Microstructure of tribologically induced nanolayers produced at ultra low wear rates

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Abstract

Wear in modern tribological systems is characterized by ultra-low rates in the order of a few nanometers per hour. Even under low-wear conditions, morphology, crystalline arrangement, and chemical bonds of surface and subsurface are modified significantly and considerable plastic deformation occurs up to 1 micron depth. We characterize these changes with the help of tribometer experiments employing the radionuclide technique and transmission electron microscopy (TEM). The tribological conditions lead to complex and strongly inhomogeneous layered structures. The top zone of the subsurface has a nano-crystalline structure with an average grain size of about 10 nm containing ferrite, austenite, and cementite phases. Below the subsurface material consists of a work-hardened, fine grained structure. Our experiments lead us to conclude that the observed combination of a nano-crystalline top layer and a work-hardened subsurface favours high wear resistance and low friction.

Key words: friction, nano-crystalline layer, low wear rate, third body, hardening
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1 Introduction

Real technical surfaces are always rough. Therefore, the real contact area of two sliding bodies is much smaller than the apparent one. The pressure in the micro-contacts is high enough to initiate severe plastic deformation, which leads to local temperature increase. Hence, the surface and the near-surface volume of both sliding partners becomes gradually modified with respect to morphology, crystalline structure and chemical composition [1–4]. Wear rate and friction coefficient are very sensitive to the appearance of the interface and subsurface of contacting bodies, which are intensively studied nowadays [5–8]. Recent achievements in the improvement of analytical tools for characterization of the chemistry and micro-structure of the interface and subsurface resulted in the amount of publication in the area of layers characterization. Unfortunately, *in vitro* studies often exaggerate load and sliding velocity so that wear rates become measurable in a short period of time with weighting or profiling techniques. It is, however, unlikely that the mechanisms for intensive wear and for ultra-low wear are identical, which asks the relevance of many tests to modern applications into question.

In this study we consider the accurate measurement of the low wear amounts by means of radioactive tracer technique, in order to apply the tribological conditions relevant e.g. for a modern engine. We use a pin-on-disk tribometer to investigate the influence of the loading conditions on the wear mechanism and appearance of the subsurface layers studied with help of transmission electron microscopy. Our previous studies dealt with chemical composition and mechanical response of the surface [1,7]. Here we focus on the structural rearrangements of the material due to friction and discuss anti-wear properties of nano-crystalline layers.

2 Experiment

2.1 Sample preparation and test details

A common pin on disk tribometer was used to stress the samples. In all experiments a chromium plated steel pin (100Cr6) with a diameter of 3 mm was pressed against a rotating grey cast iron disk. Disk surface was cut and finally lapped using a cooling lubricant. The pin surface was honed and polished. Roughness R_a of both pin and disk surfaces did not exceed 100 nm. Fully formulated engine oil was delivered to the area of the contact continuously. Radionuclide technique described in [9] allowed us tests monitoring the wear rate with a resolution of nanometers per hour. A set of experiments with nominal pressures from 15 to 90 MPa and sliding velocities from 1 to 10 m/s was run to establish tribological characteristics of the system. During experiments establishing "mild wear" conditions wear and friction coefficient were measured continuously under constant loading conditions for 68 h. Experiments with severe wear were stopped if no reduction of wear rate occured for $\approx$ 6 h.

2.2 Example selection for microstructure characterization

Out of the variety of loading conditions examples with "mild wear" (P_a = 15...90 MPa and v_{sl} = 1...2.5 m/s) and "intensive wear" (P_a = 60...90 MPa and v_{sl} = 5...10 m/s) were selected for characterization by means of transmission electron microscopy. The wear rate used for sample selection was evaluated at the end of the experiment when wear rate reaches a constant and stable value (Fig. 1) after "natural" running-in. The "mild wear" regime is characterized by wear rates under 50 nm/h in contrast to "intensive wear" regime at rates 50-5000 nm/h. A remarkable characteristics was observed for "mild wear" conditions. At low values of contact pressure the wear rate increased in direct proportion to applied pressure. However, at high pressures an inverse proportion of wear rate and nominal contact pressure was measured. No such relation was observed during "intensive wear" regime.

