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Effect of nature of nitride phases on sliding wear of plasma nitrided sintered iron

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ABSTRACT

In the present investigation, the effect of the nature of the iron nitrides (γ'-Fe_4N or ε-$Fe_{2\text{-}3}N$) on the sliding wear of plasma nitrided unalloyed sintered iron is studied. Plasma nitriding was performed in an industrial scale plasma reactor using two different sets of operative parameters to produce microstructures composed of different dominant iron nitride phases, i.e., γ'-Fe_4N and ε-$Fe_{2-3}N$. Microstructural characterisation was performed using optical microscopy, phase analysis was performed via X-ray diffraction, and topographical analysis was performed using laser interferometry. Dry, ball-on-flat and reciprocating sliding tests were used to perform the tribological characterisation. The wear loss was determined by volumetric loss of the wear scar using laser interferometry. The wear rate of the counter-body was also evaluated. Wear mechanisms were characterised using scanning electron microscopy. Compact, free of porosity compound layers with the same thickness were formed, all of which were topographically similar. The analysis of the worn surfaces showed that several wear mechanisms operate simultaneously during the wear process, with the most significant mechanisms being oxidative and abrasive wear. Based on the wear mechanisms, a model for the wear of the nitrided layers (composite layer and diffusion layer) was proposed. The tribological tests indicate that, for the tribo-system evaluated, the ε-nitride layer exhibited a superior wear performance. The volume loss for the ε-phase was two times lower than that for the γ'-phase.

1. Introduction

Powder metallurgy (PM) of ferrous components has gained outstanding importance over the past three decades. PM has been proving to be an alternative lower cost process for small parts when compared with machining, casting, stamping, forging and other similar metal working technologies [1]. In particular, iron based sintered parts have been used for many years in load bearing parts in sliding contacts, such as plain bearings, gears, cams, compressor parts (in particular connecting rods), chain pinions, pulleys, sprockets and brake linings [2].

In addition to reduction in strength and, as a consequence, in load bearing capacity, the inherent presence of porosity might influence the wear mechanisms acting on the surfaces of a PM part in different ways [3]. In order to improve load bearing capacity, fatigue and corrosion resistance, wear behaviour, and even aesthetic aspects of PM iron based alloys, heat and surface treatment (e.g. steam oxidation [4–7], phosphating [8] plasma nitrocarburising [9] and, in particular, plasma nitriding [9–12]) are often carried out.

During the sliding wear process of metals, an oxide layer formed by frictional heating is known to prevent excessive adhesive damage to the underlying metal, resulting in mild wear. Mild wear produces fine, oxidised wear debris. If the oxide is removed faster than it is formed, the resulting wear is severe, as characterised by a rough, torn wear surface with ploughing by hard asperities and the formation of large, metallic debris [13]. As discussed by Kato et al. [14], the nitriding shifts the onset of severe wear to higher loads and sliding speeds and reduces the wear rate compared with non-nitrided steel within the same wear mode.

Among the existing heat and surface treatment, nitriding is quite extensively used for the treatment of PM components. In the plasma-assisted nitriding process, N_2, H_2 and Ar gas mixtures are typically used. Dissociation of molecular nitrogen is one of the most important reactions because it provides atomic nitrogen that diffuses into the sample and forms a nitride layer. The PM parts are usually placed on the cathode of a plasma discharge (cathode configuration); as a consequence, the surface cleaning process can be enhanced by

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sputtering due to the high energy of the plasma active species bombarding the cathode [15,16].

An important aspect to be considered in the nitriding of powder metallurgy (PM) parts is the presence of pores, especially the communicating pores. In the case of liquid and gaseous nitriding, the nitride layer is formed not only on the outer surface of PM parts but also in the inner surface of communicating pores, thereby affecting the mechanicals properties of the parts. The formation of a nitride layer inside the communicating pores is prevented when plasma-assisted nitriding is used [17–19]. Moreover, the use of plasma processes also enables the production of layers with specific structure and properties because of the large number of freely adjustable treatment parameters [20–22].

