A novel technique was developed to control the concentration of water between 0.1 - 20 ppm and of oxygen between 0.3 - 2 ppm in hydrogen over a pin-on-disk apparatus. The developed technique simulates commercially available hydrogen gas at the point of use. This hydrogen usually contains sub-ppm to single-digit ppm levels of water and oxygen. The influence of impurities on the tribological properties of hardened chromium steel (JIS SUJ2) was obvious under the studied conditions, while the influence on austenitic stainless steel (JIS SUS316L) was not significant by comparison with that found in our previous study concerning higher water concentrations. The coefficient of friction of JIS SUJ2 increased with a decrease in the water concentration even at the smallest concentrations investigated in this study.

Keywords: ferrous materials, trace impurity, water, oxygen, hydrogen, pin-on-disk, wear, friction

1. Introduction

The importance of hydrogen as an energy carrier is widely recognized because of the issues around greenhouse gas emissions and the depletion of fossil fuels. Tribological parts such as bearings, seals and valves are inevitably used in hydrogen facilities, and the durability and reliability of these elements are essential for their safe and efficient use. Therefore, the tribological performance of various materials needs to be determined in a practical hydrogen environment.

Ferrous materials are the most widely used for tribological parts because of their excellent mechanical properties and low cost. However, it is known that ferrous materials such as hardened carbon steels degrade in a hydrogen environment and this is known as “hydrogen embrittlement.” Therefore, the tribological properties of ferrous materials in a hydrogen environment need to be studied in detail. In this study we used the hardened chromium steel (JIS: SUJ2) and the austenitic stainless steel (JIS: SUS316L). SUJ2 is a proven tribo-material that has been used in various atmospheres and it is on probation for use in hydrogen environments. The steel SUS316L is largely resistant to hydrogen embrittlement and it is used to fabricate vessels and mechanical components that contain or handle high-pressure hydrogen gas. Some of the internal surfaces of these components are used as parts of tribological elements and their tribological properties need to be determined.

In a previous study we confirmed that hydrogen influences the dry friction of transition metals and of metals that make stable hydrides. The chemisorption of hydrogen on the transition metals and the chemical reaction between hydrogen and the metals were determined to be the main mechanisms by changing the characteristics of the sliding surfaces. However, the tribological properties of steels are difficult to derive from these mechanisms even though the main chemical components of the steels are transition metals.

We then looked into the influence of trace impurities in a practical hydrogen environment because the wear debris and the sliding track of steels that were tested using commercial hydrogen gas were obviously oxidized in a practical hydrogen environment. The influence of 20 to 650 ppm water accompanied by 0.8 to
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over 11 ppm oxygen in a hydrogen environment has also been studied for steels\(^4\). The influence was significant as shown in Figs. 6 - 9. A water concentration of 20 ppm and an oxygen concentration of 0.8 ppm were the lowest concentrations used in our previous test rig\(^5\), but these values are not low enough to eliminate the influence of these gases. We therefore designed a sliding test rig with a better gas replacement system.

The hydrogen gas to be used as an energy carrier for FCVs (fuel cell vehicles) has been proposed by ISO\(^5\) to be more than 99.99% pure and to contain less than 5 ppm water and oxygen as impurities. We checked the guaranteed water and oxygen concentrations in a few commercial hydrogen gases with purities ranging from 99.9 to 99.999% and found that they are around single-digit ppm levels. The actual concentrations in 99.99% hydrogen were determined to be around 0.8 ppm for water and 0.2 ppm for oxygen at the point of use. We designed a pin-on-disk apparatus with a better gas replacement system and equipped it with a moisture sensor and an oxygen sensor, as shown in Fig. 1. Operational procedures were devised with the new apparatus to carry out sliding tests in hydrogen whose impurities were controlled at 0.1 to 20 ppm water and from 0.3 to 2 ppm oxygen.

