Raman scattering study of micrometer-sized spots of magnetite and hematite formed at 18CrNiMo7-6 screw rotor surfaces due to liquid-free, unsynchronized operation

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Abstract. We analyze differently worn surface positions of a screw rotor’s contact zone using confocal Raman spectroscopy with 2 μm spatial resolution. The Raman scattering spectra demonstrate signals from magnetite Fe₃O₄ and hematite α-Fe₂O₃ whose intensities and energy shifts are associated with the degree of wear of the surface locations. While magnetite is identified at the worn surface areas studied, excluding a possible white etching domain, scattered light signatures from hematite are only detected at surface positions, at which high temperatures and/or high pressure inputs were proposed to be present during the liquid-free wear process of the screw rotors. The findings may be used to gain a more general understanding of tribological layers and to develop microscopic indicators of wear.

1. Introduction
The ideal product designed for mechanical-engineering purposes remains its functionality during an infinite long lifetime. For the conditioning of the functions as well as the product’s operation, surfaces being in contact with each other are of major importance. The understanding of how the surface properties are changed and controlled needs to be developed [1]. It is well known that a tribological layer of a few nanometers thickness is formed at the surfaces [2]. This layer determines the short- and long-term behavior of the engineered product [3]. Predicting the properties of the layer by monitoring changes in the atomic and molecular structures is highly desirable, but it was up to now only realized within the framework of fundamental theoretical [4] or to some extent in complex ex-situ studies [5]. In the latter case, detailed information about the surface tribological properties on the atomic scale are drawn from x-ray scanning and transmission-electron microscopy experiments. An in-situ and a non-destructive tool for characterizing the tribological layers ideally during their formation process will be the key to understand and control the functionality and lifetime of an engineered product.

Such a key could be provided by Raman spectroscopy, which is a powerful optical technique used for a wide range of applications [6]. It was exploited to characterize and identify materials,
to discover novel effects in physics and chemistry and to enhance the understanding of elementary mechanisms in fundamental, technological and industrial research studies [7, 8]. The main advantage of the Raman spectroscopy is based on its principle mechanism, which is mediated predominantly by a quantized lattice vibration (phonon), whose energy is directly measured through the difference in energy of the incident and scattered light [6]. Combining the Raman spectroscopy with confocal microscopy adds high spatial resolution to its large set of surface-sensitive features. Confocal Raman spectroscopy could be the key technique to reveal the atomic properties of heterogeneous surfaces, such as tribological layers.

Tribological layers play a major role in the wear process of the sliding surfaces of oil-injected twin-screw rotors. Due to their cost-effective design twin-screw machines are used for the compression and expansion of gases [9]. To reduce the degree of wear and its impact on the rotor functionality by preventing a direct rotor-rotor contact, oil is usually injected into the twin-screw-rotor system. The usage of oil as lubricant is a drawback, since it has to be separated from the processed gas, which enhances significantly the total cost of ownership [9, 10]. On the other hand, dry-running screw compressors or expanders are always equipped with an oil flooded timing gear. Therefore, during operation there is no contact between both rotors. The main drawback of this type of screw machines is their reduced efficiency and the required sealing between the timing gear and the working chambers of the rotors. Hence, they are more expensive in manufacturing and operation. In order to protect the environment and to lower the manufacturing and operating costs it is desirable to design dry-running (liquid-free) screw rotor machines. Short-time experiments on twin-screw rotors with WC/C coating for different applications (supercharger, expander, and vacuum blower) have already been performed by achieving 200 to 400 hours of operation. The wear process at the rotor surfaces in the contact zones is not understood yet; however, first confocal Raman spectroscopy experiments have gained insight into the microscopic properties of the tribological layer [11].

