Properties of nitrocarburised and oxidised steel surfaces and the correlation with their tribological behaviour under unlubricated sliding conditions

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ABSTRACT

In the present study, DIN 31CrMoV9 (1.8519) steel samples were initially treated by salt bath- (SNC), gas- (GNC) and plasma-nitrocarburising (PNC) and afterwards oxidised for increased corrosion protection. The thickness and hardness of the oxide and compound layer as well as the diffusion zone were measured. Surface topographies and microstructures were analysed with optical microscopy, laser scanning microscopy and scanning electron microscopy (SEM), while the detailed chemical compositions of the sample surfaces were determined with energy-dispersive X-ray spectroscopy (EDX), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). Tribological tests for characterisation of wear and frictional behaviours of the treated samples were performed under unlubricated sliding conditions.

Results show that, although different nitrocarburising processes yield very similar hardness profiles and compound layer thicknesses, their surface morphology and oxide layer properties can be significantly different. On SNC samples, the thickest oxide layers were formed, which had a different chemical composition than those formed on GNC and PNC samples. Furthermore, SNC samples provided the highest wear resistance and only on these samples, the oxide layers were not removed during tribological testing. It is thus possible that a correlation between the oxide properties and the favourable tribological behaviour of the SNC samples exists.

1. Introduction

Ferritic nitrocarburising is a thermochemical process that consists of diffusing nitrogen and carbon into the surface of ferrous materials. It is widely used in industry to achieve enhancements of hardness, wear resistance, fatigue strength, low adhesion and corrosion resistance of tools and engineering parts operating under unlubricated or boundary lubrication conditions [1–3]. During the process, a very hard compound layer with a thickness of 0.5–10 μm is normally formed on top of a 200–500 μm thick nitrogen diffusion zone having a slightly lower hardness (which is higher than that of the untreated material). Through the enhancement of hardness and adhesion resistance, service life of machine components can be significantly extended [4–7] and through the formation of the protective compound layer, steel grades that are not resistant to corrosion can attain a relatively good corrosion resistance [8–10].

The compound layer mainly consists of ε-nitrides (Fe$_{2–3}$N) and γ′

nitrides (Fe$_4$N) and often has a porous structure. In order to achieve further enhancement of surface properties, nitrocarburising process can be combined with a post-oxidation treatment that produces a thin iron oxide film on the surface and inside the porosities of the compound layer, which brings a significant enhancement in corrosion resistance of the nitrocarburised components [5,11]. In combination with the nitrocarburising procedure, post-oxidation after nitrocarburising has also shown an improvement of frictional and anti-galling properties of unlubricated steel components [5,12]. However, under lubricated conditions, a detrimental effect of the post-oxidation on friction and wear was also reported [13].

Generally, nitrocarburising processes can be differentiated based on the processing medium used: salt bath- (SNC), gas- (GNC) and plasma-nitrocarburising (PNC). Although, different nitrocarburising processes produce nitrocarburised layers with very similar mechanical properties, their chemical composition and surface morphology can be very different, which affects their friction and wear behaviour under

Table 1
Nitrocarburising and oxidising process parameters.

		SNC	GNC	PNC
Nitro-carburising	**Time in h**	1.5	12	17/5
	Temperature in ˚C	580	540	540
	Nitriding medium	Commercially available salt melt consisting of alkali cyanate and alkali metal carbonate	Mixture of NH_3, (60%), N_2 (38%) and CO_2 (2%) gases; atmospheric gas pressure (1 bar)	Mixture of N_2 (50%) and H_2 (50%) gases/mixture of N_2 (50%), H_2 (45%) and CH_4 (5%); gas pressure 2.5 mbar
Oxidation	**Time in h**	0.25	1.75/0.75	1
	Temperature in ˚C	430	515/500	520
	Oxidation medium	Commercially available oxidation solution consisting of alkali metal hydroxide, alkali metal nitrate and alkali metal carbonate	Water vapour	Water vapour

tribological loading. In previous studies, it was already shown that different nitrocarburising processes and/or process parameters can result in very different tribological behaviours, which can be correlated with the surface microstructure and the mechanical properties of the compound layer of the treated materials [14–16]. In other studies, it was already shown that, due to its brittleness, a very thick compound layer can increase the wear rate of the treated surface through the formation of abrasive wear particles [2,17,18].

Although nitrocarburising is a well-established surface treatment technique which is being continuously analysed and developed [19–22], very few studies focused on its application for tribological applications were found; foremost for those operating under unlubricated sliding conditions. The present paper is focused on the correlation between the surface properties of steel samples treated with different nitrocarburising and oxidising processes and their tribological behaviour under unlubricated sliding conditions.