Variations in the coefficient of friction and specific wear rate of pure Fe were investigated for the studied range of impurity gases and a significant influence of these gases was confirmed\(^6\). A chemical analysis done by XPS (X-ray photoelectron spectroscopy) showed that the variations might be caused by a difference in the chemical compounds produced on the sliding surfaces under hydrogen environments with different water concentrations. The influence of trace impurities in the practical hydrogen gas on the dry friction of ferrous materials is expected to be larger than those of hydrogen itself and they govern the tribological properties.

In this study, the experimental atmosphere was determined based on a practical viewpoint. The influence of 0.1 to 20 ppm water accompanied by inevitable oxygen that ranged from 0.3 to 2 ppm on the tribological properties of SUJ2 and SUS316L was studied and compared to our previous study on the same materials under the same testing conditions except for the concentrations of water and oxygen.

### 2. Experimental

Figure 1 is a schematic diagram of the pin-on-disk apparatus used in this study. The part to be tested was placed in a vacuum chamber equipped with a turbo molecular pump to enable a high quality atmosphere replacement. Further details about this apparatus have been described in our previous paper\(^6\). The shapes and dimensions of the pin and disk specimens are same as our previous study as shown in Fig. 2. The finishing and cleaning of specimens before testing has been described in our previous reports\(^{4,6}\) as well. Table 1 lists the chemical content and hardness of the specimens.

Table 2 shows the experimental conditions other than the atmospheric conditions as they are described in detail in the next chapter. These are equivalent to those of our previous study\(^4\) though the design of a loading

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Chemical composition (%)</th>
<th>Hardness (HV1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUJ2 bal.</td>
<td>Fe 1.0, C 1.5, Ni 785</td>
<td></td>
</tr>
<tr>
<td>SUS316L bal.</td>
<td>Fe 0.018, C 12.3, Ni 16.9, Cr 2.1</td>
<td>178</td>
</tr>
</tbody>
</table>

### Table 2 Experimental conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load (N)</td>
<td>10</td>
</tr>
<tr>
<td>Sliding speed (m/s)</td>
<td>0.063</td>
</tr>
<tr>
<td>Sliding distance (m)</td>
<td>126</td>
</tr>
<tr>
<td>Lubrication</td>
<td>Non</td>
</tr>
</tbody>
</table>

![Fig. 1 Pin-on-disk apparatus](image)

![Fig. 2 Shapes and dimensions of the specimens](image)
mechanism is slightly different. The applied load, friction force and pin displacement normal to the disk surface were measured using force sensors and a displacement sensor, respectively. Measurements were triggered by 720 signals per disk rotation as generated by a rotary encoder upon which the data was transferred to a processing system.

The specific wear rate, coefficient of friction and pin displacement perpendicular to the disk sliding surface were also evaluated. For SUS316L, the weight of the specimens was determined before and after each sliding test using an electrical balance and then the difference between the readings was converted into a specific wear rate (mm³/N), which is the wear volume (mm³) per unit load (N) and a sliding distance unit (mm). The wear rates of the SUJ2 pin and disk were too small to be determined by the electrical balance and were calculated from the changes in shapes 4) using an optical microscope and a surface roughness meter.

3. Preparation of a hydrogen environment

After placing the specimens in the apparatus, the vacuum chamber was evacuated using a turbo molecular pump. Filtered hydrogen containing less than 1 ppb water and oxygen was then introduced into the chamber. Hydrogen was allowed to overflow from the chamber after reaching a gas pressure of 0.1 MPa and the overflow gas was led to the moisture and oxygen sensors. The rate of the overflow was fixed at 0.5 L/min and was chosen from the 2, 0.5 or 0.05 L/min that we used in our previous study 6).

