



Liquid Lubricants over Iron Oxides: A Scanning Probe Study

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(別紙様式 3)

論文内容の要旨

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専 攻 化学

論文題目 (外国語の場合は、その和訳を併記すること。)

Liquid Lubricants over Iron Oxides:

A Scanning Probe Study

(液中動作する走査プローブ顕微鏡を用いた潤滑油と鉄酸化物界面の研究)

指導教員 大西 洋

In Chapter 1, background on this research was described. The prevention of wear and seizure and the reduction of friction in boundary lubrication where the distance between two sliding surfaces is close and contact between solids is partially generated are still major problems. One of the solutions is a modifier contained in lubricating oil. By modifying the solid surface or adsorbing to the solid surface, the modifier reduces friction and prevents wear and seizure. Especially, in the boundary lubrication in which the single molecule adsorption film influences the friction reduction characteristic, the adsorption of the modifier to the solid surface directly leads to the performance improvement of the lubricating oil. That is, knowing and controlling the modifier adsorption film is the key to controlling boundary lubrication.

On the other hand, even today, it is not easy to characterize adsorbed modifiers of nanometer-scale thickness. The mass and chemical structure of the adsorbed modifier and the thickness of the adsorption film have been evaluated in the previous study. However, these analyses are based on the assumption that the modifier is uniformly adsorbed. It is expected that the adsorption is not uniform in the actual sliding part, and an operand method capable of evaluating the non-uniformity is required. Frequency modulation atomic force microscope (FM-AFM) has a spatial resolution in the order of sub nanometers, which is on the atomic and molecular size, in both the in-plane and vertical directions, and can detect unevenness at the molecular level of the adsorption film. In addition, it has a force detection sensitivity of the order of 10 pN, and can capture not only a solid modifier adsorption film but also a modifier adsorption layer existing in a liquid state at a solid-liquid interface. In this study, we tried to visualize the adsorption film of the modifier using FM-AFM, and succeeded.

In Chapter 2, the adsorption of orthophosphoric acid oleyl ester (C18AP) on the iron oxide film was evaluated, which is commonly used as an antifriction agent. As the base oil, poly- α -olefin (PAO) was used, which is also widely used. The antifriction agent forms a tribofilm of the reaction secondary product on the solid surface to prevent seizure and wear. The formed reaction coating is hard enough to be recognized as a solid and can be analyzed with a conventional atomic force microscope (AFM)/scanning probe microscope (SPM). However, the precursor adsorption film formed by the physical or chemical adsorption of modifier molecules on the solid surface as a preliminary step for this reaction was so soft and required the force

sensitivity of the order of 10 pN achieved in FM-AFM to detect the layer induced force response. The adsorption layer of C18AP contained in PAO, the base oil, to the oxidized iron film was evaluated. The formation state of the C18AP adsorption layer was evaluated by changing the concentration of C18AP. According to the dynamic response measurement of the ZX cross section, C18AP was adsorbed with its phosphoric acid end anchored to the films. There was fluctuation of the C18H35 chains of C18AP in the lubricant. The force maps reflected the time-averaged density distribution of the fluctuating chains and monotonically decayed to zero force at a tip-to-surface distance of 2 nm when a monomolecular layer of C18AP was completed. The oxidized iron film was intermittently covered with C18AP molecules in the lubricants containing C18AP concentrations of 0.2 and 2 ppm; it completely covered at 20 and 200 ppm. The oxidized iron film that was completely covered with the C18AP layer produced topographic images with reduced sharpness according to its fluctuating, dynamic boundary with the lubricant. And in addition to analysis with FM-AFM, the dynamic friction coefficient of the sliding steel-lubricant-steel interfaces was evaluated using the friction tester. As the results, the dynamic friction coefficient decreased with increasing the coverage of the monomolecular C18AP on the iron film. These experimental results indicate that nanometer-scale distribution of C18AP precursor adsorption film on the oxidized iron film is related with the friction characteristics of sliding surfaces, and it proved that the nanometer-scale analysis is valuable for the control of the modifier adsorption layer at the lubricating interface.

