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Hydrogen influence on material interaction with ZDDP and MoDTC lubricant additives

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ABSTRACT

In this paper the interaction of lubricant additives with hydrogen at the frictional interface has been investigated. Three different states of the base AISI 52100 alloy steel have been tested: untreated, nitrided and sulphonitrided, with different combinations of PAO6 base oil and ZDDP/MoDTC (Zinc DialkylDithioPhosphate and Molybdenum Dialkyldithiocarbamate) additives. Experiments have been carried out on pin-on-plate reciprocating tester, immersed in the lubricant heated to 100 °C. In the boundary lubricated regime the results showed the best friction behaviour for treated surfaces tested in presence of PAO6 with additives suggesting some interaction at the frictional interface of nitrided and sulphonitrided surfaces with lubricant additives. The minimum recorded value of coefficient of friction was as low as 0.05 for the sulphonitrided sample with PAO6+MoDTC oil. In the case of the treated surfaces a characteristic "low friction phase" has been observed when tested with PAO6 with additives. After a given time, the coefficient of friction was increasing to a higher steady-state value and the duration of this low friction phase varied from sample to sample. This can be explained by the mechanism of hydrogen interaction in the boundary lubrication regime, which was postulated for the base oil case by some of the authors in their previous papers. To validate the hypothesis, an experiment has been carried out where the test was stopped at the end of the "low friction phase" and during the hold period the sample was re-saturated with hydrogen. After resuming the experiment the low friction regime was again observed. The effect of a potential synergistic mechanism between hydrogen and ZDDP or MoDTC lubricant additives on frictional behaviour of nitrided and sulphonitrided surfaces is discussed in this paper.

1. Introduction

Hydrogen presence in a friction couple is usually not recommended due to the "hydrogen embrittlement" phenomenon [1,2]. This mechanism was widely examined experimentally [3,4], and numerically [5]. However, in some circumstances, hydrogen can bring some beneficial effects, which are much more significant than the hydrogen embrittlement. Both negative and positive effects are caused by hydrogen specific properties. Hydrogen is known to be the most diffusive atom, and can easily move through the crystal lattice. At lower temperatures, where hydrogen does not have enough energy to diffuse, it is still very mobile due to the quantum tunneling effect [6]. Therefore diffusivity is caused by both small size of hydrogen atoms (which usually reduces to a single proton in lattice) and its marginal mass. Moreover, hydrogen easily fits into lattice interstitials and the reason for that lies in a large energy drop of a system in the case of trapped hydrogen atoms and reactivity of hydrogen molecules (radicals) [3,6]. Self-trapped hydrogen leads to lattice deformation, which makes the material more brittle, although it is not the only phenomenon caused by this mechanism. In this paper experimental work is being carried out to verify the knowledge of the hydrogen influence on friction couples which has generally received little attention.

The question arises how can the impact of hydrogen on friction be examined by carrying out experiments in the environment where hydrogen is present? Results of [7–9,4] have shown that nitrided surfaces can be useful in such an experiment. It was proved that these surfaces naturally protect the bulk material from hydrogen diffusion (Fig. 1). Moreover in [10], the distribution of hydrogen along a nitrided surface was discovered to be more complex. Authors have shown existence of ε-iron phase, which is deformed due to abundant hydrogen presence in lattice interstitials in the outer sublayer of the nitrided layer [11,12].

The next stage of this research is to evaluate the action of hydrogen in the boundary lubrication regime. NIRAM-HSAB

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approach (Negative Ion Radical Action Mechanism—Hard and Soft Acids and Bases) was developed by Kajdas et al. as an explanation of lubricant film formation [13–15]. This mechanism is based on the fact that a triboplasma is created in the contact zone [16], which emits electrons and photons. These photons are likely to interact with negatively charged particles. If the energy of the photon is higher than the electron affinity, then it results in electron emission. Therefore in the contact zone, the density of electrons is expected to be high and these electrons are able to react with lubricant molecules. As a result, negative ions and hydrogen radicals are formed on rubbing surfaces. Afterwards, according to the HSAB mechanism, negative ions can react with positive ions on the metal surface, which were formed after triboemission of electrons.

