Effect of external magnetic field on tribological properties of goethite (a-FeOOH) based nanofluids.

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Abstract

Additives responsive to magnetic fields can be easily manipulated under the action of external stimuli and employed in various sectors, with great feasibility. In this work, suspensions of goethite nanorods were developed for anti-friction and anti-wear purposes. Goethite represents a promising additive in lubricants promoting the formation of a protective tribofilm during rubbing processes, especially under severe lubrication regime.

Nanofluids were characterized regarding both viscosity and stability. Tribological *ball-on-flat* tests were executed in presence of variably oriented magnetic field. The resulting orientation of nanorods within the contact zone influenced the friction coefficient with a maximum decrease of 22% with magnetic field oriented parallel to the sliding direction. The wear mechanism was investigated by means of SEM, X-EDS and Raman spectroscopy.

Keywords: Nanolubricants, goethite, tribofilm, lubrication, wear

1. INTRODUCTION

Friction phenomena cause wear of mechanically coupled materials and undesirable energy dissipation, and are responsible for about 20% of the world's energy resource consumption, by considering both direct and indirect effects [1]. Hence, the protection against the detrimental effects of reciprocal sliding motions has been lately recognized as a key factor in the future energy saving programs. Researchers are encouraged to develop new solutions to minimize friction and wear during the operation of various mechanical equipment, improving their efficiency, reliability, productivity and longevity and limiting maintenance costs [2].

The growing request for higher energy efficiency has brought the research towards new materials to be used as lubricant additives. In the last decades, nanofluids for lubrication, i.e. nanolubricants, are being studied and developed to meet these requirements. They are colloidal suspensions of nanoparticles in a carrier fluid. Such multiphasic systems are gaining increasing interest in tribology and energy-related fields, for their unusual anti-friction and anti-wear properties, which make them suitable for wear protection purposes, energy saving and increase of efficiency in devices operating with sliding contacts in a wide range of applications [3-5].

Nanomaterials are added to lubricating oils to improve their tribological properties and load-carrying capability. Various types of nanoadditives, typically in the 1 to 100 nm size range, have been recently considered for this purpose, including graphene-based or fullerene-based nanostructures, inorganic and organic nanoparticles, hybrid nanoparticles, quoting just the latest ones [6-10]. Nanoparticles have a mean size that allows them to enter easily the contact area, thus bringing positive effects to the lubrication activity of the base oils. Spikes [11] summarized some potential benefits of using nanometric additives in lubricants, like insolubility in non-polar oils, low interaction with other additives in oils, formation of protective film on different kinds of surface, long durability and non-volatility to endurance high temperature working conditions.

The effectiveness of nanoparticles dispersed in oils is related to their action mechanism within the contact zone during sliding, which depends on both their intrinsic properties and experimental conditions. Among suggested mechanisms, the scientific community has recently acknowledged four main actions played by dispersed nanostructures: (i) the rolling effect [12, 13], typical of spherical particles which likely act as tiny ball bearings, thus changing the sliding friction into a mix of sliding and rolling friction; (ii) the protective tribofilm formation [14, 15], which occurs due to interactions induced tribochemically, between the nanoparticles and the sliding surfaces; (iii) the mending effect [16, 17], where nanoparticles can deposit inside the grooves and the valleys of surface roughness, thus compensating for the loss of mass; (iv) the polishing effect [18, 19], that causes the reduction of the mean surface roughness of the sliding materials due to nanoparticle-assisted abrasion.

Generally, boundary lubrication is the most severe regime, and is expected to occur in start-stop phases and in periods of severe operation in the contact zone between sliding surfaces. The dispersion of nanoparticles can reduce friction and wear phenomena especially in boundary and mixed regimes [20].

The name “intelligent materials” encloses a wide group of materials whose properties can be controlled to a certain extent by external stimuli. Among them, there is goethite (α-FeOOH), which is an antiferromagnetic iron oxyhydroxide. Nanoparticles typically exhibit an acicular (needle-like) form and are often aggregated into bundles of oriented crystallites, in the sub-micrometer to micrometer size range. Goethite nanorods are typically synthesized by conversion of precursor ferrihydrite nanoparticles and precipitation of the new phase from homogeneous solutions followed by ageing [21, 22]. Variable chemical environments can produce different crystal morphologies [23-25]. Once the nanorods are formed, oriented aggregation occurs, which can provide a method for controlling final size, shape and microstructure.

Unlike bulk materials, goethite nanorods have peculiar magnetic properties, since they hold a permanent longitudinal magnetic moment, along particle long axis. They also show a negative magnetic susceptibility, along the shortest particle dimension, leading to the formation of a lyotropic nematic phase that aligns in magnetic fields [26, 27]: the nanorods orient parallel to the field at low intensities, and reorient perpendicularly when the magnetic field overcomes a threshold, typically the magnetic induction B=0.35 T [28, 29]. Goethite nanoparticles show symmetries that appear hybrid between those of nematics and ferrofluids [27, 30]. Thus, by applying a suitable external magnetic field to the mineral nematic phase, it becomes possible to steer the orientation of anisotropic nanoparticles and exploit this property to improve performance of existing systems [31]. Recently, magnetic nanoparticles have received much attention due to their great potential for technological applications, including magnetic record, drug delivery agents, imaging and therapy [32]. However, less systematic research has been reported on these materials as oil additives to date [13, 33].

In this work, stable suspensions in lubricating oil of goethite nanorods with different morphology, size and self-organization properties have been prepared to test for anti-friction and anti-wear purposes. A α-olefinic hydrocarbon synthetic oil (PAO) was selected for this purpose. Some important characteristics make PAO oils particularly interesting for developing new lubricants, such as their high thermal and oxidative stability, the low volatility, the excellent low-temperature viscosities, their wide operational temperature range, the high viscosity index, low corrosivity and toxicity and finally the compatibility with various materials of construction and with mineral oils.

Goethite represents a promising and new functional additive in lubricants to promote the formation of a protective tribofilm during the rubbing process, because of tribochemical reactions, especially under severe working conditions, such as in boundary lubrication regime [34]. The microstructure and composition of the tribofilm affects the friction coefficient, as it separates the first bodies of the tribopair and may act as a protective oxide layer against the wear of the first bodies. The final aim of this study was to investigate the influence of a variably oriented external magnetic field on tribological properties, in boundary lubricating conditions, of goethite nanorods dispersed in bare oil. Since goethite is generally investigated for water purification, sensing of humidity, coatings, lithium-ion batteries and for many other applications due to its chemical stability at room temperature, low cost and nontoxicity, the tribological performance of α-FeOOH has been rarely reported in the literature, thus supporting the originality and novelty of this study. Previously, in the tribological sector, goethite has been recently used as filler, to reduce friction and wear of polymer composites, in the case of PEEK reinforced with small amount inorganic nanoparticles [35]. Then, it has been added in form of micro-particles in a dispersion of zinc metaphosphate in oil, leading to the formation of a tribologically effective depolymerized zinc-iron phosphate tribofilm [34].