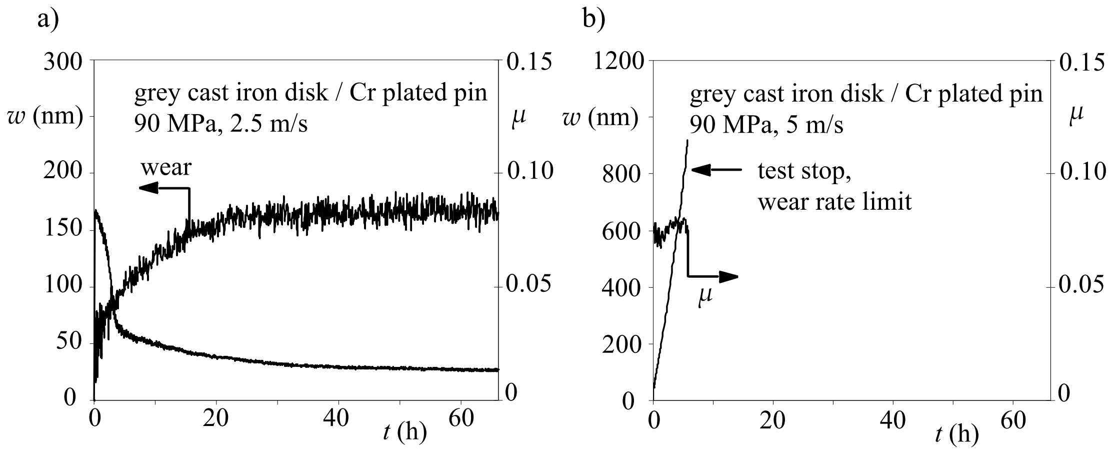

Fig. 1. Friction coefficient and wear as function of run-time under low sliding velocity "mild wear"(a) and high sliding velocity "intensive wear" (b).

2.3 Transmission electron microscopy (TEM)

In order to define the microstructure of tribologically induced layers, worn and unworn samples were prepared for observation with transmission electron microscopy (TEM). Material of the grey cast iron disk up to depth of 500 micron was cut out parallel to the surface. Two of these cuts with a thickness of 500 micron were glued together using a two-component adhesive (M-Bond 610, Bal-Tec GmbH, Witten, Germany). The as-prepared sample was then fixed in a brass cylinder (diameter: 3 mm) using a slotted pipe (diameter: 2.5 mm) as well as M-Bond 610. A heat treatment at room temperature for 30 min and at 150℃ for 2 h resulted in a satisfying bonding strength of the composite which was then cut into 400 micron thick discs using a corundum wheel on a low speed saw. After conventional wet grinding (1200 mesh SiC paper) down to a thickness of 100 micron, the specimens were further thinned from both sides using a dimple grinder (Model 656, Gatan GmbH, Munich, Germany) and an ion mill (Ion Tec 791, Ion Tec Ltd., London, UK). TEM investigations of cross-sections perpendicular to the sliding direction were performed with an accelerating voltage of 120 kV (TEM, type EM 400, Phillips, Eindhoven, The Netherlands). To get certainty about the lattice characteristics of different phases electron diffraction was used. Once a phase was clearly identified, dark and bright field images helped to locate the same phase within the observed regions.