Here, we study worn surfaces of uncoated twin-screw rotors made from 18CrNiMo7-6 steel using the confocal Raman spectroscopy. We identify magnetite \( \text{Fe}_3\text{O}_4 \) and hematite \( \alpha-\text{Fe}_2\text{O}_3 \) Raman scattering signals in dependence on the degree of wear of the surface locations. The spatial dimensions of surface areas containing hematite and magnetite are a few micrometers. Spatial Raman scattering patterns suggest that hematite is only present at surface locations, which were exposed to high temperatures and/or high pressures during the liquid-free operation. Moreover, the surface positions without heavy wear history contain primarily magnetite as iron oxidation product. Since the respective Raman line widths are not broadened, the molecular bond lengths and strengths are homogeneously distributed. Our spectroscopic findings of iron oxide compounds, which play a fundamental role in corrosion processes of surfaces [12, 13], may provide a step forward to understand wear mechanisms and properties of tribological layers at uncoated twin-screw rotors.

### 2. Experimental Details

Within the following investigation, the effects of the tribological interaction between the female and male rotor in the interlobe contact of a dry-running, unsynchronized twin-screw expander are analyzed. The twin-screw expander was operated at a constant inlet pressure of 4 bar (absolute), an inlet temperature of 90°C, and a rotational speed of 9500 min\(^{-1}\) corresponding to a male rotor tip-speed of 35.7 ms\(^{-1}\). At the expander outlet an ambient pressure of 1 bar (absolute) was applied. The rotors with an asymmetric SRM profile were in use for 40 minutes with \(4 \times 10^5\) changes of load under liquid-free conditions (dry air). In this context, we studied the surface area of a female screw rotor, which was in contact with its male counterpart. Both screw rotors were made of chromium steel 18CrNiMo7-6.

A photography of the part, which was mechanically excavated from the female screw rotor, is shown in figure 1(a). A horizontal arrow indicates the contact area which clearly demonstrates
wear traces resulting from the running process. In figure 1(b) a monochrome video-camera image shows a 150 μm × 150 μm area which was obtained after a focus stacking. The surface is mainly characterized by shallow strips and several dark discolored domains having different dimensions. Surfaces without wear history do not exhibit such black shaded spots. Hence, one can assume that the dark discolored domains were formed during the wear process. Using the vertical scanning option (perpendicular to the rotor surface) of our microscope system, we could determine the depths of the dark areas; they typically vary between 5 and 20 μm. In figure 1(c) another example of a surface area, which was inside the contact zone of the screw rotors, is depicted. In the center of the image the laser spot can be seen as bright spot with a few interference rings. At the left and right side of the image heavily worn surface domains can be identified. For the confocal Raman scattering experiments, we investigated the area marked in figure 1(d), which shows a part of panel (c) in a magnified way. This surface area of 320 μm² contains three separated domains with different degrees of wear: a worn surface domain (purple), a transition zone (dark blue) and a heavily worn domain (light blue). At every 2 μm in the x- and y-direction the surface was illuminated with a laser beam and a Raman spectrum was measured. In that way, 80 Raman spectra in the corresponding 16 × 5 scanning matrix, as presented in figure 1(d), were detected. Every spectrum was recorded during an exposure time of 600 s.

The spatial mapping of the surface area marked in figure 1(d) was performed at room temperature using a confocal Raman spectrometer (S&I MonoVista Raman Microscope System CRS+ 750/BX51). A scheme of the Raman scattering setup is presented in figure 2(a). A 532 nm single-frequency laser (Cobolt Samba) was used in the experiments. The laser power was set well below 1 mW through neutral density filters. For this laser power, a sample degradation was not detected. After each measurement, the surface was visually checked using white light illumination and a video camera installed at the microscope. The laser beam was focused with a 50× microscope objective (Olympus LMPLFLN50x, NA=0.5) on the screw rotor surface. The laser spot size did not exceed 2 μm. The scattered light was examined using a 0.75 m monochromator (Acton SpectraPro SP2750) with a liquid-nitrogen cooled charge-coupled-device (CCD) camera (Princeton Instruments PyLoN 2KF). An edge filter suppressed the laser light, so
Figure 2. (a) Scheme of the confocal Raman scattering setup. (b) Exemplary Raman scattering spectrum shows the scattered light intensity $I_{sc}$ as function of the energy shift with respect to the laser light energy. It was measured at a heavily worn surface position of the female screw rotor. The hematite (h) and magnetite (m) signals as well as the laser line are marked by arrows. (c) Raman spectra integrated over the three different spatial domains, which are marked by the light blue, dark blue and purple patterns in figure 1(d). The Raman line at 668 cm$^{-1}$ of magnetite and the two-magnon line at 1310 cm$^{-1}$ of hematite are selected for the mapping images shown in figure 3 and figure 4.

