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Friction and wear reductions under slip-rolling contact through chemically reactive tribofilm generation during pre-conditioning of steel alloys

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ABSTRACT

The running-in phase of mechanical systems is critical from a tribological standpoint, though poorly understood. Microcracks accelerate material failure and wear during this phase of heightened friction. With this in mind, the ultimate goal of this current work is to transfer the running-in phase into the final step of the mechanical finishing process through the targeted pre-conditioning of novel, high toughness steel bearings without thermo-chemical treatments and compare these to conventional, case-hardened steels. This pre-conditioning involved the targeted implementation of two specific lubricant packages, the first with $CaCO_3$ as the active ingredient and the second with MoDTC as the active ingredient, to generate chemically reactive tribolayers (tribofilms) on twin disk testing rigs. Pre-conditioning was carried out up to 10^4 load cycles (approximately 25 min). The films generated in pre-conditioning were analyzed by SEM-EDX with Element-Mapping, Raman spectroscopy, and XPS to elucidate their molecular composition and concentration on the sample surfaces. The combination of these methods of analysis gave a clear indication that 10^4 cycles were sufficient to generate stable chemical tribofilms. CaO and $CaCO_3$ were the main components of the tribofilm from the first lubricant package, while MoS_2, MoO_2 and MoO_3 were the main components from the second lubricant package. Tribofilm-protected samples were then subjected to slip-rolling endurance testing ($T = +120$ °C, 10,000,000 cycles, approximately 19 days in a factory fill engine oil) to determine any changes in friction behavior or wear performance. Some significant reductions in coefficients of friction at the end of endurance testing were observed, though in certain cases, no definitive improvement was observed. In contrast, very strong reductions in wear were observed across the entire spectrum of materials and testing loads. In some cases, sample surface wear reduction from pre-conditioning via tribofilms reached over 90%. The observed improvements to friction behavior and wear performance are indicative of a technically simple, cost- and energy-efficient pre-conditioning method that may prove to be competitive with existing thermochemical treatments for steel alloys.

1. Introduction

Lightweight material strategies used in the reduction of CO_2 emissions inevitably lead to an increase in the bending load of both the tooth base and tooth flank of gear components. One possible solution for this problem, aside from the application of wear resistant coatings, is to apply alternative alloys with increased fracture toughness and strength [1]. Such novel alloys allow expensive and energy-intensive thermochemical treatments to be circumvented, and still achieve respectable wear performance. It is also known that tribological “running-in” results in the development of protective boundary layers that reduce wear on contact surfaces, which occurs both through the introduction of compressive residual stresses via work hardening processes and the generation of chemically reactive protective films via interactions between contacting tribological surfaces and carefully selected lubricant additives under sufficient contact pressure. The reduction of friction and reduction of wear are not mutually exclusive, as increased wear can be expected in a state of heightened friction, particularly during the running-in phase. Therefore it is a worthwhile pursuit to reduce friction- and wear-related energy losses by eliminating the need for running-in during regular operation. More specifically, targeted application of the abovementioned running-in processes through a tailored pre-conditioning regime can be utilized to prepare steel alloys for

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long-term tribological operation, i.e. improve the endurance of the overall material.

1.1. Tribofilm formation

Wear protection of tribological surfaces through tribologically induced protective films, or simply tribofilms, is currently a very prevalent area of research. These tribofilms are generated from the additives in lubricants during tribological solicitation [2]. The understanding of the metallurgical and chemical processes involved is rapidly increasing with improvements to analytical techniques. There are many different types of films, as well as ways to generate them, which can make describing these processes difficult if there is not a consistent naming system. Systems for classification of tribofilms have been suggested in the literature [3].

Extensive work has been done with the additive zinc dialkyldithiophosphate (ZDDP), because it is the main anti-wear agent used in many engine oils [4,5] ZDDP is able to react chemically with steel surfaces to produce a protective tribofilm coating, typically composed of polyphosphates and metal sulfides [6]. Phosphorous, decomposed to pyrophosphates that pass through the engine combustion chamber, however, interferes with the operation of the exhaust system by forming ash or deactivation of the catalytic centers of the catalytic converter [7], so the goal of work with ZDDP is to reduce the amount of phosphorous present in engine oils, while still maintaining good friction and wear performance [8]. This is expressed by the so-called "chemical box" or the prevalence of low and mid sulfur, ash and phosphorous (SAP) engine oils. While these studies have shown some favorable results in terms of improvement of friction behavior and wear performance, they are predicated on generating, or rather, replenishing the tribofilm throughout regular operation, as opposed to generating a stable, production-ready tribofilm through pre-conditioning.