2. Experimental setup

2.1. Nitrocarburising and oxidising of the test samples

DIN 31CrMoV9 (1.8519) nitriding steel was used in the present study. This type of steel is typically used for components for high wear applications such as tools for processing of polymers, e.g. extruders and injection moulding machines, spindles on machine tools, valve spindles, control parts, superheated steam valve parts, crankshafts and similarly stressed machine elements. The chemical composition of 1.8519 steel is: 0.3% wt% C, 0.3 wt% Si, 0.8 wt% Mn, 2.5 wt% Cr, 0.2 wt% Mo and 0.2 wt% V.

The samples were cut from a rod into disc shaped samples with a diameter of 35 mm and a height between 9.15 and 9.4 mm. The flat sides of the samples were grinded to a surface roughness of R_a = 0.4 μm. This relatively high surface roughness was selected as it corresponds to a typical roughness of nitrocarburised parts used in industrial applications such as those enumerated earlier.

The steel samples were initially treated by SNC, GNC or PNC and afterwards oxidised for increasing their corrosion protection. SNC was performed in a commercially available salt melt consisting of alkali cyanate and alkali metal carbonate (Durferrit TF 1.6, Durferrit GmbH, Germany) at a temperature of 580 °C for 1.5 h. GNC was performed in a mixture of NH_3, (60%), N_2 (38%) and CO_2 (2%) gases at the atmospheric gas pressure (1 bar) and a temperature of 540 °C for 12 h. PNC was performed in two steps: first in a mixture of N_2 (50%) and H_2 (50%) gases for 17 h and then in a mixture of H_2 (50%), N_2 (45%) and CH_4 (5%) gases for 5 h. During the entire PNC process, the temperature and the gas pressure were kept constant at 540 °C and 2.5 mbar, respectively. After nitrocarburisation, oxidation of SNC samples was performed in a commercially available oxidation solution consisting of alkali metal hydroxide, alkali metal nitrate and alkali metal carbonate (AB, Durferrit GmbH, Germany) at a temperature of 430 °C for 15 min. Oxidation of both GNC and PNC samples was performed by supplying

water vapour into the process chamber. GNC samples were oxidised in two steps, first at a temperature of 515 °C for 105 min and then at 500 °C for 45 min, while PNC samples were oxidised in a single step at 520 °C for 60 min.

In Table 1, the main parameters of the nitrocarburising and oxidising processes are summarised.

2.2. Material characterisation

Material characterisation was performed on sample surfaces and on sample cross-sections. After nitrocarburising and oxidising, the surfaces of the samples were not further modified, while the sample cross-sections were prepared by cutting the samples with a Struers 50A25 precision cutting machine (Struers GmbH, Germany), embedding in Bakelite, polishing and etching with a 5% nital solution for 3–5 s.

Hardness of the samples was measured using a TukonTM 2100B indentation hardness tester (Wolpert Wilson® Instruments). Measurements were performed using a Vickers pyramid indenter at a normal force of 0.5 N, i.e. HV 0.05 values were obtained. Vickers hardness measurements were performed for the assessment of the hardness depth profiles and the surface hardness. The hardness depth profiles were measured on sample cross-sections. For statistical evaluation, 2 measurements were conducted on each analysed sample. Surface hardness was measured on the sample surfaces. Due to the high roughness of sample surfaces and the consequent non-uniform imprint shapes, scattering of the measured values was very high; therefore on each analysed sample around 15 measurements were conducted. For the representation of the measured hardness values, the average and standard deviation values were calculated.

Surface topographies of the samples and their roughness parameters were analysed with a laser scanning microscope (VHX-600, Keyence, Japan). Morphology of the sample surfaces and the cross-sections were analysed with a field emission scanning electron microscope (FE-SEM) JEOL JSM-6500F (JEOL, Japan).

Detailed chemical properties of the sample surfaces were determined with Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) by using a Microlab 310 F VG-Scientific SEM/AES/XPS apparatus. XPS surface scans were performed after sputtering with Ar^+ ions for 1200 s. Ar^+ beam of 3 keV was applied at 0.8 μA ion current over an area of $5 \times 4\ mm^2$; at these parameters the sputtering rate was approximately 0.2 nm/min, which means that after 1200 s of sputtering, approximately 4 nm of material were removed from the surface. AES depth profiles were measured during sputtering with Ar^+ ions for up to 36 h at a sputtering rate of about 0.7 nm/min.

For all XPS measurements, Al K_α radiation at 1486.6 eV with an anode voltage of 12.5 kV and an emission current of 16 mA (total power of 200 W) was used. Measurements and data acquisition were controlled by an Avantage 3.41 v data acquisition and processing software supplied by the SEM/AES/XPS equipment manufacturer. A commercially available Casa XPS software for XPS and AES data processing [23] was also used for further data processing, e.g. fitting of high resolution