2. MATERIAL AND METHODS

2.1. Preparation of nanolubricants

Nanolubricants were prepared by a two-step method, by dispersing previously synthesized α-FeOOH nanorods inside the synthetic base of PAO lubricating oils. The synthetic base of PAO was chosen to have only the olefin and no lubricant additives, thus being able to study the nano-additive effect on tribological properties, not altered by the presence of unknown compounds. Production methodologies of goethite nanorods have been described in detail elsewhere [36]. In the synthesis of goethite nanorods, $Fe(NO_3)_3{\cdot}9H_2O$ (99% pure, provided by Sigma-Aldrich) was used as metal oxide precursor; NaOH (anhydrous pellets, provided by Carlo Erba) or Tetraethylammonium hydroxide (solution, 35%$_{wt}$ in H_2O, provided by Sigma-Aldrich) were used to prepare co-precipitation ferrihydrite solutions; deionized water (Millipore, Billerica MA, USA, 18.2 MΩ) was used as solvent.

Three different samples, named RT, T and US, have been synthesized by following different preparation routes summarized as following. Sample RT has been prepared by adding $Fe(NO_3)_3$ to NaOH solution, leading to a ferrihydrite precipitate which was aged afterwards at room temperature for three days. Sample T has been prepared by adding dropwise Tetraethylammonium hydroxide (TEAH) to $Fe(NO_3)_3$ solution at room temperature until the solution reached pH 12, followed by ageing an oven for 24 hour at T=60°C. Finally, sample US has been prepared by adding TEAH to a $Fe(NO_3)_3$ solution at room temperature, followed by an ultrasound irradiation treatment.

After the ageing period, the obtained goethite precipitates were purified by centrifugation and the pH adjusted to 12 with NaOH to gain adequate stability. In order to achieve stable suspensions of goethite nanorods into PAO, solutions containing 0.2%$_{wt}$ dioctyl sulfosuccinate and 0.1 %$_{wt}$ α-FeOOH in water were stirred to favour the adsorption of surfactant on the surface of nanorods and then centrifuged to precipitate them. The 0.1%$_{wt}$ concentration was chosen based on typical concentrations tested in nanolubricant studies [3-5]. After drying at 105 °C for 1h, a suitable amount of PAO was added to obtain 0.1%$_{wt}$ suspensions by sonication using a Sonics VCX130 (Sonics & Materials, Inc.) operating at 20 kHz and 130 W, equipped with a 6 mm diameter Ti_6Al_4V alloy tip, operated at 70% power. The main features of used PAO oil are summarized in Tab. 1.

Properties	
Viscosity	
- @ 40°C	20 cSt
- @ 100°C	5.6 cSt
Density @20°C	0.818 g cm^{-3}
Boiling Point	>316°C
Flash Point	>113°C
Viscosity-pressure coefficient α* @25°C	19.7 GPa^{-1}

Tab. 1. Main properties of PAO lubricating oil used as base fluid (So-Klaus method)*

2.2. Physical and tribological characterization

Dynamic Light Scattering (DLS) measurements were carried out on prepared nanofluids, containing dispersed goethite nanorods, for the stability characterization. DLS data were obtained with a Malvern Zetasizer Nano ZS, by evaluating the mean size of suspended aggregates for 20 days, in order to detect possible aggregate settling.

Rheological characterization of nanolubricants was carried out at room temperature by a rotating disk type rheometer with a cone-plate geometry (AR G2, TA Instruments). The declared experimental uncertainty is 5%. The viscosity measurements were functional to the tribological characterization, which was performed at room temperature with a Bruker UMT-2 tribotester, set for pure sliding contact geometry and operating in *ball-on-flat* configuration. The non-conformal contact between the Al_2O_3 counterbody and the AISI 304 SS substrate, was investigated, with and without the presence of a variably oriented 50 mT applied magnetic field, i.e. parallel, perpendicular and axial with respect to sliding direction. The Al_2O_3 balls were supplied by RGPBALLS S.r.l., with a certified hardness of 1500 HV and produced according to ASTM F 2094 standard. The substrates were obtained from a commercial bar with certified hardness of 165 HV.

The reason for choosing Al_2O_3 as counterbody material was dual: on one side, aluminum oxide is considerably harder than stainless steel, thus being able to provide significant wear on the metal surface, remaining almost unchanged. On the other side, eventual contamination from counterbody would not create misunderstanding in the interpretation of results obtained from post-mortem characterization, especially in Raman and X-EDS analyses.

The mean roughness prior to wear tests for SS substrate and Al_2O_3 ball was R_a=0.025 µm and R_a=0.005 µm, respectively. Tribological experiments lasted for 120 min and an average sliding speed of 10 mm/s was set, via linear reciprocating motion mode in order to develop boundary lubrication conditions. The normal load was kept constant in order to obtain 500 MPa of initial Hertzian contact pressure [37]. The schematic representation of the setup is reported in Fig. 1.

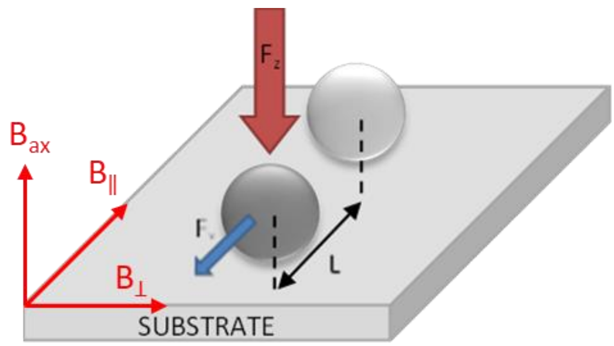


Fig. 1. Scheme of the used configuration for tribological tests.

Experiments were implemented in presence of a ring magnet, diametral or axial depending on the desired orientation for the applied magnetic field, positioned on the steel substrate, so that field lines crossed the contact area and were variously oriented, i.e. parallel and perpendicular in respect to the sliding direction of the counterbody and to the sliding plane. Ring magnets, diametral and axial ones, were selected for the simplicity of orientation of the magnetic field in the desired directions for conducting the experiments. The magnet was firmly fixed on the substrates, while the counterbody was free to move inside it, progressively developing the wear track for succeeding characterizations.

