thus a defined amount of activation energy can be brought in the sample [43]. To carry out the HCA measurements, washer segments are firstly confined within a glass tube. After a 24 h effusion heat treatment, the effused hydrogen of the entire sample is present in the free volume of the glass tube in a concentrated form. The concentrated hydrogen is then released in an external sample chamber which is connected to a conventional hydrogen analysis system through a thermal conductivity measuring cell (ONH 2000 of the company Eltra). Therefore, the HCA measures the effused hydrogen quantity in a short period (~1 min) while the TDA measures it directly and continuously over a longer period (> 20 min). This results in a lower measuring error of the HCA compared to the TDA.

2.6 Test procedure
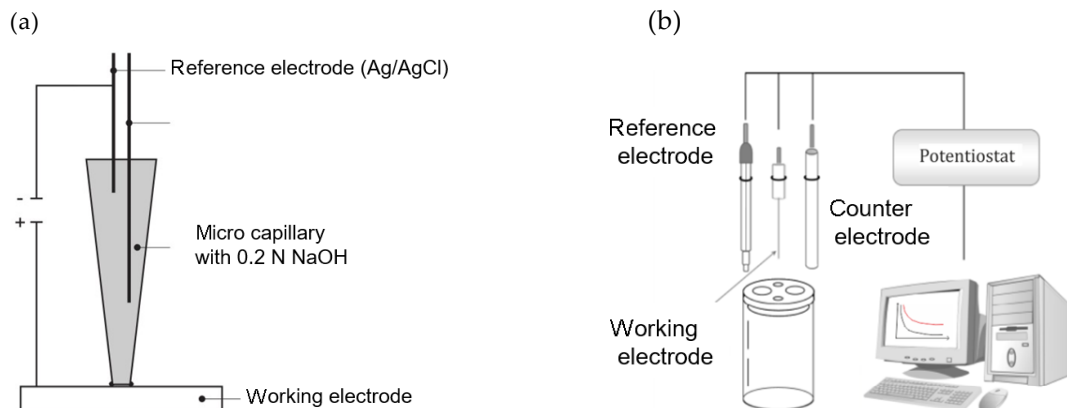
The results of the hydrogen measurements from

Fig. 3 Schematic structure of (a) LHA measuring method and (b) measuring cell.

the test using the mineral oil are presented in Section 3. The hydrogen content of each shaft washer of each test on the roller bearing test rig (1 × 30 h, 4 × 50 h, 2 × 70 h) was measured by LHA. For HCA measurements at 210 and 400 ℃, the test number at 50 h was reduced to three. The LHA results are shown in Section 3.1, the HCA results at 210 ℃ are shown in Section 3.2, and the HCA results at 400 ℃ are shown in Section 3.3. In all figures, the hydrogen content is given as parts per million (ppm) for the different test durations (0, 30, 50, and 70 h). The measured values of each washer represent the arithmetic mean value from three to six measurements on each washer for LHA and a minimum of two measurements for HCA on each washer. The mean value and the empirical variance were calculated for each test series (all tests of the respective measuring time with the same oil). The showed empirical variance of the test series considers the variance of a single washer and the variance between the washers of the test series themselves.

The results of the hydrogen measurements on the samples of the bearing washers after a rolling test using the PFAE oil are shown in Section 3.4.

For each test condition, one washer was examined by ultrasound analysis and by metallographic sectioning. As already shown in Ref. [32] ultrasonic analysis allows detecting cracks and defects in the materials. Under the selected conditions with the mineral oil, it has been previously shown by metallographic sectioning that bearing failure is caused by WEC [28, 30]. A further discussion of the ultrasound analyses and metallographic examinations is not within the scope of this work. The ultrasonic analyses were carried out by Schaeffler Technologies AG & Co. KG and the metallographic investigations were carried out by the Institute for Material Applications in Mechanical Engineering, RWTH Aachen University (IWM).

3   Results

Regarding the macroscopic and microscopic appearance of the conducted tests, it should be noted that tests with a duration of 30 h showed no abnormalities in the ultrasonic analyses nor could WEA or WEC be detected in the examination of the metallographic sections. At the tests with a duration of 50 h showed several abnormalities in the ultrasonic analyses, which could also be identified as sub-surface WEC by metallographic investigations. Flaking on the raceway was only identified after a test duration of 70 h. Metallographic investigations of these areas confirmed the expected damage due to WEC.

3.1   Hydrogen measurement with LHA from the tests with mineral oil

The results of the hydrogen measurement with LHA from the experiments with mineral oil are shown in Fig. 4.