that scattered light signals with energy shifts of 50 cm$^{-1}$ with respect to the laser line position at zero energy shift could be resolved. The excavated part of the female screw rotor was placed on a microscopy table, whose position could automatically be changed with sub-micrometer spatial scanning resolution.

3. Results and Discussion

In a typical Raman scattering experiment the incident laser light interacts with a molecular vibration at the surface leading to scattered light whose energy is reduced or enhanced. The energy difference between the incident and scattered light is given by the energy of the elementary excitation, which has mediated the scattering process [6]. The energy shift, which provides information about the vibrational modes, indicates the type of the bonding; thus, the Raman shift can be used to identify chemical compositions. Light-weighted atoms give rise to large Raman shifts, while a weak bonding of atoms results in small Raman shifts. One can assume that the Raman shift $\Delta E$ is in good approximation proportional to the coupling strength $\sqrt{W}$ of the respective atoms and inversely proportional to the length $d$ of the bonding and effective mass $\sqrt{m}$ of the interacting atoms: $\Delta E \propto \frac{1}{d} \sqrt{\frac{W}{m}}$ [14]. Each type of bonding is characterized by unique motions of the atoms or molecules, respectively. One can distinguish between translational, rotational and vibrational motions. Accordingly, the molecules and chemical bondings can be described. Moreover, in amorphous samples the Raman lines are typically inhomogeneously broadened, since the chemical composition, molecular chain length and, for example, morphology underlie considerable variations at different sample positions. Since each variation causes slightly different Raman line energies, the integrated spectrum of the ensemble of molecular vibrations can be broadened significantly. Thus, the width of a Raman line is an essential parameter.
to describe local changes in the molecular vibrations and, in turn, to identify chemical and mechanical property changes across the surface.

To begin with, the experimental Raman scattering data for the excavated part of the female screw rotor are presented. In figure 2(b) an exemplary Raman spectrum obtained from a heavily worn surface position is shown. Six Raman lines are typically observed, their Raman shifts are approximately 230, 292, 405, 544, 668, and 1310 cm\(^{-1}\). Here, the error tolerance in the absolute spectral position is set to approximately ±10 cm\(^{-1}\). Within the scope of this article we do not want to go into details on line shifting and broadening. These lines can be attributed to molecular vibrations of iron oxide being present in different oxidation stages. Relying on the analyses of de Faria et al. and Shebanova et al. [15, 16], we assign the Raman lines detected at 544 and 668 cm\(^{-1}\) to magnetite, Fe\(_3\)O\(_4\). The lines with energy shifts of 230, 405, and 1310 cm\(^{-1}\) stem from hematite, α-Fe\(_2\)O\(_3\). The Raman line with an energy shift of 292 cm\(^{-1}\) cannot be related definitely to an iron-oxide vibrational mode. However, the integrated Raman spectra evaluated from the spatial mapping experiments, see figure 2(c), indicate that this line is most probably due to a magnetite molecular vibration.