In order to ensure complete separation of the mating surfaces, it was important to predict the film thickness under actual operating conditions for the applied lubricant. In this study, the lubrication regime, accounted from the central film thickness (h_c) and the lambda ratio λ, i.e. ratio of estimated lubricant film thickness to composite surface roughness, were estimated with the classical theory of Hamrock and Dowson [38-41]. It is a well-established empirical power-law film thickness expression for elliptical contacts that is used by many investigators to predict the film thickness as a function of the operating conditions. In this work, h_c was estimated as 0.01 µm.

The family of Hamrock and Dowson formulas are interpolation formulas fitted on numerical results for specific lubrication regimes, and the film thickness approximation is defined in different sets of non-dimensional groups. [38, 42, 43].

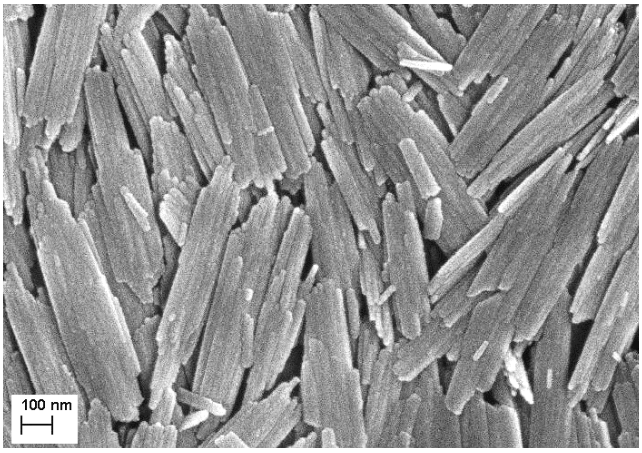
The general classification of lubrication regimes based on lambda ratio is: $\lambda>3$, $0.5<\lambda<3$ and $\lambda<0.5$ [44] corresponding, respectively, to thin film/EHD, mixed and boundary lubrication. The calculated value for λ was 0.28, well below the limiting value 0.5 for mixed regime, thus indicating that boundary lubrication conditions were achieved during wear tests. All experiments were repeated three times and showed very low variation in friction, so only responses of one representative experiment were presented here.

The topography of worn surfaces was examined by optical microscopy and by FE-SEM (Sigma, Zeiss). For each sample, wear tracks dimensions and depths were measured with a stylus profiler (Dektak XT, Bruker). The worn volume was also been estimated according to ASTM G133-02 [45]. The volumetric wear loss was calculated using the geometrical relations given in the standard, by measuring the wear tracks after the test with the stylus profilometer. The evolution of the expected tribofilm was analysed by means of X-EDS spectroscopy (Oxford Instruments) and µ-Raman spectrometer (InVia Renishaw) with excitation at 488 nm.

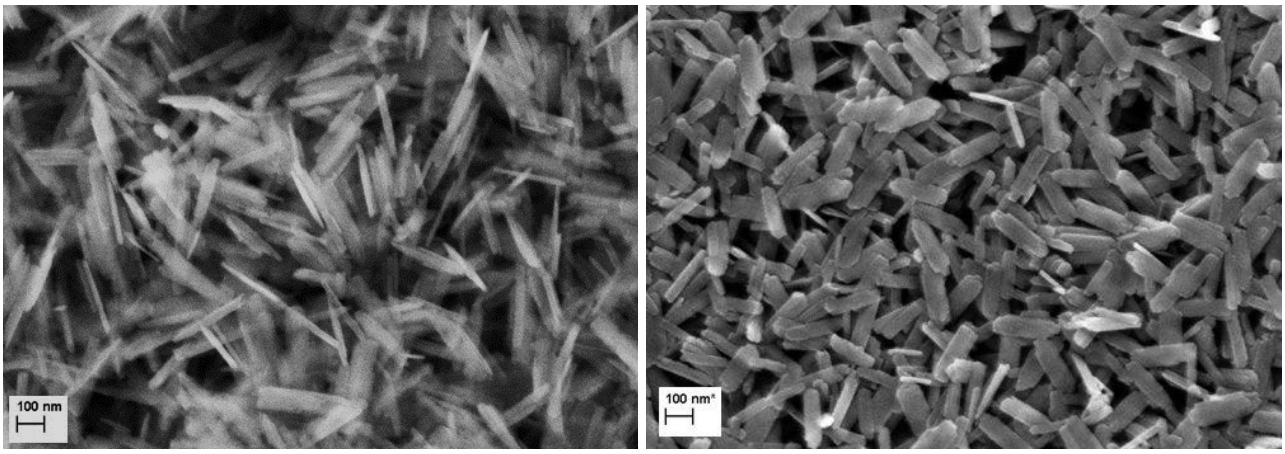
3. RESULTS AND DISCUSSION

3.1. Morphology of goethite nanorods

Produced goethite nanorods have been analysed morphologically by means of scanning electron microscope, before being dispersed inside the PAO lubricating oil, in order to evaluate their shape, size and aggregation state. Collected micrographs are reported in Fig. 2(a-c):



(a)



(b) *(c)*

Fig. 2. SEM pictures of synthesized goethite nanorods: samples (a) RT, (b) T and (c) US

From morphological analyses, some relevant differences appeared among samples: RT nanorods, produced with NaOH as alkaline reactant and aged at room temperature, were (460 ± 80) nm long, a few tens of nanometers thick and appeared strongly packed into sub-micrometric nematic arrangements, also called mesocrystals [46]. Within a nematic single domain, all rods spontaneously tend to align in the same direction, in contrast with the isotropic phase in which the rods point in random directions. Differently, T and US nanorods were not organized and showed different aspect ratio appearing thinner and/or shorter, about (240 ± 30) nm in length and 10 nm thick for sample T, and (210 ± 20) nm in length for sample US. In addition, the shape was unalike, since sample T exhibited an acicular morphology, while US one looked mainly constituted by small platelets with rounded edges.

XRD characterization of goethite samples was performed and Rietveld refinement was carried out to analysed collected patterns. The complete conversion from ferrihydrite to goethite has been achieved for all samples. The detected crystal structure was orthorhombic with space group *Pbnm*. Detailed characterization is reported elsewhere [36].