The freely movable hydrogen content of the material reference is 0.01±0.04 ppm. Due to the conversion of a quantity of charge into hydrogen content, minimal negative values can occur due to the measurement deviations but these negative values should be neglected. After a test duration of 30 h, the freely movable hydrogen content has increased to 0.03±0.12 ppm, which is 300% of the hydrogen content of the material reference. By increasing the test duration to 50 h the freely movable hydrogen content increases to 0.11± 0.16 ppm, which is 1,100% of the hydrogen content of the material reference. Finally, at 70 h the hydrogen content is 0.22±0.17 ppm and, therefore, 2,200% the material reference.
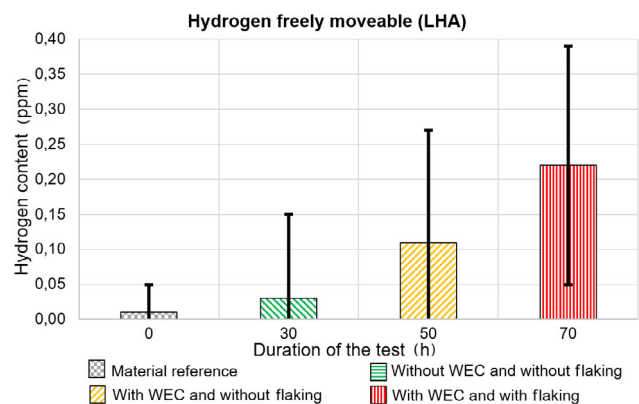

Fig. 4 Hydrogen measurements with LHA from tested roller bearings at roller bearing test rig with mineral oil.

3.2 Hydrogen measurement with HCA at 210 ℃ from the tests with mineral oil

As aforementioned, the HCA at 210 ℃ determines the freely movable hydrogen content (I) in a washer segment. Like the LHA, the HCA at 210 ℃ measures the freely moving hydrogen content; however, the measured values cannot be compared with one another. The reason for this is that the LHA refers to the measurement signal to the surface and the HCA refers to the measurement signal to the volume. The results for the analysed axial bearing washers are shown in Fig. 5. It can be seen that the material reference has a freely movable hydrogen content of 0.055±0.003 ppm. The content of the freely movable hydrogen has increased to a value of 0.159±0.028 ppm after a test duration of 30 h, which corresponds to a value of 289% of the material reference. By extending the test duration to 50 h, the content of the freely movable hydrogen increased to a value of 0.212±0.054 ppm and thus by 385% compared to the material reference. At a test duration of 70 h, the freely movable hydrogen content reduces to a value of 0.146±0.042 ppm, which corresponds to a value of 265% of the material reference.

3.3 Hydrogen measurement with HCA at 400 ℃ from the tests with mineral oil

As mentioned in Section 2.5.2, the HCA at 400 ℃ determines the diffusible hydrogen content according to Fig. 2. The results for the analysed

axial bearing washers after an effusion heat treatment at 400 ℃ are shown in Fig. 6. The material reference has a diffusible hydrogen content of 0.873±0.006 ppm. The content of diffusible hydrogen has increased to a value of 1.032±0.008 ppm which is 118% the content in the material reference after a test duration of 30 h. In the case of a test duration of 50 h, the amount of diffusible hydrogen content increases to 1.047±0.078 ppm, which corresponds to a value of 119% of the material reference. The further extension of the test duration to 70 h results in a diffusible hydrogen content of 1.060±0.051 ppm and thus an increase of 121% compared to the reference.

3.4 Hydrogen measurement from experiments with PFAE

Additional tests with the hydrogen-free PFAE lubricant were carried out. This should serve as a validation that the measured hydrogen content did indeed has its origin in the mineral oil. The results of the hydrogen measurements from the test using the PFAE are shown in this section. The hydrogen content of each shaft washer of each test with PFAE on the roller bearing test rig (2×70 h) was measured by LHA and by HCA at 210 and 400 ℃. For each test condition, one washer was examined by ultrasound analysis and by metallographic sectioning. Regarding the macroscopic and microscopic appearance of the conducted tests, it should be noted that these tests
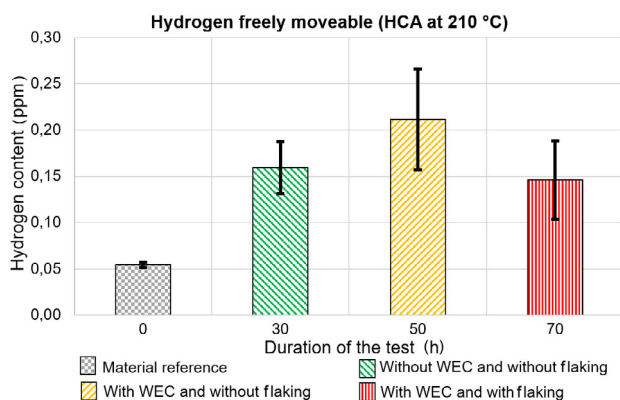

