**Short Communication**

**Generation of Ammonia during Wear Processes in Adhesive Wear of Titanium**

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We report a short note of preliminary and new experimental results that the generation of ammonia (i.e. nitrogen fixation) can occur on tribologically activated surfaces formed as a result of the frictional sliding of pure titanium when this is performed in a mixed gaseous environment of dinitrogen and dihydrogen at a total pressure of $6 \times 10^{-4}$ Pa. Gaseous ammonia, synthesized at the tribologically activated surface on the actual area of contact and/or on fine debris of wear elements with a size of the order of ten or a few tens of nanometers, was detected by analyzing the partial pressures for each species between amu 1 and amu 50 present in the environmental gases during the sliding friction: this analysis was performed using a quadrupole mass spectrometer (QMS). This process, however, depends on the mode of wear, i.e. it is expected to occur only under mild conditions of wear.

**Keywords:** adhesive wear, generation of ammonia, wear elements, chemisorption, titanium

1. **Introduction**

In the friction and wear processes a surface becomes quite active for environmental materials, and then environment gas molecules adsorb or chemisorb to the surfaces of the transition metals that have a high chemisorption activity for gas molecules [1-5]. The increase in chemisorption sites for gas molecules produced in the tribological process will promote chemical reactions on the sliding surfaces by the tribological process. Here we report a short note that generation of gaseous ammonia can occur on tribologically activated surfaces formed as a result of the frictional sliding motion of pure titanium against titanium when this is performed in a mixed gaseous environment of dinitrogen and dihydrogen at a total pressure of $6 \times 10^{-4}$ Pa.

Because of the need to rupture the strong N≡N triple bond that is present in dinitrogen, the fixation of nitrogen in nonbiological process requires catalysis by transition metals or their complexes [6,7]. However, we will show the possibility of generation of ammonia on a pure transition metal by demonstrating that it occurs when a tribological process is applied to titanium under conditions that lead to a mild wear mode in adhesive wear. The complexes of the transition metals molybdenum, tungsten, and zirconium are well known to be capable of catalyzing nitrogen fixation [8-10]. From a tribological point of view, however, these hard transition metals show very little wear, so that they cannot generate a sufficient surface area to achieve the chemisorption of nitrogen and hydrogen gases that is a prerequisite for the formation of gaseous ammonia. By taking account of the two necessary conditions for achieving generation of ammonia; i.e. a high catalytic activity and the probability of achieving large amounts of wear under given tribological conditions, we selected titanium and iron as candidate transition metals for study, and we found ammonia was clearly detectable in the tribological process of sliding friction in the case of titanium. To obtain evidence for the synthesis of gaseous ammonia through the frictional action of titanium, we chose the method of measuring of the partial pressures of the species amu17 (the parent peak of NH3) and amu16 (the secondary peak of NH3).

2. **Methods and materials**

The tribological experiment was performed with a pin-on-disk type tribometer set in a vacuum chamber. The sliding system consisted of a 4-mm flat-ended pin and the flat surface of a 25-mm disk. The pin was pressed onto the rotating surface of the disk at an applied load of...
2.2 N₂, and the disk was rotated with a sliding velocity of 251.3 mm/s at room temperature without a lubricant. These conditions of friction were selected to achieve optimal nitrogen fixation after preliminary experiments for some kinds of environmental gaseous pressure. The pin and disk consisted of commercial titanium with purity of 99.7% and Vickers hardness of 181. To compare the wear process with titanium, iron with purity of 99.9% and Vickers hardness of 118 was used for the experiment because iron is a transition metal and it can chemisorb both gases, although an activity of iron for chemisorptions of both gases is less than that of titanium [4]. We identified generation of ammonia by performing the frictional sliding procedure in a mixture of dinitrogen and dihydrogen gases at a pressure of 6 × 10⁻⁴ Pa and a N₂/H₂ ratio of 1:1. The two gases with a high purity of 3-5 N were introduced into the chamber after it was evacuated to 10⁻⁵ Pa. The total pressure quite sensitively affected the detection of spectrum of each amu-number. When a total pressure was higher rather than 10⁻³ Pa, the changes of spectrum of amu17 were not clearly appeared. At a pressure less than 1 × 10⁻⁴ Pa the value of generated gases was hardly detectable change. From these process of setting of the pressure was chosen at 6 × 10⁻⁴ Pa and a N₂/H₂ ratio was set at 1:1, and then we could gain available changes in the spectrum was observed with reappearance. Fig. 1 shows the spectrum between amu17 and amu50 of gaseous environment after a mixture of dinitrogen and dihydrogen gases was introduced into the chamber at a total pressure of 6 × 10⁻⁴ Pa. We can see strong peaks of H₂, N₂ in the spectrum, and weaker spectrum of H₂O. Gaseous H₂O is impurity in both gases or in the chamber.