Finally, these nanorods did not show any packing effect, similar to that observed for sample RT, and instead the isotropic phase could be recognised [28]. This last characteristic could bring to a higher and faster mobility of nanorods, in presence of an applied variable external stimulus, expected for T and US samples in respect to RT, for which a higher inertia was speculated. The peculiar small size of US nanorods could let them change more rapidly their orientation, providing lower response times, also compared to T type [47].

A picture of prepared nanolubricants, containing various type goethite nanorods are shown in Fig. 3. The typical goethite ochre colour characterized the three samples.

Fig. 3. Pictures of goethite-based nanofluids.

3.2. Stability and viscosity of nanolubricants

The suspensions of PAO base oil containing 0.1%$_{wt}$ α-FeOOH nanorods were analysed by Dynamic Light Scattering (DLS), in order to determine its stability over time, by measuring the average size of the suspended aggregates, showed in Fig. 4.

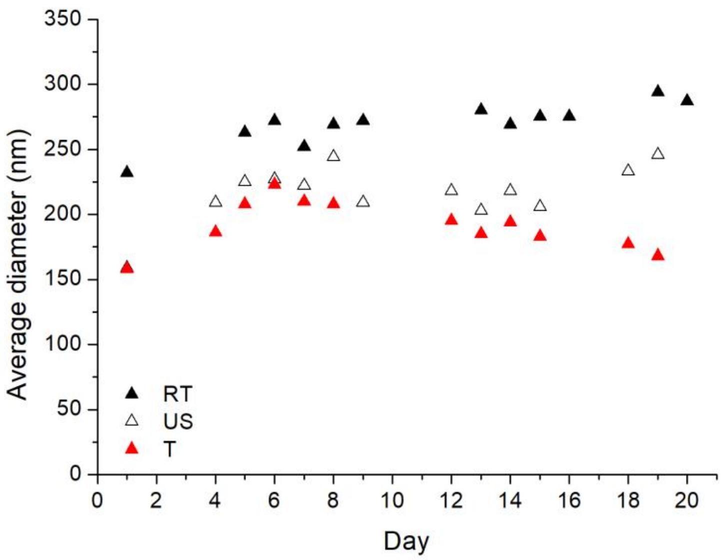


Fig. 4. DLS data collected over 20 days from prepared nanolubricants.

Dynamic Light Scattering (DLS) measurements confirmed the stability of nanolubricants for over two weeks. DLS data showed stable size trends for nanolubricants, since measured average size of suspended nanorods did not change significantly during measuring time, leading to infer that no important aggregation phenomena took place during the evaluation period, thus revealing a satisfactory stability with time.

After the dispersion of goethite nanorods, viscosity measurements were carried out in order to evaluate the influence of the additives on the behaviour of the PAO oil. The viscosity trend with shear rate is reported in Fig. 5, and shows the Newtonian behaviour of the nanofluids containing 0.1 $\%_{wt}$ of all types of nanorods: viscosity appeared nearly constant with shear rate for all tested samples.

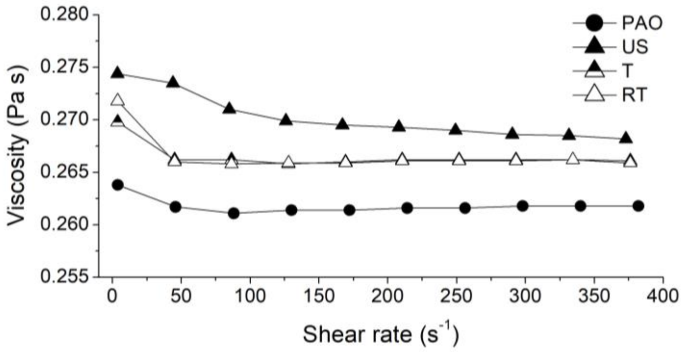
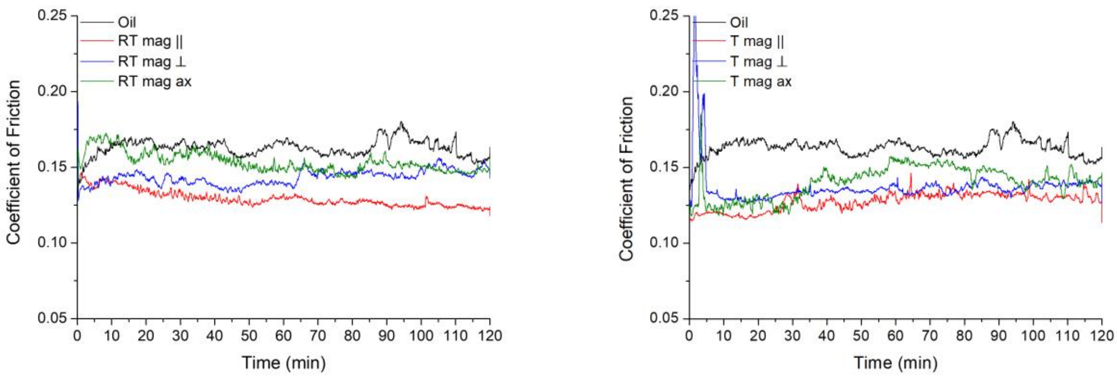


Fig. 5. Dynamic viscosity measured for nanolubricants containing different type of goethite nanorods

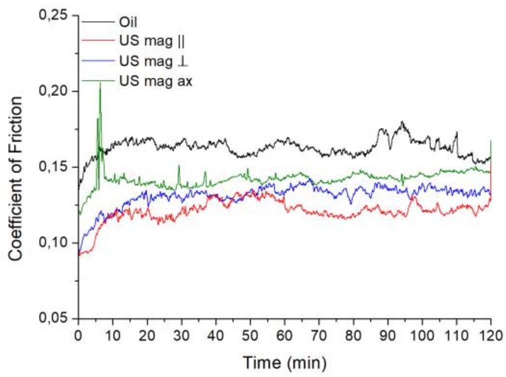
A maximum variation of 2.7% for US sample was recorded, which was within the rheometer uncertainty. Thus, results stated that the addition of α-FeOOH in PAO did not significantly affect the physical properties of the raw oil.

3.3. Tribological behaviour of goethite based nanolubricants

Collected data referring to Coefficient Of Friction (COF) versus sliding time are reported in Fig. 6 pointing out the trends developed during each experiment for differently oriented applied magnetic field, i.e. parallel, perpendicular and axial direction in respect to the sliding path.



(a) (b)



(c)

Fig. 6. Friction coefficient versus sliding time for differently oriented magnetic field. (a) RT, (b) T and (c) US based nanofluids.