3 Results and discussion

3.1 Coarse scale picture of the specimen structure

Proposing a coarse-scale picture of the tribologically stressed surface will help us to understand the results of transmission electron microscopy observed on different locations of the specimen. Friction and wear are explicitly connected with physical properties of the interface and mechanical properties of the subsurface. In the tribosystem chromium plated pin/ grey cast iron disk intensive shear occurs predominantly on grey cast iron surface. Chromium layer because of its superior physical and mechanical properties does not change its structure as much as grey cast iron does. The grey cast iron intensively involves into tribological interaction on pearlite-ledeburite grains, which obtain a significantly larger yield stress in comparison to ferrite-graphite phase (see Fig. 2). The zones of the contact shown schematically in the Fig. 2 have an area A an thickness h. This thickness is related to the depth of shearing when sliding occurs. We will relate to this thickness when analyzing the TEM photographs. The quantitative distributions of A_i and of h_i depend on the topography, mechanical properties of subsurface and physical properties of the interface as well as on the loading parameters [10,11]. In reverse friction and wear depend on the A_i and h_i probability distributions. We will only give short remarks regarding these distributions. However, we consider the influence of loading parameters on the microstructure of the subsurface and on the thickness h_i.

Due to limitations of our sample preparation technique, TEM photographs only show the microstructure as cross-sections perpendicular to the wear path (the same plane of cross-section as in Fig. 2).

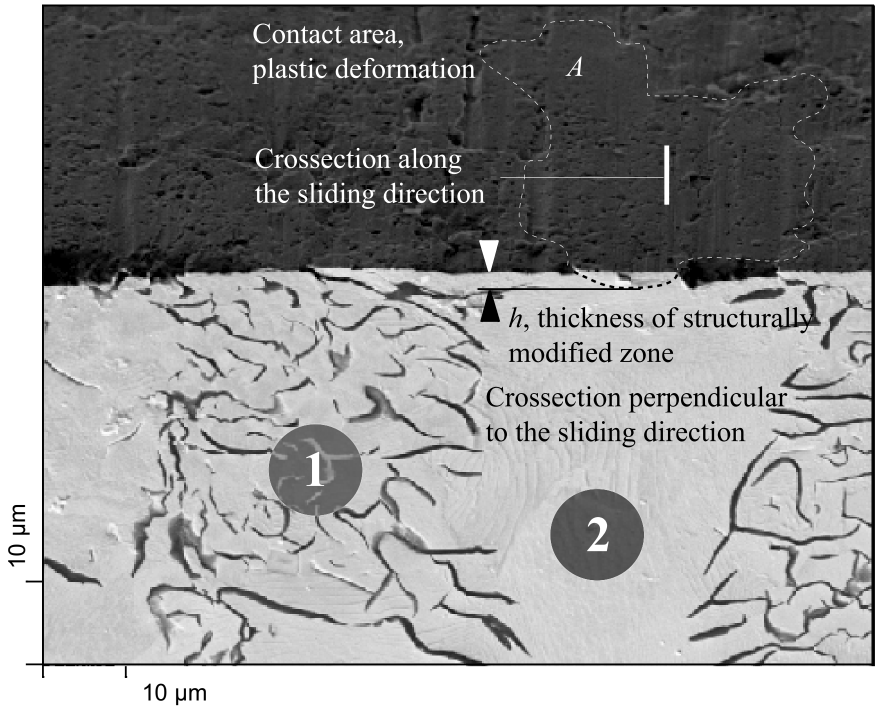

Fig. 2. A cross-section of grey cast iron surface after tribological contact (secondary electron photograph, dark area - contact surface, bright area - polished cross–section). 1: the ferrite-perlite-graphite phase with weak mechanical properties. 2: pearlite-ledeburite grain responsible for carrying the load from counterpart. The zone of intensive plastic deformation has an area A and thickness h (rescaled for clarity, usually less than 1 micron thick at low wear rates).