Fig. 5 Hydrogen measurements with HCA at 210 ℃ from tested roller bearings at roller bearing test rig with mineral oil.
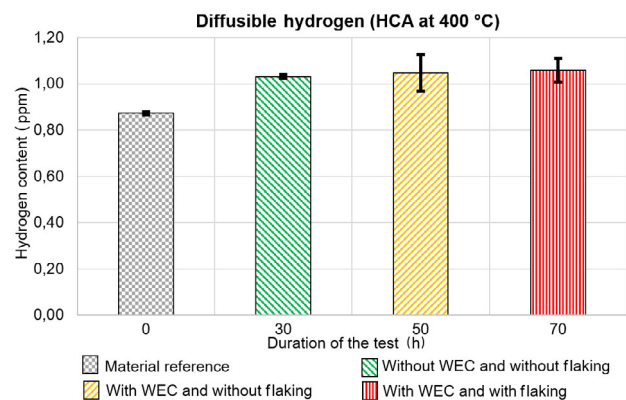

Fig. 6 Hydrogen measurements with HCA at 400 ℃ from tested roller bearings at roller bearing test rig with mineral oil.

showed no abnormalities in the ultrasonic analysis nor could WEA or WEC be detected in the examination of the metallographic sections.

The results of these hydrogen measurements are shown in comparison to the material reference in Fig. 7. Using the LHA, a value of 0.014±0.042 ppm is measured for the material reference (0 h) and a value of 0.108±0.174 ppm is measured after 70 h test duration.

Using HCA at 210 ℃, a value of 0.055±0.003 ppm is measured for the material reference and a value of 0.039±0.008 ppm is measured after 70 h test duration. This unexpected reduction of the hydrogen content was also observed at 400 ℃. In this case, the material reference had a hydrogen content of 0.873±0.006 ppm and the sample after 70 h of 0.811±0.060 ppm.

The analysis of the hydrogen content from the specimens of tests with PFAE shows that the hydrogen content remains almost constant compared to the content from the material reference and confirms the expectation.

4 Discussion

In this work, the applicability of the two hydrogen analysis methods is investigated by comparing the measured values of the specimen with the material reference. The LHA measurement shows an increase in the freely movable hydrogen content over the test duration in the specimens tested with the mineral oil. Thus the LHA does show an

Fig. 7 Hydrogen content from the tests with PFAE using three measurement methods: LHA, HCA at 210 ℃, and HCA at 400 ℃.

increase of the freely movable hydrogen content during the formation or propagation of WEC in direct comparison to the material reference. However, the measured increase using the LHA is under consideration of the empirical variance of the measured values not significant. It is to be mentioned that the correct function of the measuring method was proven by artificially loading test specimens with a defined hydrogen content and subsequent measurements with LHA. These measurements were then validated by measurement with HCA.

A possible explanation for the strong empirical variance of the individual measured values may be a locally varying hydrogen concentration. This could be an indication that the freely movable hydrogen accumulates locally in the material/defects and promotes the local formation of WEC. However, this hypothesis cannot be further investigated in the context of this study and thus cannot be clarified.

Therefore, it can be concluded that the LHA is not applicable for the measurement of the freely movable hydrogen content of cylindrical roller thrust bearings under operating conditions which leads to bearing failure due to WEC.