It can be noticed that the curves relative to nanofluids appear lower than that referring to the raw oil alone, indicating that goethite nanorods acted as effective friction modifiers during sliding, thus providing sensitive decrease of friction phenomena within the tribological pairs. Best results were obtained by orienting the applied magnetic field parallel to the sliding direction of the counterpart during tribological experiments, for all tested samples.

Fig. 7 shows the mean values of the friction coefficient in the steady state, recorded during wear tests, after the run-in period, when the stabilization of the signal occurred.

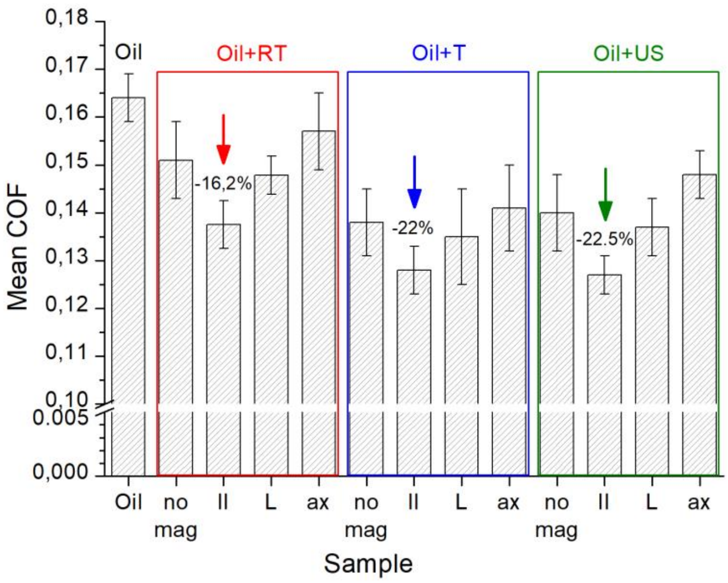


Fig. 7. Mean COF values during sliding tests with variably oriented external magnetic field

Evident friction reduction was noticed, due to the addition of goethite nanorods, in each tested configuration. The best results were obtained, for all three nanolubricants, by orienting the magnetic field parallel to the sliding direction ($B_{\parallel}$), which accordingly represented an optimal arrangement to make the additives the most effective as possible as friction modifiers. The reason of this preferential orientation of the magnetic field is that nanorods aligning parallel to the sliding direction can better compensate the formation of wear scratches, thus maintaining the contact zone smoother and reducing mostly friction phenomena. Moreover, another phenomenon has recently gained great interest inside the scientific community and could be considered in this case: the frictional anisotropy that has been observed in some anisotropic materials [48].

Accordingly, since friction force can be anisotropic with respect to the crystallographic direction of sliding, the variation of nanorods alignment with differently applied magnetic field can cause a superior beneficial effect on friction for a particular direction [49]. The nanorods could provide significant resistance while the counterbody slides perpendicularly over them, i.e. in the perpendicular and axial orientation of magnetic field, while when the tip moves along the alignment of nanorods, they present the most favourable crystallographic direction in terms of friction.

Generally, at high applied loads, typically over 1 GPa, the deformation is the dominant mechanism of friction, as opposed to adhesion at lower loads [50]. Therefore, an increase in contact area as the tip touches the sides of the nanorods brings to a behaviour that is similar between a conventional thin film and the nanorods trapped into the contact area, limiting the gaps between them, because of tribologically induced deformation phenomena. A similar effect, but gradually less marked, could be ascribed for the other orientations of the applied magnetic field.

The maximum decrease of friction coefficient was observed for nanofluids containing nanorods from samples T and US, for which the reduction was estimated around 22%.

Therefore, T and US morphologies resulted the most effective in reducing the severity of friction phenomena, probably owing to their higher mobility and because they were more likely to adapt their orientation in respect to both the applied magnetic field and the evolving topology of the rubbing surfaces.

3.4. Action mechanism of goethite nanorods

Since the most promising tribological results were obtained with the orientation of the applied magnetic field parallel to the sliding direction, their tracks were in depth characterized. Size and morphology of wear scars were inspected by means of stylus profilometry. Linear profiles were collected for each scar and are shown in Fig. 8.

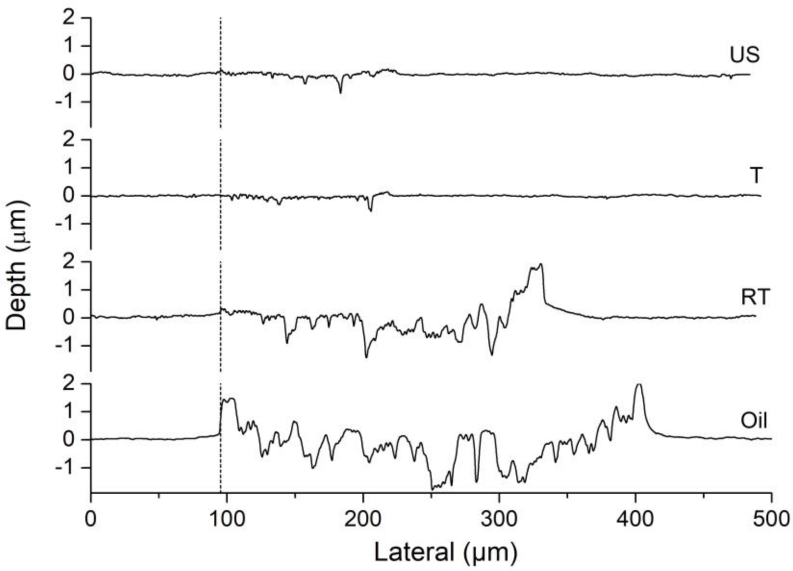


Fig. 8. Linear profiles of wear scars for each nanolubricant

It clearly appeared that US and T samples outperformed both the raw oil and RT sample, and exhibited the best tribological behaviour. In fact, the scar width was approximately 110 µm for both these specimens, while scar widths of 220 µm and 300 µm were measured for the RT sample and PAO oil, respectively. Thus, US and T type nanorods were able to reduce the dimension of the wear scar of more than 60% in respect to raw oil, and proved to bring beneficial effects to the overall tribological coupling during sliding. Also RT sample provided a smaller benefit, and the width of the produced track was reduced by 25% compared to PAO.

Furthermore, the roughness at the bottom of the tracks was measured for each sample and results are reported in Tab. 2.