Hydrogen radicals are the only products of the NIRAM process not used in HSAB. Hence the more electrons are emitted, the more hydrogen radicals are present in triboplasma. In that case the issue is how do they influence the film formation and is it affected by the hydrogen presence? The answer to that question was discussed independently in [17]. In these papers the influence of hydrogen on the coefficient of friction in the boundary lubrication regime was examined and the hypothesis of a hydrogen exchange mechanism between the lubricant hydrocarbons and the metal surface was postulated. This hypothesis meant that hydrogen should act as a link between the metal surface and the lubricant, which results in the formation of a thin tribofilm. This tribofilm was proved to effectively decrease the contact area between the samples during a friction test. The authors have shown that this separation is more effective in the case of nitrided or sulphonitrided materials, which is caused by high hydrogen concentration in the outer layer (Fig. 1).

The above studies were considering additive-free lubricants only. However additives are always present in lubricants yet there have been no prior studies of how hydrogen-additives interact. Hence, the aim of this paper is to provide a preliminary assessment of the effect of hydrogen presence in friction couple, when lubricant additives are used.

2. Experimental method

2.1. Materials

The material used in this study was AISI 52100 alloy steel in three different states: untreated, nitrided and sulphonitrided (both pin and plate were of the same type). Untreated AISI 52100 will be further called as the "base material". Nitriding was performed using NITROVAC vacuum technology [18], and sulphonitriding was carried out with SULFONIT gas sulphonitriding method [18,12]. Pins were designed to have the radius of 20 mm at the ends. Roughness values of the samples are presented in Table 1. In terms of hardness, nitrided and sulphonitrided samples exhibit approximately 600 HV comparing to 200 HV of untreated sample. In the case of sulphonitrided steel the maximum hardness has been measured on the surface, while in the case of nitrided it was approximately 50 μm underneath the surface, below the layer containing iron sulfides [19].

Table 1
Roughness of samples used in this study.

	Pin roughness Ra [μm]	Plate roughness Ra [μm]
Base material	0.3	0.2
Nitrided	0.4	0.2
Sulphonitrided	0.3	0.4

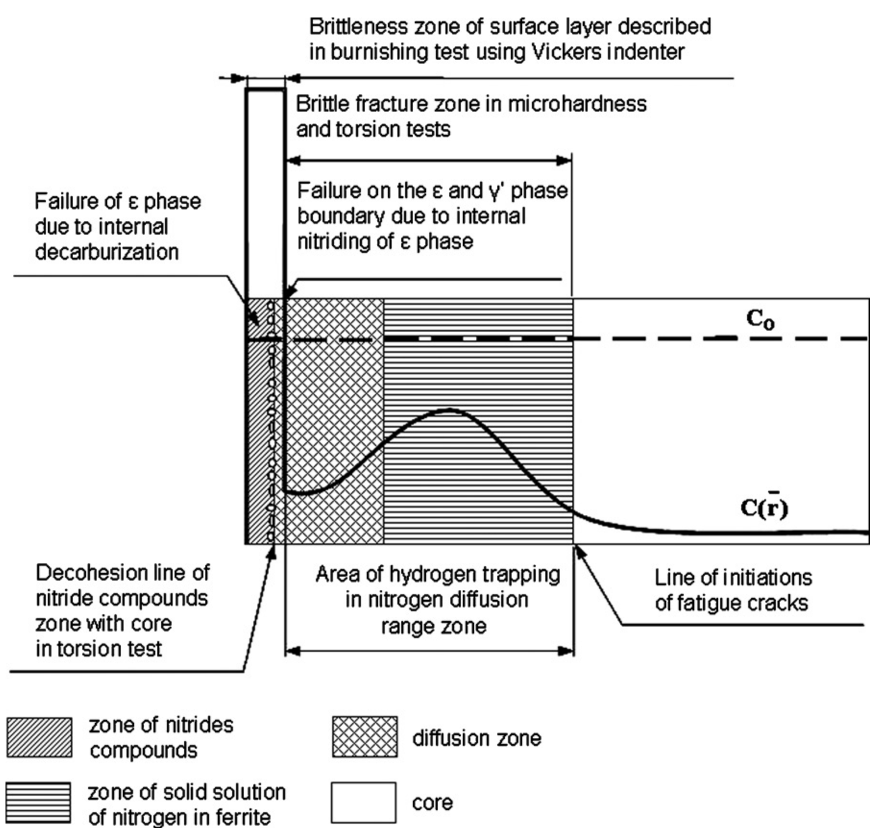

Fig. 1. Hydrogen concentration distribution in sublayers of nitrided sample $C(\bar{r})$. Concentration is much higher in the very outer sublayer, where ε-iron phase is created, comparing to concentration in non-treated, base material C_0.