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Surface investigation and tribological mechanism of a sulfate-based lubricant deposited on zinc-coated steel sheets

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ABSTRACT

Phosphatation is a well-known technique to improve friction and wear behaviour of zinc coated steel, but has a variety of economic and ecologic limitations. In this study an alternative coating based on ammonium sulfate ($(NH_4)_2SO_4$) is applied on skin-passed hot-dip galvanized steel sheets in order to investigate its surface chemical and tribological behaviour in a Pin-on-Disk Tribometer. Raman- and X-ray photoelectron spectroscopic results revealed a formation of ammonium zinc sulfate ($(NH_4)_2Zn(SO_4)_2 * xH_2O$) on the surface, which is primarily located in the skin-passed areas of the steel material. Sulfate coated samples exhibited a superior friction behaviour in Pin-on-Disk Tests using squalane as a model substance for oil-like lubricated conditions and a formation of a thin lubrication film is obtained in the wear track. Squalane acts as a carrier substance for ammonium zinc sulfate, leading to an effective lubrication film in the wear track.

1. Introduction

Solid lubricants are often used to ensure low friction even in extreme environments, where liquid lubricants can fail in case of high temperatures and pressures. A major application field of solid lubrication is in cold forming operations in the automotive assembling industry using hot dip galvanized (HDG-) steel sheets as a semi-manufactured product [1]. In the progress of metal finishing usually a phosphate layer is created on the material. Only in combination with applied oils/soaps these inorganic layers provide low friction and wear conditions in stamping operations for e.g. outer vehicle parts [2,3]. However, there are serious disadvantages of this pretreatment process like inefficient process parameters, toxicity and high environmental impact [4]. Regarding these ecological and economic aspects, new environmentally benign systems have to be developed.

Different alternative coatings based on reinforced zinc-alloys [5,6], different organic [7,8] and inorganic layers [9–12] have been recently investigated as solid lubricants on various steel materials. Lovell et al. studied the frictional behaviour of boric acid as a solid lubricant on zinc-coated steel sheets [13]. Dispersed in canola oil, these particles showed a significant friction reduction in a specialized forming operation at room temperature conditions. The lubricicous properties of boric acid were referred to its lamellar structure. In frictional environments this layered structure allows an intramolecular shearing preventing metal-to-metal contact. Kang et al. investigated a Zn/ZnS reinforced zinc-alloy for friction reduction [5]. Therefor the authors treated the samples in an ion-sulfurizer to create a Zn/ZnS matrix alloy. The Zn/ZnS coating showed a magnificent friction reduction by this novel coating in a Pin-on-Disk setup. They concluded an easy transfer of the crushed ZnS-film during the friction test onto the counterpart, which finally provides lubrication and reduces wear.

John et al. investigated earth alkali sulfates ($CaSO_4$, $BaSO_4$, $SrSO_4$) for use as high temperature solid films on M50 steel samples [9,10]. The authors showed low friction coefficients for these coatings at temperatures up to 600 °C. A formation of carbonates was obtained after Pin-on-Disk Tests. It was concluded that the layered structure of these carbonates contributed to the lubrication of the sulfate coating. Murakami et al. furthermore investigated the tribological behaviour of strontium and barium sulfate, deposited by Pulsed laser deposition (PLD), on different steel surfaces [11,12]. The authors employed different surface analytical tools (XRD, Energy dispersive x-ray spectroscopy – EDX and Scanning electron microscopy – SEM) for their investigation. In their studies the authors showed low friction coefficients for lump- and flake-shaped $BaSO_4$ on aluminium oxide and stainless steel substrates. They concluded the better frictional properties of flake-shaped $BaSO_4$ to lump-shaped crystals due to its larger crystal planes. So

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these crystal shapes provide easier sliding than crystals containing smaller planes.

The mentioned studies generally showed an opportunity to use non-complex compounds for solid lubrication on different materials and might be a serious alternative to the conventional phosphatation process. However, sulfate salts are easy-to-use chemical compounds and mostly non-toxic whereby they are predestined for industrial usage. Most of sulfates can be dissolved in water, so they can be used without special efforts in commercial processes. A formation of a sulfate-based layer on zinc-alloy coatings can be performed by treatment with solutions containing sulfates. Mainly focusing on the corrosion of zinc in sulfate containing environments [14–17], no information about the tribological behaviour of applied sulfate layers on zinc-coated steel were found. But the exceptional easy handling of these salts let them come into question for lubrication films especially on commercially used zinc-coated steel.