The HCA at 210 ℃ shows that the freely movable hydrogen content increases over the test duration from 0 to 30 to 50 h, and thus during the formation of WEC. This result indicates that the HCA at 210 ℃ is applicable for the analysis of the freely movable hydrogen content of cylindrical roller thrust bearings under operating conditions which leads to bearing failure due to WEC. However, an unexpected reduction of the hydrogen content from 50 to 70 h is measured. Nevertheless, the freely movable hydrogen content after 70 h is higher than the material reference by 265%. Within the framework of this investigation, the analysis of the freely movable hydrogen content by the HCA at 210 ℃ proves the expected increase in the freely movable hydrogen content during the WEC damage process in the tests with mineral oil. The measured increase with HCA 210 ℃ is under consideration of the empirical variance of the measured values significant.
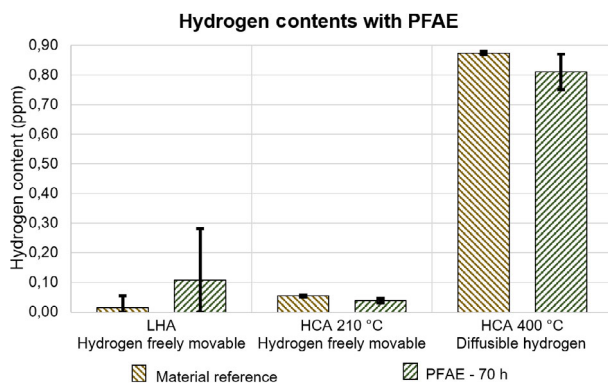
A possible explanation for the reduction of the hydrogen content during the 70 h measurement compared to the 50 h measurements could be the material spalling from the damage on the raceway as a result of WEC at 70 h. The segments measured at 70 h had material spalling from the raceway and the segments at 30 and 50 h showed no material spalling from the raceway not even macroscopic material damage. Under the requirement that the freely movable hydrogen is contained to a large extent in the near-surface area, the spalled material of the raceway contains a large amount of the freely movable hydrogen. Therefore, a large part of the freely movable hydrogen is no longer available for HCA measurement, resulting in a lower measured value at 70 h compared to 50 h. Another possible explanation for the reduction of the measured hydrogen content from 70 to 50 h, is that the surface area is increased due to the crack formation at the surface and the spalling of the material from the raceway increased during the test and thus an increased effusion of the freely movable hydrogen can take place in the breakout during the test and the disassembly time.

From the investigation of the HCA at 210 ℃, it is concluded that the HCA at 210 ℃ is suitable to investigate the freely movable hydrogen content of cylindrical roller thrust bearings under operating conditions leading to bearing damage due to WEC, as long as no material spalling from the raceway has occurred.

The investigations of the HCA at 400 ℃ show an increase of the diffusible hydrogen content at 30, 50, and 70 h compared to the hydrogen content of the material reference. Within the scope of the empirical variance of the measured values, no statistically relevant difference between the tests at 30, 50, and 70 h can be identified. The diffusible hydrogen content remains at a constant value over a period of 30 to 70 h and neither increases nor decreases.

It could be possible that the occurrence of macroscopic material damage or material spalling from the raceway also leads to a decrease in the diffusible hydrogen content between 50 and 70 h, analogous to the freely movable hydrogen.

However, this assumption cannot be supported within the limited number of experiments.

The conclusion of the investigation of the HCA at 400 ℃ is their suitability to investigate the diffusible hydrogen content of cylindrical roller thrust bearings under operating conditions leading to bearing damage due to WEC, as long as no material spalling from the raceway has occurred. Another conclusion is that the diffusible hydrogen content is higher than the material reference over the whole test because the diffusible hydrogen content shows an increase from 0 to 30 h at the beginning, but a further increase over the remaining test duration (from 30 to 70 h) cannot be detected.

A comparison between the analytical methods LHA and HCA is only possible to a limited extent, since the LHA, resolved locally, measures the hydrogen escaping from a relatively small surface area and the HCA, resolved globally, determines the hydrogen content of an entire volume. However, only with the HCA, taking into account the empirical variance, a statement can be made about the freely moving hydrogen content and not with the LHA.

It is therefore concluded from the measurements that the HCA analysis method is suitable for making statistically relevant statements about the change in hydrogen content after the test under operating conditions that lead to WEC-related bearing damage, whereas the LHA analysis method is not suitable.

In direct comparison with similar investigations in Ref. [26], it can be concluded that the increase in hydrogen content measured in the context of this investigation is only one-twelfth of the increase in hydrogen content shown in Ref. [26]. A possible explanation is based on the size of the test bearings. The type 81212 test bearings used for this investigation have 16 times the volume of bearing steel in comparison to the type 81104 test bearings used in Ref. [26]. Also, a segment of the bearing washer was used for this investigation and a cylindrical roller in Ref. [26]. The comparison between this investigation and Kürten and Kailer [26], due to the different measured bearing

elements, and different bearing sizes, can be made through the surface-to-volume ratio. The surface-to-volume ratio in this investigation is considerably lower than in Kürten and Kailer [26], it is approximately one-tenth according to Table 4.

In the carrier gas hot extraction method, which Kürten and Kailer [26] used and to which the HCA belongs, the measured hydrogen is related to the total sample weight and thus a hydrogen content for the entire sample is determined. If the hydrogen is homogeneously distributed in the volume, the hydrogen content should be the same despite the different sizes. The hydrogen content in Ref. [26] is, however, higher in comparison to the presented results. Furthermore, the tested test specimens in Ref. [26] also show a higher surface-to-volume ratio. Thus it can be concluded that the hydrogen is not homogeneously distributed in the specimen volume, but diffuses only in the areas close to the surface due to the rolling stress. Thus, in the case of smaller bearings, the volume proportion in which hydrogen diffuses in relative to the total volume is larger, which would explain the higher sensitivity in Ref. [26].