3.2 Microstructure and metallic phases

3.2.1 Microstructure of the sample before friction test

In this section we present the microstructure of the surface after machining. Machining is the first step altering the subsurface. Depending on the technique used for surface finish not only different topographies but also different mechanical properties could be set. Lapping of grey cast iron surface induces a reduction of the average grain size to a value of 100-500 nm as could be seen in Fig. 3. Reduction of grain size leads to increase of yield stress [12,13] unless the grain size reaches a critical value (20-30 nm) [14,15]. This fact was measured for machined surfaces with help of nanoindentation in [7]. Hardness increased 10-20% in relation to the bulk values. However, phase components of the grey cast iron do not change as shown in diffraction pattern (Fig. 3 b).

A mixed structure containing α-Fe, γ-Fe, and Fe_3C-phase is characteristic for the subsurface intensively sheared up to 2 microns in the depth (Fig. 4). At higher depths a microstructure not distinguishable from bulk structure could be found. Such structure shows monocrystalline features in electron diffraction pattern taken from spot with diameter of 1 micron. The undistorted ledeburite structure with Fe_3C lamellae exists at depths $>$ 2 micron (Fig. 5). The effect of lapping on the microstructure used here as surface finish does not differ significantly from a friction process. Although a further grain size decrease was observed during friction.

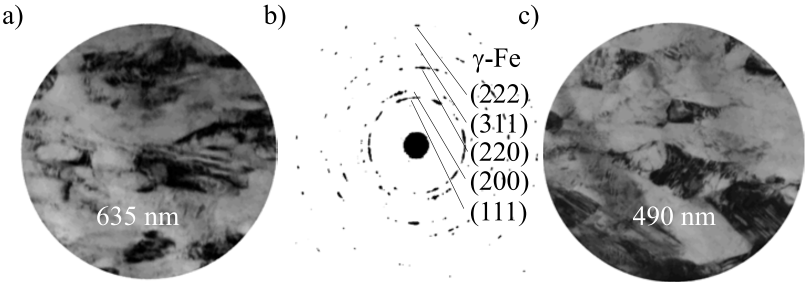

Fig. 3. Microstructure TEM photographs (a) and (c) and diffraction pattern (b) of near surface austenite region after surface finish (depth <1 μm). The number in nanometers shows the diameter of the circle for scaling.

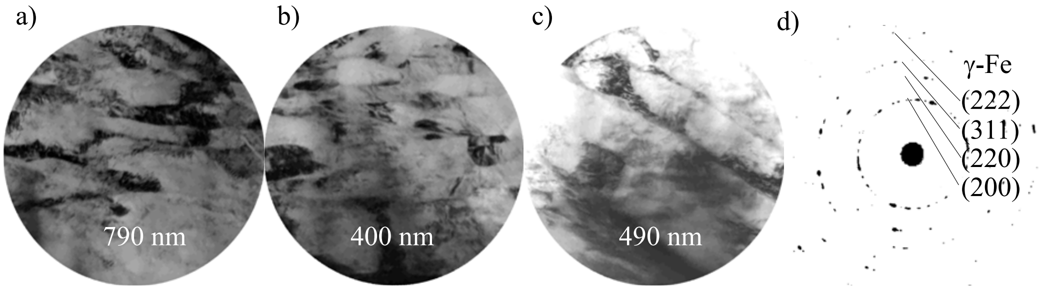

Fig. 4. Microstructure TEM photographs (a-c) and diffraction pattern (d) of an austenite region after surface finish (depth 1 μm-2 μm). The number in nanometers shows the diameter of the circle for scaling.

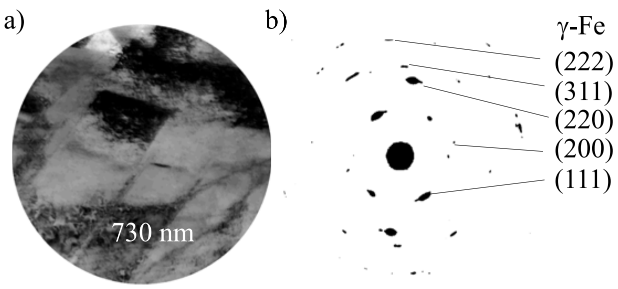

Fig. 5. Microstructure TEM photograph (a) and diffraction pattern (b) of ledeburite region after surface finish (depth >2 μm). The number in nanometers shows the diameter of the circle for scaling.