A new model of the interactions of lubricant additives with metallic surfaces was introduced by Schulz and Holweger [9]. Furthermore, the behavior of specific additives and their interactions with specific metallic surfaces were discussed in detail at the GfT-Meeting in 2011 in Göttingen, Germany [10]. In light of this research, lubricant formulations containing calcium carbonate were chosen for the current study with the hope of observing synergistic interactions [11]. Organomolybdenum compounds also offer the ability to form tribofilms through rubbing contact with metal surfaces, and are already well known for their potential for friction modification [12,13]. At the same time, extreme pressure performance is enhanced by organosulfur compounds through the formation of a chemisorbed load-carrying surface layer between rubbing metal surfaces [14]. Therefore competition for access to the metal surface arises when both Mo-based friction modifiers and organosulfur extreme pressure additives are present in the same lubricant mixture. This may lead to a reduction in performance of the friction-reducing extreme pressure (or anti-wear) additive, i.e. antagonism. Therefore it appears that, at a very selective ratio of Mo to S, a compromise on metal surface access between the two is reached.

The focus of this work is to generate stable chemical tribofilms during the last stage of mechanical finishing so that the additives used for the initial tribofilm generation are not needed for tribofilm generation during regular operation. This contrasts with a vast majority of the research on chemical tribofilms for friction and wear reductions, particularly involving ZDDP or molybdenum dialkyl-dithiocarbamate (MoDTC). The negative eco-toxicological properties of MoDTC suggest reduced use of this additive, while still obtaining improved frictional behavior through the chemical tribofilms generated from MoDTC, is a valuable pursuit. With the prominence of greater friction and wear during running-in, it is particularly crucial that protective tribofilms are effective during this initial tribological contact. Therefore the extension of the abovementioned goal is to remove running-in from regular operation by accomplishing this during the last stage of mechanical finishing, ultimately yielding better friction behavior and wear performance.

2. Experimental procedure

2.1. Applied materials

In continuation of prior research, three different steels were applied in this study: the gear steel 20MnCr5 (1.7147, SAE 4820/SAE 5120), the hot working tool steel 9966 Super C from Buderus (36NiCrMoV1-5-7) and the silicon alloyed spring steel V300 from Aubert & Duval (45SiCrMo6, 1.8062). 20MnCr5 has been used for decades as a "classical" case-hardening gear steel, and serves as a reference material in this study. Both 36NiCrMoV1-5-7 and 45SiCrMo6 are industrially available materials, as their trade names suggest, and were not case-hardened. Detailed descriptions of the applied heat treatment regimes and elemental analyses, as well as characterization of material microstructures and residual stresses, have been previously provided for all testing materials [1]. All testing was performed on twin disk testing rigs, which are described later under *Slip-rolling endurance testing*. Therefore disks of a specified geometry (in this case, cylindrical samples and spherical counterbodies) were machined from the heat treated material for twin disk testing. The heat treated and machined disks were then mechanically finished: the cylindrical samples were grinded and polished, while the spherical counterbodies were simply grinded. The roughness values, R_a and R_z, that resulted from mechanical finishing are given in Table 1. In essence, a comparison of operational performance is sought between the case-hardened reference steel and the non-case-hardened steels, and furthermore, how this operational performance is impacted by the generation of chemically reactive tribofilms through targeted pre-conditioning.

2.2. Pre-conditioning via generation of tribofilms

The reactive tribofilms were generated on cylindrical sample surface using both Optimol 2Disk and Amsler type twin disk machines, which are described in greater detail under *Slip-rolling endurance testing*. Table 2 provides further information on the conditions under which pre-conditioning was carried out. Two specific lubricant packages were applied to generate chemically reactive tribofilms on the steel surfaces: Wisura LS514, which is a customized fine cutting fluid from Wisura GmbH (Bremen, Germany) with an enhanced concentration of $CaCO_3$ as the active ingredient, and VPX*+Molyvan 822 [CAS: 71342-89-7], which is from Vanderbilt Chemicals, LLC (Norwalk, CT, USA) and comprised principally of MoDTC. These lubricants, and the corresponding

Table 1
Roughness values, R_a and R_z, of mechanically finished cylindrical samples and spherical counterbodies.

	Cylindrical sample		Spherical counterbody	
	R_a (µm)	R_z (µm)	R_a (µm)	R_z (µm)
20MnCr5 (6% RA)	0.0042	0.0245	0.22	1.52
20MnCr5 (14% RA)	0.0039	0.0237	0.26	1.79
36NiCrMoV1-5-7	0.0070	0.0790	0.19	1.35
45SiCrMo6	0.0048	0.0314	0.17	1.30