Magnetite, which has a spinel structure at room temperature and contains both Fe\(^{2+}\) and Fe\(^{3+}\) cations [16], possesses several Raman bands. The two Raman peaks assigned above belong to the \(T_{2g}\) and, respectively, \(A_{1g}\) mode: The \(T_{2g}\) mode at 544 cm\(^{-1}\) is an asymmetric stretching of Fe and O, the \(A_{1g}\) mode is a symmetric stretch of the oxygen atoms along the Fe-O bondings [17, 18]. Apart from magnetite, maghemite \(\gamma\)-Fe\(_2\)O\(_3\), which also has a spinel structure with iron cations only in the trivalent state and is the second most stable polymorph of iron oxide [19], could give rise to the Raman lines observed. Nevertheless, the Raman signatures owing to vibrations of maghemite have a doublet-like structure thus being much broader than the Raman lines of magnetite [15]. Since the detected Raman lines are quite narrow, we rule out the presence of maghemite at the worn surface areas of the female screw rotor. In the following, the intensive \(A_{1g}\) Raman mode with an energy shift of about 668 cm\(^{-1}\) is considered as indicator of magnetite.

In comparison to that, hematite belongs to the rhombohedral (hexagonal) crystal space group. The Raman line at 230 cm\(^{-1}\) is an \(A_{1g}\) mode, which reflects a symmetric stretching of the iron and oxygen ions, the Raman line at 405 cm\(^{-1}\) describes a symmetric bending of the iron and oxygen ions (\(E_g\) mode), while the 1310 cm\(^{-1}\) line results from a two-magnon scattering process [15, 20]. In the antiferromagnetic hematite two magnons, which are collective spin waves, are excited at adjacent lattice sites with antiparallel spin orientations [20]. This two-magnon scattering line is not a feature of magnetite [15]. Accordingly, this line in the scattering spectra shall be exploited in the following to designate hematite.

The presence of wustite FeO and a participation of hydrogen in the iron oxide bondings forming oxyhydroxides cannot clearly be identified. However, the focus of future Raman scattering studies shall be drawn on the possible impact of those compounds on the tribological properties of the screw rotor contact zones. Moreover, we have carefully chosen the laser power to avoid a degradation of the laser illuminated surface domains. As underlined by de Faria et al. [15], we also observe changes of the Raman line features depending on the laser light power applied to the screw rotor surface. For high laser powers, we obtain Raman scattering spectra containing only signatures of hematite; we detect the laser-induced transformation called martitization of magnetite into hematite [21]. For future studies, it would be interesting to study the dependence of this transformation on the surface morphology of the screw rotors. A detailed laser wavelength dependence is also out of the scope of the present article, which will however be essential to identify the photochemical behavior of the iron oxides as well as oxyhydroxides.

In figure 2(c) the integrated Raman spectra characteristic for the heavily worn (light blue), transition zone (dark blue) and worn (purple) surface areas are shown. For the three differently worn domains, the Raman spectra of each \(2 \times 2 \mu m^2\) pattern square are summed up to provide an averaged spectrum. At the heavily worn surface positions hematite is present, while it is absent...
Figure 3. Confocal mapping of the $A_{1g}$ Raman mode of magnetite at about 668 cm$^{-1}$ across the three surface areas marked in figure 1(d). The energy shift (a), intensity (b), full width at half maximum (c), and integral intensity (d) are shown. These parameters result from Lorentzian peak fittings.

at the two other areas. Raman signals from magnetite are detected for all surface domains, while their intensities are considerably weaker at the transition zone. The change in the energy of the $T_{2g}$ magnetite Raman mode is interesting: Its line shifts from large energies at the heavily worn positions, 580 cm$^{-1}$, to small Raman shifts of 572 and 547 cm$^{-1}$ at the transition and worn areas, respectively. The position of the Raman line at about 300 cm$^{-1}$ also depends on the degree of wear, but it demonstrates an opposite trend (299 cm$^{-1}$ $\rightarrow$ 307 cm$^{-1}$) compared to the previously described Raman line. The shift to high energies, as demonstrated for the $T_{2g}$ magnetite Raman line, could be caused by compressive pressure leading to a reduction of the bonding length and an enhancement of the interaction strength [17]. Since a hematite Raman signal is less probable at the worn surface positions, one can propose that the Raman signals observed at the worn positions including the Raman line at about 300 cm$^{-1}$ belong to magnetite.