The residual gas concentrations at different vacuum pressures were determined by quadrupole mass spectrometry (ANELVA M-201GA-DM) using the analysis software QUAD VISION2, as shown in Fig. 3. The partial pressure of each residual gas was attributed to the differential between out-gassing from the internal surface of the chamber and evacuation by turbo molecular pump. Therefore, those gases became contaminants in the replaced hydrogen because

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**Fig. 3** Concentrations of the residual gases in the evacuated chamber

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**Fig. 4** Relationship between the chamber pressure just before hydrogen introduction and water concentration in the introduced hydrogen

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**Fig. 5** Range of water concentration for a) this study, b) our previous study 4) and c) conventional studies with corresponding oxygen concentrations for a) and b) and relative humidity at 298 K for reference
evacuation had to stop before the introduction of hydrogen and out-gassing continued during the introduction and overflow of high purity hydrogen. The residual gases were water, nitrogen, oxygen and carbon-dioxide in this order by quantity. Quantities of the other gaseous species were negligibly small. Water and oxygen were investigated in this study because they are known to be chemically more active than the other gaseous species. Nitrogen and carbon-dioxide\(^7\) are known to influence tribological properties; however, their low quantities were thought to not have an influence.\(^7\)

The concentrations of water and oxygen were controlled by out-gassing the gases that absorb and/or adsorb on the internal surface of the chamber. The relationship between vacuum just before hydrogen gas introduction that ranged between \(5 \times 10^{-3}\) and \(10^{-5}\) Pa and the concentration of water in the replaced hydrogen was determined by repeat gas replacement as shown in Fig. 4. The ratio between the concentrations of water and oxygen were not constant at different vacuum pressures as shown in Fig. 3. Therefore, a relationship between the concentrations of these gases was determined as shown in Fig. 5a). The concentration of water was controlled between 0.1 and 20 ppm and that of oxygen was around 10% that of water when the concentration of water was more than 2 ppm. For a water concentration of less than 2 ppm, the oxygen concentration was almost constant at around 0.3 ppm.

Even with the devised technique explained above, the concentrations of water and oxygen could not be controlled precisely and, therefore, the concentrations were needed for each test and were determined using a moisture sensor and an oxygen sensor. The concentration of water was used as a parameter to show the tribological data in the following results. Figure 5 shows b) the relationship between the concentrations of water and oxygen in our previous study\(^4\) and c) the range of water concentrations as relative humidity, and its influence on the tribological properties has been reported in many conventional studies.\(^8,9\)

A sliding test was conducted once for each water concentration because the precise control of the concentration was difficult as described above while that was relatively easy for higher concentration used in our previous study\(^5\). The repeatability of the sliding test was good enough to show the specific trend of the variation of tribological data at the different concentrations in this study.

### 4. Results and discussion

Figure 6 shows the variation of the coefficient of friction of SUJ2 at different concentrations of water. The data from this study and the previous study\(^4\) show a discontinuous trend. Possible reasons for this might be i) a sudden change in tribological phenomena at around 10 ppm water, ii) scattering of data and iii) the difference in test rigs especially with regards to the rigidity of the pin supporting part\(^10\).

The specific wear rates of the SUJ2 disk and pin varied with water concentration as shown in Fig. 7.
all sliding tests, the volume of the SUJ2 disks increased and the increase was almost proportional to the decrease of the pin. The disk increase is attributed to the transferred substances from the pin; however, the increase is more than the decrease for all the sliding tests. The volume expansion due to oxidation of transferred material form the pin might be one of reasons for the increase but it is not enough to explain all. Some adhered material originated form the disk that made a round trip to the pin should also be oxidized and contributed to the increase. In addition, some micro structural change accompanied by the formation of a low density compound such as ferric hydroxide might take place at the sliding surfaces. The variation of the specific wear rate at different concentrations of water shows continuous change, which implies that the difference in testing apparatus did not influence the tribological phenomena significantly.