In Chapter 3, the adsorption films of carboxylic acids were evaluated such as stearic acid and oleic acid, commonly used as oiliness agents, onto iron oxide single-crystalline wafers. As the base oil, PAO was used, which is also widely used. The adsorption film formed by the oiliness agent is also expected to be soft enough not to be recognized as a solid, as is the case with the precursor adsorption film formed by the extreme-pressure agent and the antifriction agent, and the detection required the force sensitivity of the order of 10 pN achieved in FM-AFM. As in Chapter 2, topography and dynamic response measurements of the ZX cross section were used to evaluate. In the topographic measurement, it was found that adsorption of the carboxylic acid onto the wafer is enhanced by pseudo sliding caused from the interaction force generated when the probe was scanned on the surface of the wafer. In frequency-shift mapping on ZX plane, by comparing the analytical results of five carboxylic acids with different molecular structures,

their adsorption on the wafer was elucidated on a molecular scale. The carboxylic acid was chemically adsorbed with its polar group to the wafer and inhibited the direct contact of PAO with the wafer by forming a monolayer on the surface of the wafer. In case of single chain carboxylic acid, the carboxylic acid in the lubricant formed the liquid layered structure on the monolayer with a layer-to-layer distance of 0.56 - 0.75 nm. This is the first time that the behavior of carboxylic acids at the solid-liquid interface has been identified in the order of molecular scale.

In addition, the temperature dependence of the oleic acid adsorption onto the iron oxide single-crystalline wafer was verified by measuring the frequency-shift maps at temperatures from 25 degrees centigrade to 65 degrees centigrade. The repulsive force from the fluctuating tail of the oleic acid adsorbed to the wafer, became thinner with increasing temperature, and disappeared at 60 degrees centigrade. On the other hand, the dynamic friction coefficient of the sliding carbon steel-lubricant-iron oxide single-crystalline wafer interfaces, which was determined using the ball on disk friction tester at each temperature from 25 degrees centigrade to 150 degrees centigrade, increased at 150 degrees centigrade compared with it from 25 degrees centigrade to 90 degrees centigrade. These results indicated that the adsorption of oleic acid to the wafer is activated at a temperature much lower than the temperature at which the effect is lost. The mechanical probing with FM-AFM provides a new knowledge in a molecular scale that cannot be found only from friction phenomena in the macroscopic dimensions.

In Chapter 4, it was confirmed for the first time that KPFM works normally in PAO-based lubricant. In addition, it was detected that the surface potential of the sliding part simulated with the AFM probe was different from that of the non-sliding part. This indicates that sliding in a lubricating oil using a nonpolar organic solvent as a base oil changes the charged state of the iron oxide shingle-crystalline wafer surface. In the present experiment, PAO containing only oleic acid was used, but several kinds of modifiers are added to the actual lubricants to improve the performance, which makes the behavior of the modifier more complicated. It is very useful in designing a modifier formulation to know which modifier preferentially forms an adsorption film and provides a good effect, when multiple modifiers are mixed. The KPFM proposed as a new analytical method adds an index of electrical characteristics in addition to topographic and

mechanical response. This can be of great help in identifying the type of modifier and the amount adsorbed.

In Chapter 5, this research was summarized. In this study, the behavior of the modifier molecule in the lubricant at the solid-liquid interface was identified at the molecular resolution by the excellent spatial resolution and force sensitivity of FM-AFM. Not only an adsorption film hard enough to be recognized as a solid, but also an adsorption film existing as a liquid was captured. The relationship between the adsorption film and the macroscopic frictional properties was confirmed, and it was clarified that the behavior of the modifier at the molecular level affected the macroscopic frictional properties in no small way. FM-AFM and KPFM can be expected as new methods to accelerate the development of lubricants by clarifying the behavior of lubricants at friction interfaces on a molecular scale and providing a theoretical basis for lubricant design.