The presence of gaseous ammonia in the gaseous environment was detected by measuring amu17 and amu16 species in measurements from amu1 to amu50 using a QMS. The measurements were performed before, during, and after the sliding procedure. The sliding friction was continued during 300 s, and measurements were performed over a period of 540 s.

3. Results and discussion

To obtain evidence for the synthesis of gaseous ammonia through the frictional action of titanium, we chose the method of measuring of the partial pressures of the species amu17 (the parent peak of NH₃) and amu16 (the secondary peak of NH₃); the pattern coefficient \( p_c = 80/100 \), which is the ratio of spectral peaks of amu16 and amu17 for ammonia provided additional evidence. The pattern coefficient of the fragment for each gas which has spectral peaks around amu17 is shown in Table 1. We first show the existence of a change in the original partial pressure line of the mass spectrum of species amu17 (Fig. 2a). We measured the partial pressure of amu17 for 540 s, and performed sliding friction with titanium for a 300 s interval during this period (shown by the arrow from 120 s to 420 s in Fig. 2a). A significant increase in the partial pressure in amu17 was detected only while sliding friction was occurring. The increase in the partial pressure shows the formation of gases with amu17 at the sliding surface and/or the desorption of such gases from the sliding surfaces, or possibly the presence of secondary or higher spectral peaks of other gases that are formed or desorbed. In the spectral analysis, the line of amu17 in Fig. 2a includes two kinds of partial pressures.

![Figure 1: Spectrum between amu1 and amu50 after inlet H₂ + N₂ gas in the chamber before sliding friction (secondary peak of each gas)](image)

<table>
<thead>
<tr>
<th>amu</th>
<th>CH₄</th>
<th>NH₃</th>
<th>H₂O</th>
<th>NO</th>
<th>O₂</th>
<th>CO₂</th>
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<td>14</td>
<td>9.0**</td>
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<tr>
<td>16 (CH₄)</td>
<td>100</td>
<td>80.0**</td>
<td>1.1</td>
<td>1.5</td>
<td>11.4**</td>
<td>8.5</td>
<td>5.0</td>
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<tr>
<td>17 (NH₃, OH)</td>
<td>1.2</td>
<td>100</td>
<td>25.0**</td>
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<td>18 (H₂O)</td>
<td>100</td>
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<td>28 (CO₂, N₂)</td>
<td>0.001</td>
<td>100</td>
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<td>30 (NO)</td>
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<td>32 (O₂)</td>
<td>100</td>
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<td>44 (CO₂, N₂O)</td>
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(*secondary peak of each gas*)
corresponding to that of ammonia (NH₃ = amu17) and the secondary spectral peak of water vapor (H₂O = amu18); the latter may be desorbed from the sliding surface as a result of frictional action, which had been once adsorbed onto the sliding surface before or during frictional motion from atmospheric gas. If we examine the pattern coefficient of H₂O for the QMS used in the present experiments, the usable pattern coefficient of amu17/amu18 was \( p_c = 25/100 \) from Table 1. The partial pressure of H₂O in the amu17 spectrum was identified by multiplying the partial pressure of the species with amu18 in the parent spectrum by 25/100, because the partial pressure of amu18 is, fortuitously, almost entirely produced by H₂O. Fig. 2b shows the result after subtracting the partial pressure of amu18 multiplied by 0.25 from the original partial pressure of amu17 in Fig. 2a. The line in Fig. 2b shows the real partial pressure of ammonia formed during the sliding friction. A maximal increase of about \( 4 \times 10^{-8} \) Pa was detected during the frictional process.