Sample	**R_a (µm)**	**Var**
Oil	0.363 ± 0.008	-
Oil+RT	0.258 ± 0.008	-29 %
Oil+T	0.045 ± 0.004	-88 %
Oil+US	0.042 ± 0.003	-88 %

Tab. 2. Mean roughness at the bottom of wear scars

A noticeable decrease of mean roughness was detected for substrates treated with nanolubricants containing US and T type nanorods, confirming their outstanding wear protection properties. The measure of R_a was found to be almost an order of magnitude lower than what observed for PAO alone. The smoothing effect could be ascribed to a certain polishing action played by dispersed additives on rubbing surfaces and has been already suggested by several authors, for nanoparticles which cannot roll inside the contact zone because of their shape and hardness, and therefore are dragged along the wear scar by the counterbody [19].

Since there was no significant ball wear (no worn area was detected on alumina balls surfaces by optical microscopy), the estimated worn volume was calculated for stainless steel substrates, and it is reported in Fig. 9 for each sample, appearing significantly reduced in all tests performed with nanolubricants.

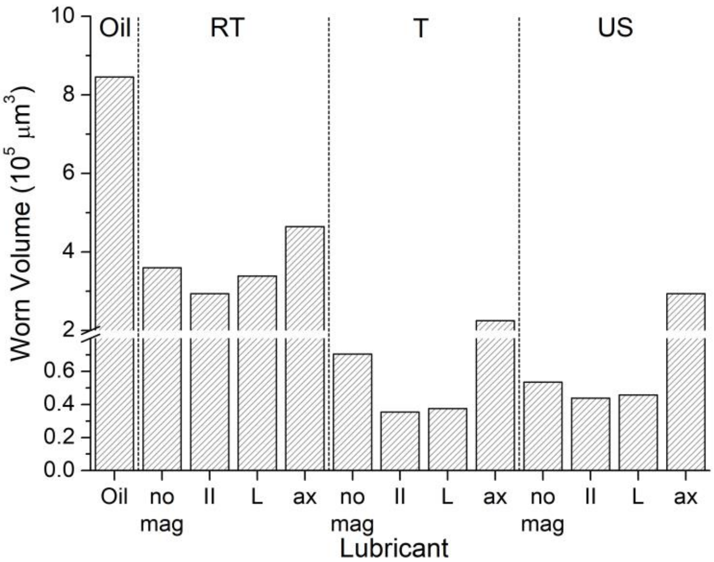
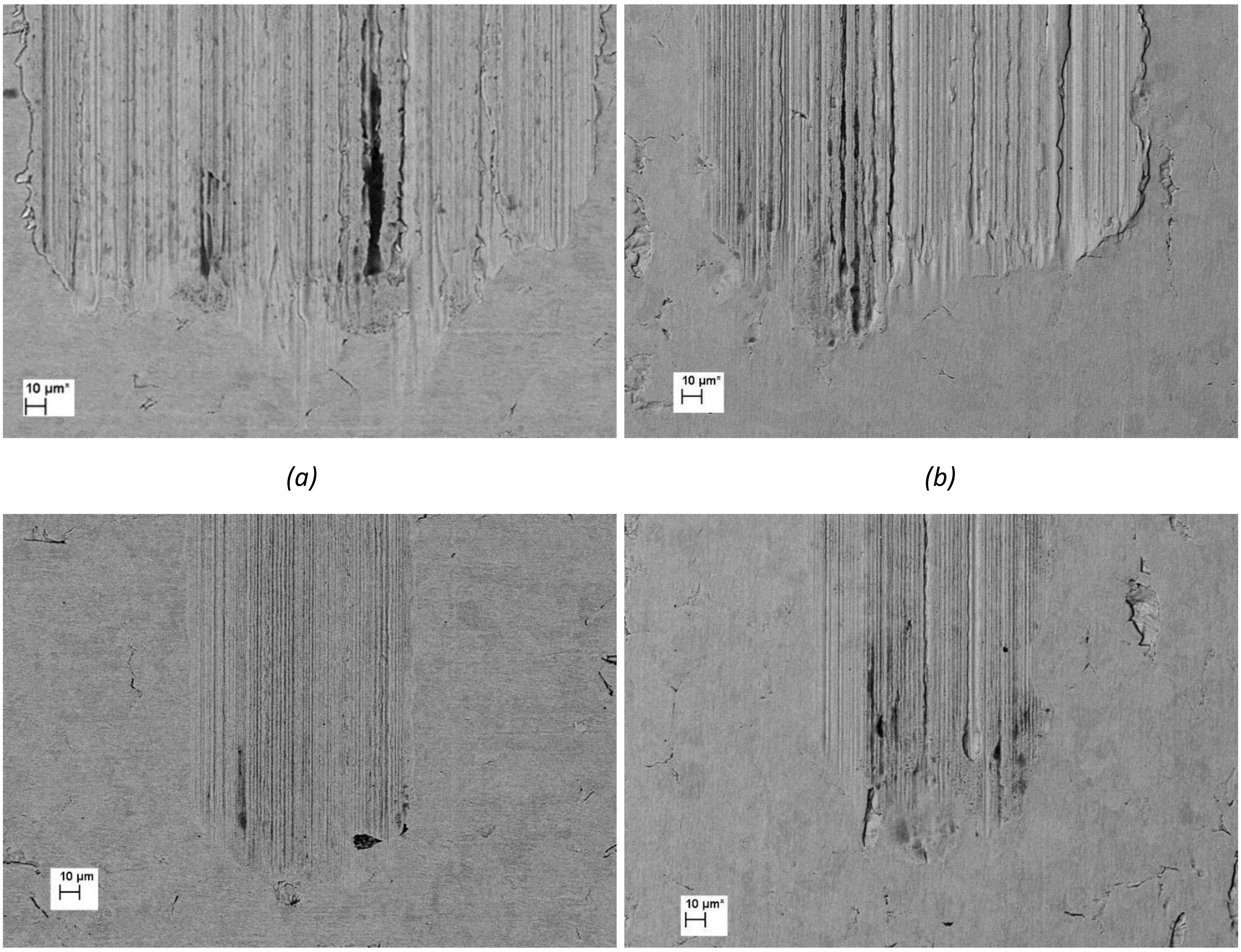


Fig. 9. Estimated worn volume after wear tests.