3.2.2 Microstructure of the sample after "mild wear" conditions

As for machining during friction the reduction of grain size of subsurface continues. Many grains obtain size in the vicinity of 10 nm (Fig. 6). The average grain size lies between 10 and 50 nm. Thickness of the zones with such nano-crystalline structure seem to depend upon specific friction power. Its amount is represented by the product of friction force and sliding velocity in the contact area spot A_i. The amount of friction power strongly depends on the interface properties e.g. properties of the boundary lubricant, which governs the amount of shear and thickness of the material responsible for dissipation. Under "mild wear" regime the thickness of the nano-crystalline layers does not exceed 500 nm. It is important to note that the probability to find a nano-crystalline zone increases (ΣA_i and $\overline{h}$ increase) when contact pressure increases from 15 to 90 MPa. Besides a refining of the grains the microstructure components remain detectable as a mix or variation of nano-crystalline α-Fe, γ-Fe, and Fe_3C-phases (Fig. 6 c). The microstructure of locations deeper than 1 micron appear to be similar with structure after surface finish.

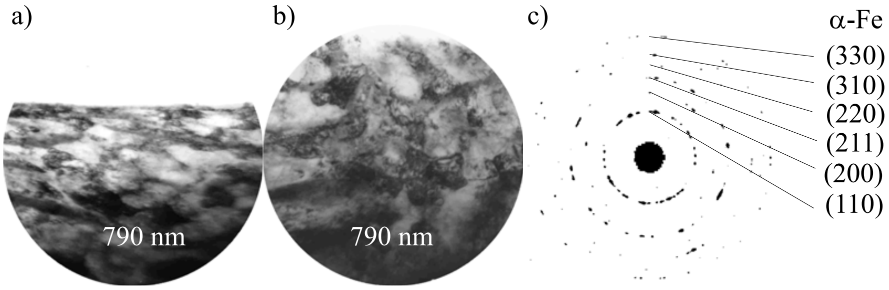

Fig. 6. Microstructure photographs (a-b) and diffraction pattern (c) of tribologically induced nanolayers (surface). The number in nanometers shows the diameter of the circle for scaling.

3.2.3 Microstructure of the sample after "intensive wear" conditions

Near surface regions of the surface experienced an intensive wear are represented by Fig. 7. The significantly larger specific friction power and hence shear led to nano-crystalline zones up to depth of 1 micron. The average grain size does not show a reliable difference to the top layer microstructure obtained under mild wear regime. The only difference seems to be the thickness of nano-crystalline areas and more densely covered area with such material. The transition from nano-crystalline layer to fine-crystalline material appears at the depth of 1-2 micron. The microstructure of such fine-crystalline material is shown in Fig. 4. At depths between 1-10 microns highly distorted areas with shear bands were found Fig. 5. Material there was not involved in an intensive plastic flow, as the original average grain size remains unchanged. Although development of cracks could be considered. Regarding friction power higher by factor 10 in comparison to "mild wear" conditions a significant increase of temperature in near surface regions could be expected. High temperature gradients and thermally induced stress fluctuations are well known factors leading to crack propagation. There is also another aspect which could intensify crack propagation. Maximum of Hertzian pressure lies in the depth of 5-10 micron when radius of contacting body is about 50-150 micron. This radius fairly represents the size of mechanically stable pearlite-ledeburite phase assuming it would have a spherical shape. At depths higher than 10 micron the bulk