We tried to confirm the formation of gaseous ammonia by examining the secondary peak of NH₃ in the spectrum of amu16. The partial pressure of amu16 includes methane (CH₄ = amu16) and some secondary or higher-order spectral peaks. Among the known species that form amu16 species are dioxygen \( (O₂ = \text{amu32}; p_c = 11/100 = \text{amu16/amu32}) \), carbon dioxide \( (CO₂ = \text{amu44}; p_c = 8.5/100 = \text{amu16/amu44}) \), nitrogen dioxide \( (N₂O = \text{amu44}; p_c = 5.0/100 = \text{amu16/amu44}) \), water \( (H₂O = \text{amu18}, \text{ and used pattern coefficient } p_c = 1.1/100 = \text{amu16/amu18}) \), nitrogen monoxide \( (NO = \text{amu30}; p_c = 1.5/100 = \text{amu16/amu30}) \), and ammonia \( (NH₃ = \text{amu17}; p_c = 80/100 = \text{amu16/amu17}) \). Fig. 3a shows the partial pressure after subtracting the partial pressures for higher-order peaks of gases from the original partial pressure of amu16, except for ammonia \( \{\text{amu16} - (\text{amu32} \times 0.11) - (\text{amu44} \times 0.0675) - (\text{amu18} \times 0.011) - (\text{amu30} \times 0.015)\} \), where 0.0675 multiplied by amu44 is the mean value for carbon dioxide and nitrogen dioxide. The possibility of methane being present is very small because of the partial pressure of amu15, whose line includes the secondary spectrum of CH₄ \( (p_c = 86/100 = \text{amu15/amu16}) \), was less than \( 4 \times 10^{-9} \) Pa. Next, we tried to compare the parent pressure of ammonia in Fig. 2b and the secondary spectral peak of ammonia at amu16 of Fig. 3a. In Fig. 3b, the two lines are compared between the green line in Fig. 3a and the secondary spectral peak of ammonia at amu16 of Fig. 3b (pink line). The two lines are very similar to each other. Evidently, the result indicate that ammonia was formed only when titanium was subjected to tribological sliding action titanium in an environment of dihydrogen and dinitrogen gases, although the total volume of ammonia that was formed was very small.
Similar experiments were performed using iron as the transition metal, because iron produces a considerable wear volume; nevertheless, we could not find any significant increase in the partial pressure of amu17 under the present sliding conditions. There is a significant difference between the tribological wear modes of titanium and iron. Fig. 4 shows the sliding surfaces of titanium disk (a) and iron (b). With iron shown in Fig. 4b, large transfer particles were formed in a severe wear mode because of less chemisorption of gas molecules onto the surfaces rather than titanium [1,4,5]. On the other hand, the surface of titanium showed relatively smooth with small transfer particles only (Fig. 4a), and that the wear mode was almost mild wear as a result of strong chemisorption of environment gas molecules. Sliding surface of the pin specimen was shown similar to the mating disk surface for each same metal combination by means of microscopic

Fig. 3  Proof of the existence of ammonia in the secondary-peak spectrum on the amu16 line. a, Partial pressure of amu16 after subtraction of secondary or higher-order spectra of dioxygen, carbon dioxide, nitrogen dioxide, water vapor, and nitrogen monoxide from the original line of amu16. b, Fit to the corrected line (green shown in online) in Fig. 2a and the secondary spectrum of ammonia line (pink shown in online) from Fig. 1b with a pattern coefficient \( p_c = 80/100 = \text{amu16}/\text{amu17} \) of ammonia

![Fig. 3](image_url)

Fig. 4  a; Sliding surface of titanium disk after sliding with titanium pin in gaseous environmental \( \text{H}_2 + \text{N}_2 \); b; sliding surface of iron disk after sliding with iron pin with reference to show the difference of surfaces and wear mode for the two metals (Titanium shows almost mild wear mode and iron shows severe wear mode)