The properties of the magnetite-related Raman line with an energy shift of 668 cm$^{-1}$ evaluated from the mapping across the three surface domains, which are marked in figure 1(d) by the light blue, dark blue and purple colors, are shown in the panels of figure 3. While the changes in the Raman shift do not exceed considerably the $\pm$10 cm$^{-1}$ error tolerance, the line intensity varies significantly. At worn positions (left area) the intensity is homogeneously distributed. At the transition zone the magnetite-related Raman line practically vanishes, and at the heavily worn domain the intensity fluctuates remarkably. The same behavior can also be observed for the full width at half maximum (FWHM) of the line, see figure 3(c), and the integral intensity, see figure 3(d).

For the two-magnon scattering line with an energy shift of approximately 1310 cm$^{-1}$, which is clearly attributed to $\alpha$-Fe$_2$O$_3$, the spatial mapping yields distinct differences, see panels of figure 4: At the worn and transition areas, the two-magnon line is not observed. It is only present at the heavily worn surface positions, as concluded from figure 2(c). At the latter region, the line parameters furthermore demonstrate strong fluctuations. The energy shift ranges from 1300 to 1400 cm$^{-1}$ at several positions. The relatively weak intensities and large line widths indicate a great distribution of different energies of the magnon scattering process and a small amount of hematite across the surface area selected.

The appearance of hematite at the heavily worn surface positions of the female screw rotor may result from high temperatures being present during the liquid-free wear process at the contact zone of the screw rotors. Temperatures of about 400°C are necessary to initiate the transformation of magnetite to hematite [15]. Due to the significant spatial variations in the hematite signal parameters one may propose that such high peak temperatures were present and
Figure 4. Confocal mapping of the two-magnon scattering line of hematite at about 1310 cm\(^{-1}\) across the three surface areas marked in figure 1(d). The energy shift (a), intensity (b), full width at half maximum (c), and integral intensity (d) are shown; they are evaluated from Lorentzian peak fittings. A black colored square indicates the absence of the hematite related two-magnon scattering line.

locally different. Not only a high temperature input, but also a mechanical deformation combined with a high pressure transfer in the GPa range may cause the formation of rhombohedral $\alpha$-Fe\(_2\)O\(_3\). Besides that, it is surprising that the surface positions without heavy wear history contain primarily magnetite as iron oxidation product. The line width is not broadened thus highlighting a homogeneous distribution of bond lengths and strengths. At those surface positions neither the temperature nor the pressure input was so high that the chemical bonding structure was considerably changed. The transition zone with its bright reflective character may hint at a white etching crack. At this domain the formation of iron oxides seems to be less probable, or the related Raman lines cannot be probed by the laser illumination due to a weak absorption. For future experiments, it would be interesting to identify the detailed chemical composition profiles of the surface domains and to solve the reason of their formation and their coupling with the substrate material. Since a phonon spectrum provides insight into the lattice vibrations and thermodynamic features, one may think about the description of the specific heat and magnetic contribution to the thermodynamic properties of the iron oxide compounds in further studies.

4. Conclusion
On the whole, we demonstrate that micrometer-sized areas of magnetite and hematite are detected at differently worn 18CrNiMo7-6 steel surfaces of screw rotors through confocal Raman scattering. A thermally activated transformation of magnetite to hematite during the liquid-free screw rotor operation is proposed to be the reason for the appearance of $\alpha$-Fe\(_2\)O\(_3\) at the heavily worn surface domain, where material was worn out. Magnetite-related Raman signals are found at the heavily worn and, in particular, worn surface domains. At the latter area their line widths do not change significantly thus indicating a weak distortion of the Fe-O bonding length and strength.

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