The wear debris and the sliding surface of SUJ2 were red at a water concentration of 650 ppm. It changed to black and then to metallic shine with a decrease in the water concentration, as found in the previous study4). This phenomenon is due to a reduction in the degree of oxidation with a decrease in the concentration of water and/or oxygen. The sliding tests of SUJ2 in this study with a water concentration of less than 10 ppm showed similar results to that obtained with 20 ppm water in the previous study. The coefficient of friction and the specific wear rate varied even at 0.2 ppm water, which was the lowest water concentration used in this study and the concentration of oxygen was almost constant at 0.3 ppm.

Figure 8 shows a variation in the coefficient of friction of SUS316L at different concentrations of water. The discontinuous trend in data between this study and the previous study4) is evident again and the reasons for the discontinuity are presum ably the same as for the data discussed in Fig. 6. Because of the sudden increase in the coefficient of friction between 10 and 20 ppm water in this study the possibility of a sudden change in the phenomena might be responsible; however, the continuity should be confirmed by increasing the water concentration range towards a higher value with the test rig that we used in this study. The present test rig is not able to supply test gases with more than 20 ppm water and the issue of the discontinuity will be studied in future.

For SUS316L, the individual specific wear rate of the pin or disk showed large scattering because of an unstable mutual transfer of the adherent substance between the pin and disk. Therefore, Fig. 9 shows a variation in the total specific wear rate of SUS316L, which is the sum of the rates of the pin and disk. The variation in the specific wear rate seems to be consistent between this study and our previous study. The variation obtained for SUS316L does not show a clear tendency at different water concentrations in this study, while that for SUJ2 showed an obvious tendency.

Although the coefficient of friction was at around 0.6 and was not as large as that found in vacuum, the phenomena observed for SUS316L in this study was
similar to that of the metals tested in vacuum. The gases that prevent the adhesion of metals did not have a strong enough influence to discharge many wear particles while water and/or oxygen enhanced the discharge in the range of the concentrations tested in the previous study.

The difference in the influences of trace water and oxygen between SUJ2 and SUS316L can be attributed to the difference in the chemical compositions of these ferrous alloys. The influence of water at less than 20 ppm and oxygen at less than 1 ppm are significant for SUJ2 as is the case for pure Fe. Oxide and/or hydroxide formation with a small amount of water and/or oxygen might be enough to determine the tribological properties of SUJ2 and pure Fe. SUS316L contains Ni and more Cr than SUJ2 does. The free energy of oxide formation for Ni is higher than that of Fe and this is independent of temperature. Therefore, Ni is more inactive than Fe in terms of oxidation. Cr is more active for Fe oxidation but Cr forms a dense oxide film on the surface, which prevents further oxidation of the subsurface. These two chemical components might restrict the influence of trace water and/or oxygen in smaller concentrations.

The concentrations of water and oxygen in commercial hydrogen gases vary and our study shows that these variations can significantly influence the performance of tribo-elements. Materials for tribo-elements for use in a hydrogen environment should be chosen from the viewpoint of robustness over hydrogen and also over variable of water and oxygen content.

Four issues are left unresolved; a) distinguishing the influence of hydrogen alone on the tribological properties of alloys, b) finding evidence for the causes of the difference in influences of impurities between SUJ2 and SUS316L, c) verifying the continuity of data at a water concentration of 20 ppm using a higher water concentration with the test rig from this study and d) finding a ferrous material that shows good tribological properties regardless of impurity concentrations.

5. Conclusions

The influence of trace water and oxygen, as found in commercial hydrogen gas was studied using hardened chromium steel (JIS SUJ2) and austenitic stainless steel (JIS SUS36L). The following summarizes our experiments using a pin-on-disk apparatus.

1. Variations in the coefficient of friction and specific wear rate of SUJ2 were found for a range of impurities consisting of 0.1 ppm to 20 ppm water accompanied by 0.3 ppm to 2 ppm oxygen.
2. The coefficient of friction of SUJ2 increased with a decrease in the water concentration even at the lowest concentrations studied, viz. 0.1 ppm.
3. A variation in the tribological properties of SUS316L was not clear using the tested concentrations of water and oxygen in this study but they were significant at higher concentrations.

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7. References