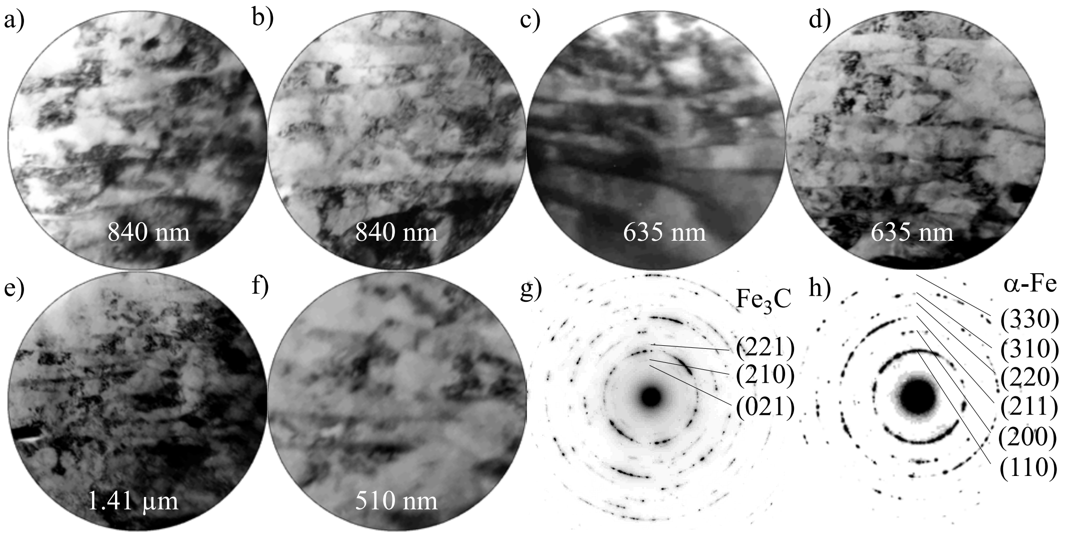

Fig. 7. Microstructure photographs (a-f) and diffraction patterns (g-h) of tribologically induced nanolayers (surface). The number in nanometers shows the diameter of the circle for scaling.

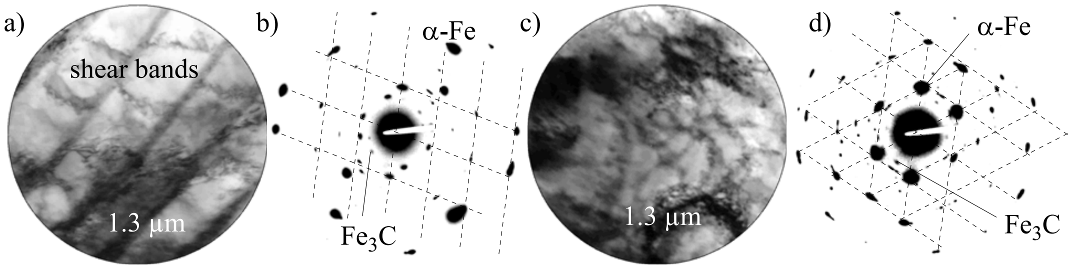

Fig. 8. Microstructure photographs (a and c) and diffraction patterns (b and d) of near surface region after tribological stressing (depth 1-10 μm). The number in nanometers shows the diameter of the circle for scaling.

structure of grey cast iron is observed (see Fig. 9).

Regarding the microstructures measured with transmission electron microscopy a discussion of anti-wear properties is presented in this section. Mild wear conditions as well as intensive wear conditions show a significant decrease of the grain size at depths up to 1 micron. The average grain size of 10-50 nm in top surface areas could govern the very special mechanical properties of the material. Unfortunately the direct measurement of the shear strength of such layers under conditions similar to a tribological stress are connected with many difficulties. The use of grain size for evaluation of the properties could give conflicting results. In the literature exist a variety of explanations for anti-wear action of nanocrystallyne layers [3]. We discuss two the mostly appropriate here:

1. Nano-crystalline layers are extremely hard and therefore can protect the surface from pressure peaks. Moreover they reduce friction while acting predominantly elastically. This fact is supported by preparation of TEM lamellae, where these layers remain if surrounding material was etched away. These layers, once they are formed, should sustain for long time until they will be fractured due to crack propagation, delamination or failure of the substrate.