The maximum wear protection occurred in presence of T and US samples and with applied magnetic field in the rubbing plane, regardless of the direction of the magnetic field. Good results were also obtained without the magnetic field, although slightly lower than those observed with the field parallel or perpendicular to the sliding direction. The axial orientation of the magnetic field revealed to be the less performing, since nanorods should be oriented perpendicular to the sliding plane, thus providing the maximum resistance to the movement of the counterbody and consequently enhancing the active friction phenomena as they beneath the indenter tip deflect against the sliding direction. Similar results were achieved also by Mohanty *et al* [49] and by Hirakata *et al* [51] who analysed the effect of sliding direction against variably tilted molybdenum nanorods and titanium nano-column arrays. The overall wear decrease detected for US and T samples was one order of magnitude in respect to the raw oil. Wear tests in presence of variably oriented magnetic field were also carried out with the raw oil, in order to exclude that there was a possible magnetic response from the oil itself rather than from dispersed goethite based additives. Results (not reported here for brevity) revealed high reproducibility for PAO regardless the direction of the applied magnetic field.

The difference in tribological behaviour among different nanolubricants lies in the variable packing properties of nanorods, since those having high motion freedom (T and US type) appeared more effective for wear reduction purposes than steadily packed ones (RT). In fact, both T and RT sample, despite individual goethite nanorods exhibited a similar acicular shape, performed very differently, just because they show a very different aggregation state. Moreover, T sample tribologically behaved like US, although the last one was constituted by shorter and thinner nanoplatelets. Thus, the explanation of such dissimilar action mode was attributed to the packing tendency of different goethite nanomaterials rather than to their peculiar shape. In fact, RT type nanorods tend to form oriented aggregates, building larger particles held together by weak bonds or stronger magnetic interactions, even reaching micrometric size. Such aggregates are less tribologically effective, because of great inertia of movement and slower response to the applied magnetic field. Moreover, they are less prone to enter the contact zone for their large dimensions. Fig. 10 (a-d) shows SEM micrographs of wear scars.



(a) *(b)*

(c) *(d)*

Fig. 10. SEM images of the topology of the wear scars obtained with (a) raw oil, (b) RT, (c) T and (d) US.

The micrographs confirmed the superior protective and anti-wear effects provided by US and T samples, as observed by profilometer. Beside the polishing effect, the other most probable action mechanism for such promising results could be ascribed to the formation of a protective tribofilm at sliding interfaces, due to tribochemical reactions between the additives in lubricating oil and the sliding materials, which can prevent metal-to-metal contact [52].

In the formation of a tribofilm, three different routes can be generally followed: the nanorods can be melted and welded on the shearing surface, can be tribo-sintered to the surface or can react with the sliding materials to form a protective layer [53]. In this case, the third process is the more likely, since nanometric α-FeOOH is considered unstable relative to more oxidized phases and hence the evolution of dispersed additives and their conversion in a Fe-O rich protective tribofilm could be supposed [54].

According to the "third body approach" [55, 56], the wearing surfaces are separated by a debris layer, which protects the sliding materials by supporting the bearing load and providing a means for the accommodation of the shear displacement between the faces. In this case, the particles were artificially supplied to the contact zone by the lubricant itself, thus the formation of a compacted oxide film could be responsible of the wear reduction in the contact area, due to the interruption of metal-metal contact by oxide.

The formation of the tribofilm was investigated by means of micro-Raman spectroscopy and X-EDS, both applied to worn samples in the post-mortem state, to get a cross-check and better evaluate the composition and final state of surfaces. Raman mapping provides chemical information coupled with spatial information.

μ-Raman spectra were useful for determining the changes in the surface induced by sliding. Fig. 11 reports, as an example, the Raman maps for raw oil and US sample, where the differences in maps were more evident. Image contrast results from multivariate analysis of the information contained in collected Raman spectra. Principal Component Analysis (PCA) [57] was applied to obtain the most relevant spectral features present on the sample, which can be observed in Fig. 11(b) and 11(d). The absence of the principal components found inside the scar in the region outside the scar shows that the transformation could be observed only within the scar.

The PC loadings on Fig. 11(d) could be attributed to a sliding oxide conversion of the pristine goethite (band at 390 cm^{-1}) to a mixture of contributions from more phases, including hematite (band at 290 cm^{-1}) and magnetite (band at 640 cm^{-1}) [58], in line with the tribological results above. μ-Raman chemiometric maps, in Fig. 11(a) and 11(c), were so reconstructed by the abundances of the features found respectively on Fig. 11(b) and 11(d).