The investigations with the mineral oil showed an increase in the freely movable hydrogen (I) in the course of the WEC damage process. Considering this knowledge, it was examined whether the tendency of the system to fail due to WEC under the operating conditions can be reduced by using a lubricant without hydride compounds. By using the PFAE under otherwise identical conditions, no bearing damage occurred even after 500 h. Two further tests with the PFAE, which were stopped after 70 h, also showed no surface damage.

Table 4 Surface-to-volume ratio comparison between 81104 rolling elements and 81212 shaft washer segment from axial thrust roller bearings.

Parameter	81104 bearing	81212 bearing
Volume of the bearing steel	4,819 mm³	78,155 mm³

Parameter	81104 rolling element	81212 shaft washer segment
Surface of the test specimen under rolling stress	84.82 mm²	~66 mm²
Volume of the test specimen	95.43 mm³	~758 mm³
Surface-to-volume ratio	0.889 mm⁻¹	0.087 mm⁻¹

Furthermore, these showed neither abnormalities in ultrasonic analysis nor could WEA or WEC be identified by metallographic investigations.

The interpretation of the LHA results is not meaningful because it has been shown that the LHA measurement is not suitable for determining the freely movable hydrogen content of cylindrical roller thrust bearings under the selected operating conditions.

The investigations with PFAE showed that no WEA or WEC occurred after 70 h and that there was also no increase in the diffusible hydrogen content ((I) and (II)) occurred. This observation also correlates with the results of Kürten [45] on axial cylindrical roller bearings of type 81212-TV using a PFPE lubricant.

The investigations from the tests with PFAE analysed with HCA show a minimum decrease of the freely movable hydrogen content (I) at 70 h measured with HCA at 210 ℃ compared to the material reference and, considering the empirical variance, no reduction of the diffusible hydrogen content ((I) + (II)) measured with HCA at 400 ℃ compared to the material reference.

The empirical variance at 70 h much higher than the empirical variance at 0 h (factor 10). This could be because four different bearing washers were measured at 70 h and only one bearing washer at 0 h. Thus, at 70 h, the measurement deviation between the repeat measurements of one bearing washer, and the measurement deviation between the bearing washers were added together, which is why a higher empirical variance occurs.

Through the comparison of the analyses with HCA from the tests with PFAE to the tests with mineral oil, the measured hydrogen increase with HCA on the test specimens tested with mineral oil can be purely related to the lubricant.

5   Conclusions

The first aim of this work was the assessment of the applicability of two different hydrogen analysis methods for measuring the freely movable hydrogen content in cylindrical roller thrust bearings after testing under operating

conditions which leads to bearing failure due to WEC. The second aim was to examine whether a continuous increase in hydrogen content occurs during the formation and propagation of WEC and to correlate hydrogen content with the lubricant composition.

Within the scope of this work, tests with two lubricants under operating conditions promoting WEC were stopped manually after defined test durations. The lubricants used were a mineral oil-based lubricant with hydride compounds and a PFAE without hydride compounds.

The test durations were 30, 50, and 70 h. Subsequently, the hydrogen content of these samples was determined and compared to the initial state. The two hydrogen analytical measuring methods "Local Hydrogen Analysis" and "Hydrogen Collecting Analysis" were used.

This work shows new insights into the change in hydrogen content during the formation and propagation of WEC on cylindrical roller thrust bearings and the key findings are listed below:

1) In contrast to the LHA, the HCA can be used for making statistically relevant statements on the change of the freely movable hydrogen content in cylindrical roller thrust bearings under operating conditions which leads to bearing failure due to WEC.

2) In the tests with mineral oil, the analysis of the hydrogen content by HCA clearly shows an increase in both the freely movable hydrogen content and the diffusible hydrogen content.

3) The freely movable hydrogen content increases over the test duration as long as no macroscopic material damage occurs.

4) The diffusible hydrogen content was higher than the material reference over the whole test because the diffusible hydrogen content showed an increase at the beginning, but a further increase over the remaining test duration cannot be detected.

5) Comparative measurements with a PFAE without additive showed that the system under the same operating conditions and by using a lubricant without hydride compounds in a time frame of 500 hours no failure due to WEC occurs.

Besides, it could be shown that the measured hydrogen increase with HCA on the test specimens tested with mineral oil resulted purely from the lubricant.

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