Ammonia effects on hydrogen embrittlement mitigation and induction -Experiment and theoretical understanding of the mechanisms-

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論 文 名　：Ammonia effects on hydrogen embrittlement mitigation and induction
　　　　　　-Experiment and theoretical understanding of the mechanisms-
　　　　　　(水素脆化の抑制と誘発に及ぼすアンモニアの影響
　　　　　　-実験とメカニズムの理論的考察-)

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論　文　内　容　の　要　旨

The objective of this study is to obtain a mechanistic insight into the NH_3 effects on hydrogen embrittlement (HE) in order to enable the safety of NH_3 utilization for carbon-neutral purposes. Transitioning to a hydrogen-powered society is one of the promising directions to decrease carbon dioxide emissions. However, steels and alloys used for hydrogen gas containment systems can suffer from hydrogen embrittlement, which is the degradation of material strength due to the hydrogen. Ammonia (NH_3) has been considered a hydrogen carrier and non-CO_2 fuel. It is expected that NH_3 will play an essential role in a carbon-neutral society.

In this study, fracture toughness tests of SCM440 low-alloy steel were carried out in H_2 and NH_3-added H_2 gases to characterize the HE mitigation effect by NH_3. In addition, the experiments in the N_2 and NH_3-added N_2 gases were also performed to examine the interaction of NH_3 with the Fe surface. As a result, we determined two NH_3 effects conflicting with each other, which are HE mitigation and HE induction. Regarding the HE mitigation effect, it was more pronounced by increasing the NH_3 concentration. Regarding the HE induction effect, an inverse NH_3 concentration dependence that the HE was reduced by the increase in the NH_3 concentration was found. The mechanisms were elucidated by theoretical considerations using the density functional theory (DFT). For the Fe (110) surface, which is the representative crystallographic plane cracking during hydrogen embrittlement, the NH_3 adsorption rate, NH_3 decomposition rate, H_2 dissociation rate, and hydrogen atom coverage were calculated.

In chapter 1, the background and objective of this thesis were described. First, the role of NH_3 in the recent world energy situation was explained following introduction of the physical properties of NH_3. Second, general trends in the HE during the fracture toughness test and state-of-the-arts of the mitigation of HE by impurities mixed in hydrogen gas were introduced. Third, applications of DFT calculations regarding the interaction of gaseous species and solid surfaces were described. Finally, the motivation and objective of

this study were identified.

In chapter 2, fracture toughness tests of JIS SCM440 low-alloy steel were conducted in H_2 and 1,000 volume ppm (vppm) or 10,000 vppm NH_3-added H_2 gases. As a result, it was confirmed that NH_3 had a mitigation effect on the HE. According to the DFT calculations, the NH_3 reaction rate on the Fe (110) surface was 2.773×10^{19} /s at 11 % NH_3 coverage, while the H_2 reaction rate on the Fe (110) surface was 5.887×10^9 /s. As the result that NH_3 has a significantly higher reaction rate, NH_3 was preferentially adsorbed on the Fe surface. According to the Langmuir adsorption model, when 25 % of the Fe surface is covered by NH_3, only 0.01 % of the Fe surface is available for hydrogen atoms. These are the mechanisms by which NH_3 mitigates the HE.

In chapter 3, fracture toughness tests were conducted in N_2 and 1,000 vppm NH_3 added H_2 gases. In the NH_3-added N_2 gas, a significant reduction in the fracture toughness was found. The cause was determined as HE by examination of the fracture surface. This NH_3 effect of the HE induction was strongly affected by the loading rate. For its expression, a 2×10^{-5} mm/s loading rate, which is extremely low, was required. By comparing the NH_3 adsorption rate coefficient ($k = 3.140 \times 10^{20}$/s) with the NH_3 decomposition rate coefficient ($k = 1.368 \times 10^8$/s), which were obtained by the DFT calculations, it was found that the NH_3 decomposition was a relatively very slow reaction. Therefore, NH_3 induces the HE only if the loading rate is sufficiently low.

In chapter 4, 10,000 vppm NH_3 in N_2 gas was added to the fracture toughness test in order to investigate the NH_3 concentration dependence on the HE induction effect. Interestingly, the HE by NH_3 decomposition diminished as the NH_3 concentration increased. This was opposite to the prediction based on the theoretical result that atomic hydrogen coverage on the Fe surface increased with an increase in the NH_3 concentration. The main reason for this reverse trend was the change in the NH_3 decomposition rate with the NH_3 concentration. The DFT revealed that NH_3 can achieve ($NH_2 \rightarrow NH + H$) following ($NH_3 \rightarrow NH_2 + H$) when the NH_3 concentration was sufficiently low, whereas it can achieve only ($NH_3 \rightarrow NH_2 + H$) when the NH_3 concentration was high because the NH_3 decompositions require vacant sites on the Fe surface. A higher NH_3 concentration limits the NH_3 decomposition resulting in a reduction of the hydrogen supply.

Furthermore, for the NH_3 and H_2 competitive coadsorption on the Fe (110) surface, a kinetic model, which can quantitatively determine the coverage of each species on the Fe surface, was established. It was revealed that the hydrogen atom coverage on the Fe (110) surface was 8.422 % for the H_2 + 1,000 vppm NH_3 gas and 15.2 % for the H_2 + 10,000 vppm NH_3 gas, if NH_3 can undergo total decomposition. However, the NH_3 decomposition rate decreased as the NH_3 concentration increased resulting in hindering the NH_3-derived hydrogen supply. As a result, the hydrogen atom coverage on the Fe (110) surface was 8.422 % for the H_2 + 1,000 vppm NH_3 gas and 4.375 % for the H_2 + 10,000 vppm NH_3 gas. This was the reason for the NH_3 concentration dependence on the NH_3 mitigation effect.

In chapter 5, the obtained results of this study were summarized and conclusions listed.