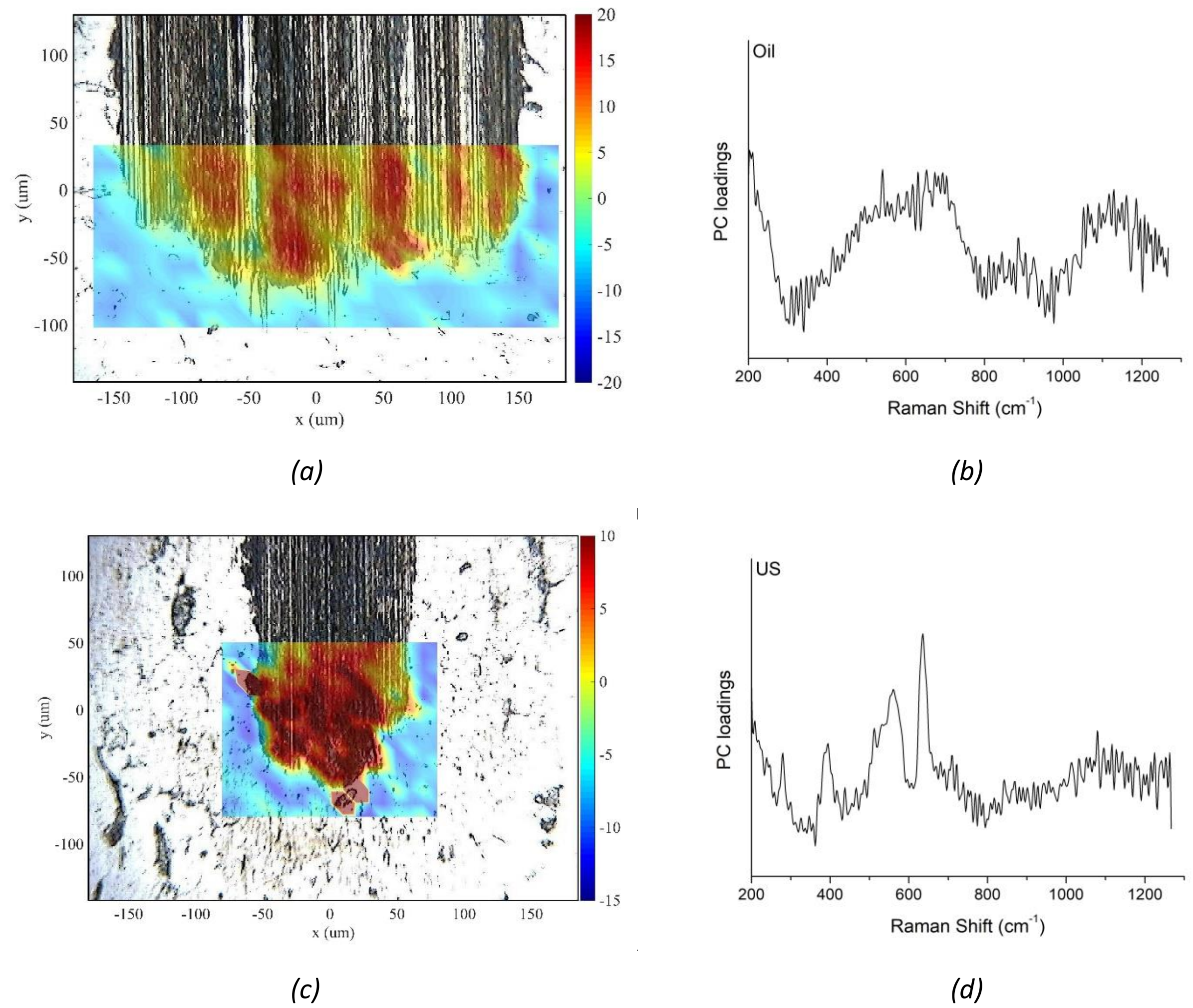


Fig. 11. Raman maps and spectra from wear scars obtained with PAO oil (a, b) and US sample (c, d)

Raman map of RT sample, not reported for brevity, was similar to the raw oil one, and exhibited the same broad bands localized at about 600 cm^{-1} and 1100 cm^{-1}. At the same time, no obvious signals from preceding goethite could be detected in collected spectra of each sample, thus confirming that goethite nanorods underwent tribochemical reactions during sliding, thus evolving towards the formation of a compound having a different chemical nature.

These results allowed to presume that US type goethite nanorods were particularly prone to evolve towards a more stable oxidized form, compatible with Fe_3O_4 (magnetite), through tribochemical reactions during sliding and by forming a protective tribofilm, capable of hindering detrimental effects of friction and wear and limit damages of the substrate [59]. The formation of oxide-based tribofilms, when supplying Fe-based nanoadditives within the tribopair, has been already observed by several researchers [60-62].

The freedom of individual nanorods, which were able to easily enter the contact zone and favourably orient with the applied magnetic field, was responsible of higher efficiency of US type goethite and accounted for the formation of a stable adsorbed film and a robust tribofilm, which resulted in excellent antifriction and antiwear properties. Moreover, the tribologically induced conversion of goethite nanorods to adherent iron-oxide tribofilm explained the low friction coefficient detected for nanolubricants, since the oxidized layer joined to the sliding surfaces and acted as a high performing lubricant [63, 64].

In order to validate the supposed action mechanism of such additives, X-EDS characterization was carried out on the same areas already analysed by μ-Raman spectrometry. Elemental analyses confirmed the large amount of oxygen into the wear scars, for all substrates, especially for those treated with nanolubricants containing US and T type goethite. The relative concentration of oxygen, related to iron content, is reported in Tab. 3.

Sample	$\frac{\mathbf{O}}{\mathbf{Fe + O}}$
Oil	0.21
Oil+RT	0.28
Oil+T	0.54
Oil+US	0.58
outside wear scar	0.00

Tab. 3. X-EDS results from wear scars treated with different lubricants.

X-EDS measurements provided further support to what emerged from Raman characterization. Worn surfaces treated with nanolubricants containing T and US goethite nanorods showed much higher oxidation degree in respect to other samples. This aspect conformed to the massive formation of a more oxidized phase, possibly Fe_3O_4, which did not appear in the same amount when raw oil or RT type goethite were used during tribological tests.

Outside wear scars, no oxygen was detected by X-EDS technique. Moreover, oxidized material was observed into the wear track produced in presence of raw oil alone, due to the oxidation phenomena that are generally associated with the sliding operation and severe conditions achieved inside the contact zone, i.e. high temperature and local stress. This oxidized layer is supposed to be initially formed during rubbing and removal of material from the mating surfaces within the contact zone, where oxidation, nucleation and agglomeration processes took place due to sliding operation, followed by plastic deformation and work-hardening of underlying material which supports the growing tribofilm. However, the oxidized species resulted different in presence of goethite. This aspect suggests that an oxidized protective tribofilm came mainly from a tribologically induced evolution of initial goethite nanorods, which underwent structural and chemical modification due to sliding process and brought to the formation of a more effective protective layer. In RT sample the oxidized layer tended to form more hardly, since the aggregates were too much relevant to easily enter the contact zone. Therefore, tribologically induced conversion of goethite was less evident and effective in building the protective tribofilm.

It has been perceived that the role of oxide films was very significant in minimizing the wear and friction phenomena on alloy steels [65]. Thus, since the formation of protective iron oxide seems deriving and being favoured by the presence of free and individual goethite nanorods, these dispersed additives can bring important benefit to the overall tribological pair operation.

4. CONCLUSIONS

The friction and wear behaviour of PAO-based nanolubricants containing goethite (α-FeOOH) nanorods has been investigated by means of tribological experiments in presence of variably oriented magnetic field and *post-mortem* characterization of produced wear scars.

Goethite nanorods with different morphology and aggregation state have been dispersed in the raw oil to obtain nanofluids for anti-wear and anti-friction purposes. Closely packed nanorods revealed to be less effective in reducing wear and friction than those with high motion freedom and response velocity, for which a maximum decrease of 22% for the friction coefficient was achieved during ball-on-flat experiments. In fact, these types of dispersant proved to be beneficial in decreasing detrimental effects of reciprocative sliding in boundary regime by means of both frictional anisotropy phenomenon and tribochemical formation of protective oxidized tribolayer.

A significant friction reduction was reached with such free nanorods, with magnetic field oriented parallel to the sliding direction, thanks to the favourable orientation of dispersed additives due to the effect of the applied field.

A noteworthy decrease in wear detrimental effects was observed for the same samples, due to the formation of an oxidized tribofilm, which could efficiently preserve the sliding surface from the direct metal-metal contact.

AKNOWLEDGEMENTS

This work has been funded by the Italian National Research Council – Italian Ministry of Economic Development agreement "Ricerca di Sistema Elettrico Nazionale", PAR 2015-2017.

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