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論文 題目	Liquid Lubricants over Iron Oxides: A Scanning Probe Study (液中動作する走査プローブ顕微鏡を用いた潤滑油と鉄酸化物界面の研究)		
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要 旨			
申請者（森口志穂）が提出した学位論文を、本研究科の学位論文評価基準に照らして審査するために、物理化学講座教員（大西）・無機化学講座教員（富永）・有機化学講座教員（茶谷）・京都大学工学研究科機械理工学専攻教員（平山）からなる審査委員会を組織した。令和2年8月4日13時40分から審査委員全員の出席のもとで、森口氏による学位論文発表会を開催して発表60分にひき続き60分にわたって論文内容と関係学術分野に関する口頭試問をおこなった。試問終了後ただちに審査委員会を開催して、学位論文評価基準が定める以下の5項目について各委員の心証を意見交換し、ついで可否を判定した。 (1) 専攻分野に関する高度な学術的価値を有する研究結果を含むこと 真空中あるいは気体中においた固体表面を分子論的な視点で理解する研究は1960年代から大きく発展し Gerald Ertl のノーベル化学賞（2007年）に結実した。Ertl に続く界面研究者に課された課題は、二つの凝縮相（液体または固体）が接する界面の分子論的理解である。森口氏はこのような背景のもとで、潤滑油が鉄および鉄酸化物に接する界面を、潤滑油から取り出すことなく実験計測し、界面におかれた潤滑油液体の構造と機能を分子論的に理解する研究をおこなった。リン酸エステルを添加した炭化水素液体を計測した成果（学位論文2章）は、アメリカ化学会（ACS）が発行する <i>ACS Omega</i> 誌に2019年10月に上梓されこれまで10ヶ月間に3回引用された。液体と固体が接する界面の分子科学ならびに潤滑理工学（トライボロジー）において世界最先端の学術的価値をもつと認められる。 (2) 先行研究や関連研究をふまえて適切な課題設定をおこなっていること 既存の液体-固体界面研究のほとんどが水溶液を対象とするなかで、あえて未踏領域である潤滑油（有機溶液）をターゲットに選んだことは適切であり、新しいことを忌避しない森口氏の挑戦性をあらわしている。			

氏名	森口 志穂
(3) 課題に対して適切な研究方法を選択し研究を実施していること 液体と固体が接する界面の計測評価は簡単ではない。真空中あるいは希薄ガス中では低速電子やイオンビームなどをプローブとした表面分析が可能であるが、これら浸透力の弱いプローブは液体に埋没した界面に到達できない。この困難を回避するために、最近 10 年間に著しく性能が向上した原子間力顕微鏡 (AFM) を計測機器として選択し、潤滑油に添加する微量成分の吸着を顕微計測した手法は適切である (2 章および 3 章)。計測対象を化学分析できない AFM の限界を突破するために、AFM をベースとする表面電位計測法であるケルビンプローブ顕微鏡を潤滑油界面の計測にはじめて活用したことも適切である。さらに、これらの分子スケール顕微計測の結果のみで完結せずに、摩擦係数というマクロ物理量と比較対照する研究方針は適切であり、関連分野の海外研究者 (Prof. Roland Bennewitz ら) から高く評価されている。	
(4) 研究結果を適切に考察し結論を得ていること AFM は固液界面に存在する分子を画像化することに優れた手法であるが、外乱に起因するノイズをも敏感に検出してしまう短所がある。液体は真空や気体に比べて熱伝導率が大きく弾性波の伝搬性も高いために、液体中での安定した画像計測の難易度は非常に高い。そのような中で計測した画像から物理的に意味ある情報を抽出するために、計測結果の再現性に留意し、さらに AFM 探針の先端にかかる力を定量化したことは適切である。このような解析によって、リン酸エステル単分子吸着層の出現 (顕微計測結果) が摩擦係数低減 (マクロ物性) の原因であることを結論できた (2 章)。	
(5) 章立て・引用を含めて論理的で明瞭な記述をおこなっていること 研究背景と計測手法 (1 章)・リン酸エステルを添加したポリアルファオレフィンと鉄薄膜界面の計測 (2 章)・鎖長の異なるカルボン酸を添加したポリアルファオレフィンと酸化鉄結晶界面の計測 (3 章)・ケルビンプローブ顕微鏡を用いた潤滑油中での電位計測 (4 章)・総括 (5 章) からなる学位論文 (160 ページ) の章立ては適切である。各章ともに目的・実験手順・実験結果・先行研究との比較にもとづく考察が順序よく英語で記述されている。潤滑油界面の液中計測は未踏分野であるため先行研究は多くないが、十分な検索と適切な引用がなされている。	
【結論】以上の認識にもとづいて本審査委員会は、森口氏が提出した学位論文が学位論文評価基準をみたし、液体-固体界面の分子科学ならびに潤滑理工学を進展させた成果として学位授与にふさわしい内容をもつと全員一致で判定した。	