From this point of view we investigate the surface layer characteristics and tribological behaviour of zinc-coated steel sheets coated with $(NH_4)_2SO_4$. A common roll-coating method is used to apply ammonium sulfate on to the surface. As substrate hot dip galvanized steel in the skin-passed state was used because of its wide application especially in the automotive industry. Novel aspects of this study are the investigation of such layers on skin-passed steel, its deposition behaviour and tribological properties under dry and oil-like lubrication. The friction performance of the applied layer is studied in a Pin-on-Disk test. The surface layer chemistry before and after tribological testing is characterized by means of Confocal Raman Microspectroscopy (CRM), Field-Emission Scanning electron microscopy (FE-SEM) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Sample preparation

For this study, industrially produced skin-passed hot dip galvanized steel sheets (*ThyssenKrupp Steel Europe AG,* Germany) with an average roughness (R_a) of 1,25 μm were used. The galvanized layer contains of 99.27% Zn and 0.73% Al by weight. To ensure a reproducible preparation all samples were cleaned in an automatic cleaning system (*WESERO GmbH*, Germany) to eliminate organic and inorganic residues on the surface. The procedure contains following steps:

1. Ridoline® C72 (*Henkel AG & Co. KGaA*, Germany) – pH 11, 8 s
2. Ridoline® 1340 (*Henkel AG & Co. KGaA*, Germany) – pH 9, 8 s
3. Rinsing with deionized water (50 °C)
4. Drying in warm stream of air

The deposition of the sulfate layer was performed directly after alkaline cleaning in a laboratory scale roll-coating plant (*Werner Mathis AG*, Switzerland). Therefor $(NH_4)_2SO_4$ (*Merck KGaA*, Germany) was dissolved in dest. H_2O ($\kappa < 0.05$ μS/cm). The concentration of SO_4^{2-} in the solution was 0.5 mol/L. The pH-value of the solution was 5.4. After the coating procedure the samples were placed manually in a temperature controlled furnace to evaporate the used water (Peak metal temperature: 77 °C; duration: 30 s).

For the tribological investigation different coating weights of 36, 26, 16 and 11 mg sulfur/m^2 (further abbreviated as mg S/m^2) were applied onto the steel material to evaluate the tribological behaviour depending on the sulfate amount. Layer weights were determined by inductively coupled plasma – optical emission spectroscopy (ICP-OES), corresponding to an aqueous dissolution method of the deposited sulfate coating from the steel surface [18].

Table 1
Testing parameters for the Pin-on-Disk Test.

Testing parameter	
Sliding velocity	1,05 mm/s
Applied Load	30 N
Total sliding distance	~60 cm
Sample temperature	60 °C
Environment	ambient air

The amount of sulfate in the solutions was determined in a Spectro Arcos (*SPECTRO Analytical Instruments GmbH*, Germany).

2.2. Surface analysis

2.2.1. CRM

Raman spectroscopic studies were carried out on an Alpha 300R confocal Raman microscope (*WITec GmbH*, Germany). All spectra were recorded with a 488 nm Ar^+-laser (*Spectra Physics*, USA) on a CCD-Detector in a WITec UHTS 300 Spectrometer, cooled down to −60 °C. The laser power was set to 32 mW. The exposure time was between 10 and 20 s for each spectrum to inhibit any damage of the laser to the sample. The imaging of the collected scans was performed through WiTec Project® (Version 2.10).

2.2.2. FE-SEM

The morphology of coating layers and friction tracks were studied with a high resolution FE-SEM Merlin® microscope (*Carl Zeiss Microscopy*, Germany) equipped with an Energy-dispersive X-ray spectroscopy (EDX) analysis device (*EDAX Ametek*, Germany). The primary electron beam acceleration was in a range of 5–10 kV and the working distance between 4 and 13 mm. The microscope was equipped with an SE2 detector.

2.2.3. XPS

The chemical compositions of the sulfate layers were investigated by a Quantum 2000 ESCA Microprobe (Physical Electronics Inc., USA). A monochromated Al K-beam with a spot size of 100 μm × 100 μm recording in a take-off angle of 45 °C to the surface normal was used. The C1 s peak at 284,4 eV was used as an internal reference. The quantification of the elements in the surface layers is based on the recorded high-resolution spectra.

2.2.4. Confocal microscopy

Topographical measurements were conducted in a μsurf mobile confocal microscope (*NanoFocus AG*, Germany). The illustration of the surface topography is performed through μsoft analysis premium (Version 6.2).

2.3. Tribological tests

Tribological investigations were performed in a conventional Pin-on-Disk setup using an adjusted 100Cr6 steel ball as the counterface rotating on the prepared samples. For all measurements, the zinc-coated steel samples were cut into disks of 50 mm diameter. The friction measurements were performed with a normal load of 30 N and a rotational speed of 1 rotation per minute in a 20 mm diameter track. Friction tests were run for 10 cycles resulting in a total measuring time of 10 min for each sample. All tests were carried out at 60 °C. An implemented heating plate ensured a constant temperature throughout the test. Table 1 summarizes the testing parameters.

Two different environmental conditions were used in this study to investigate the friction behaviour of the sulfate coating. At first, the samples were tested in a dry environment (no additional oil) to obtain the tribological properties of the applied coating itself.