2. Nano-crystalline layers are superplastic and soft. Superplastic means, that once they are sheared, they do not show significantly large viscosity or shear strength. This fact is supported by nanoindentation in [7]. These layers would form every time when two asperities of counterparts collide in the direct contact. They would form the so called third body [16,17] which would act as a lubricant and intermix the elements of both tribopartners. The wear mechanism of such layers would be diffusion and squeezing [4] out of the contact zone.

In fact these both explanations could be correct at the same time. The properties of the layers are dependent on the critical average grain size for phases mix structure when the so called inverse Hall-Petch effect takes place. The

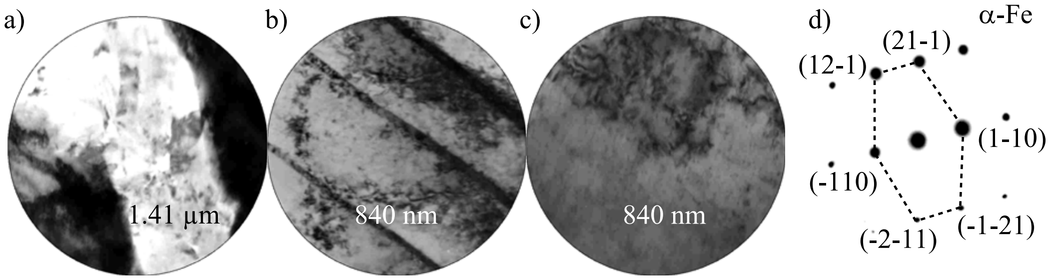

Fig. 9. Microstructure photographs (a-c) and diffraction pattern (d) of bulk material (depth >10 µm). Graphite lammelae (a), pearlite structure (b), and ferrite grain (c and d). The number in nanometers shows the diameter of the circle for scaling.

Hall-Petch relation governs the connection of the average grain size with the yield strength of the material. The plastic deformation driven by motions of dislocations would depend on the average dislocation jump which is limited to the grain size. Motion of dislocations is gradually suppressed when reduction of the grain size occurs. The material becomes harder. However, when grains reach a critical size and the volume of grain boundaries takes a significant part of material volume, the diffusion driven (fluid like) deformation mechanism becomes active [14,15,18,19]. In this case material exhibits low shear strength and probably non Newtonian fluid like characteristics.

A combination of properties 1 and 2 at different depths could explain our observations of tribological properties of the system as well as the microstructure in TEM. After shearing occurred on the asperity the very top layer with smallest grain size act as a lubricant when additives and boundary lubricant fail. The layer underneath is work hardened and deforms predominantly elastically for long period of time. Combination of these properties provides low friction and wear only when the tribological stress does not exceed a limiting value, which could be expressed in terms of specific friction power.

4 Summary

Experiments in a pin-on-disk tribometer were performed using a grey cast iron disk rotating against one resting chromium-plated steel (100Cr6) pin under lubricated sliding conditions. During the experiment the friction, normal force, running speed and wear were simultaneously measured. Wear was continuously measured based on the radionuclide technique with accuracy of 0.5 nm/h and in real time. The normal force and speed were varied from test to test in such a way that the tribological state ranged from "mild wear" regime to "intensive wear" regime. The wear properties of the system were related to the microstructure of the subsurface of the friction pair. A sufficiently large friction power is necessary to induce an intensive plastic flow and therefore a grain size reduction. The grain size reduction leads to increased wear resistance of material and friction reduction. This process is a result of work hardening of the near surface regions and possible softening of top region due to decrease of the grain size below a "critical value". The examination of microstructure by means of TEM has shown that grain size of top region of the material approached a value of 10 nm, which could be critical for transition from dislocation driven deformation mechanism to diffusion driven deformation mechanism.

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