![Fig. 4](image_url)
observations. From the tribological point of view, the possibility of synthesizing ammonia from dihydrogen and dinitrogen is limited to the case of mild wear. Fig. 5 shows the sliding surface of titanium observed by means of AFM (atomic force microscope), and we can observe many transfer particles in Fig. 5a. Fig. 5b shows the enlarged picture of the particles in symbols as “A” in Fig. 5a. Transfer particle consists of a large number of fine particles of wear elements with a size of the order of ten to a few tens of nanometers [11-13]. Wear element is the unitary debris of wear particles in adhesive wear and it has a large specific surface area (the ratio of the total surface area to the volume) with a large number of sites available for chemisorption of gases. Therefore, the tribologically formed surface is chemically active and assists to synthesize ammonia during the sliding contact of titanium. From the tribological points of view, we supposed that the possibility to synthesize ammonia from dihydrogen and dinitrogen is limited to the case of mild wear.

In the industrial process to synthesize ammonium by Harbor-Bosch method it needs a high gaseous temperature of about 670-780 K as well as a high gaseous pressure of 20 - 100 MPa. Under the given conditions, reaction \( H_2 + 3N_2 \rightarrow 2NH_3 (\Delta H_0 = -92.4 \text{ kJ/mol}) \) is possible with a catalysis of iron main compounds [7]. According to the present experiments, we can suppose that the generation of ammonia is possible to achieve in the adhesive wear without similar severe conditions of Harbor-Bosch method. We will propose an assumable model of Fig. 6 in the process of adhesive wear. Fig. 6a shows the process of dissociation of dinitrogen and dihydrogen gases to chemisorb onto the titanium surfaces as a prerequisite for the formation of gaseous ammonia through the increase of chemisorption sites on the newly generated naked-surface of wear elements, transfer particles, and sliding surfaces. In a subsequent accumulation process of wear elements to form transfer particles accumulated by wear elements

![Impression of a model](image)

**Fig. 6** Model of the generation of gaseous ammonia by chemisorbed nitrogen and hydrogen in the formation process of wear elements and transfer particles in the adhesive wear.
particles of adhesive wear [11-14], wear elements involve catalytically chemisorbed nitrogen and hydrogen in the accumulation process and then gaseous ammonia will be generated by a chemical reaction between desorbed nitrogen and hydrogen at the surface as shown in Fig. 6b.

Lastly, in general, environmental oxygen is actively chemisorbed in preference to nitrogen or hydrogen on the surfaces that are generated when transition metals are subjected to friction [1-3]. At this stage, if the chemisorption sites are occupied by oxygen, no ammonia will be synthesized, since nitrogen and hydrogen will be chemisorbed to a smaller degree than oxygen. Only when large numbers of chemisorption sites are produced in the tribological process will ammonia be synthesized after chemisorption of nitrogen and hydrogen. The necessary condition for generation of ammonia under tribological conditions is therefore the formation of a large number of fine particles with sufficient numbers of chemisorption sites for gases, and this condition is met when the wear mode is that of mild wear in which wear elements measuring of the order of ten or several tens of nanometers are successively generated during the frictional sliding process. Of course, an oxygen-free environment is also advantageous for the generation of ammonia from dinitrogen and dihydrogen gases.

4. Summary and concept

We reported the generation of ammonia during sliding friction of titanium when this was performed in a mixed gaseous environment of dinitrogen and dihydrogen at a total pressure of $6 \times 10^{-4}$ Pa. The result of generation of ammonia was quite sensitive to environmental gaseous pressure as well as wear mode of transition metal which has a high chemisorption activity for gas molecules. We believe that the present result may be the first experience of the generation of ammonia by a tribological process, although the volume of ammonia generated was small. The volume of ammonia synthesized during tribological process may increase at a higher environmental gaseous pressure, but it will become difficult to separate the partial pressures of the species amu17 or amu16 for the generation of ammonia from other overlapped spectrum.

References