Plasma nitriding is a thermochemical surface treatment widely used to enhance wear, fatigue and corrosion resistance and provides surface hardening to sintered steels components. The plasma nitriding process has been used commercially and has many advantages over conventional salt bath or gas nitriding. Plasma nitriding is environmentally acceptable when compared to other nitriding processes. The relatively low temperatures used ($\sim$ 540 °C) prevent dimensional distortions, thereby eliminating post-machining work, and the treatment times are shorter for plasma-assisted nitriding [17,23–26].

The microstructure of the nitrided zone, which develops upon nitriding pure iron (or iron-based alloy) using a certain nitriding potential consists of a compound layer (surface layer) and a diffusion zone underneath the compound layer. Depending on the nitrogen concentration in the gas mixture used during plasma nitriding, the compound layer may be constituted by ε-$Fe_{2-3}N$ (hcp arrangement of Fe atoms with ordered occupation of the N atoms at the octahedral interstitial sites) or γ'-Fe_4N (fcc arrangement of Fe atoms with ordered occupation of the N atoms at the octahedral interstitial sites) phases or a mixture of both. In the diffusion zone, nitrogen is either dissolved interstitially in the octahedral interstitial sites of a bcc ferrite matrix or precipitated as γ'-Fe_4N and α''-$Fe_{16}N_2$ (bct arrangement of iron atoms with ordered occupation of N at the octahedral interstitial sites) nitrides [27–29].

Nitrided layers have been used to improve the tribological behaviour of PM parts [20,21]. The variation of the nitriding process parameters results in different nitride layer characteristics: phase type, depth, hardness, hardness profile, etc. [24]. By varying the composition of the nitrided layer, at least one characteristic of the tribological system can be modified, which results in different tribological behaviour.

In comparison with the extensive studies on wear of non-sintered iron based alloys, there has been little work on the tribological behaviour of PM ferrous materials [30–37]. Important contributions include the works of Straffelini and Molinari [4,5,9,10,38–40] and those of de Mello and co-authors [6–8,20].

Molinari et al. [41] investigated the wear behaviour of two non-sintered nitrided (gas and plasma nitriding) steels in order to evaluate the tribological properties of the compound layer and of the diffusion layer. The specimens were treated under different conditions, in order to obtain different microstructural and compositional characteristics of the nitrided surfaces. The tribological results demonstrated the importance of designing the microstructure of nitrided layers to maximise the wear resistance of the treated components. They concluded that in order to maximise the dry rolling–sliding wear resistance, the nitriding conditions should be selected to form a thin, monophasic, compact compound layer and a homogeneous but not too hard diffusion layer.

Pavanati et al. [21] studied the tribological behaviour (dry sliding wear tests, block-on-ring configuration) of plasma nitrided sintered iron (with and without Cr enrichment). A large scatter in the experimental results was observed for the unnitrided samples. This effect was attributed to the capacity of the materials to undergo a severe-to-mild wear transition during sliding. Nitriding was found to reduce the wear rate by at least one order of magnitude. In particular, the nitrided samples enriched with chromium (540 °C) did not display any damage at 25 N, the lowest normal load used in the investigation.

Park et al. [42] investigated the microstructure and wear behaviour of ion nitrided and nitrocarburized sintered steels. The specimens were steamed at 520 °C after sintering at 1120 °C to improve the density. The wear resistance properties of steamed specimens and ion nitrocarburized specimens were better than those of nitrided specimens from the pin-on-disk wear test. A mixture of abrasion and adhesion occurred on the worn surface of nitrided specimens, but abrasion was believed to be the dominant wear mechanism for the nitrocarburized specimens.

Molinari et al. [9] studied the effect of plasma nitriding and nitrocarburising on the microstructure, the microhardness and the wear resistance of two sintered alloys, Fe–Cr–Mo and Fe–Cr–Mo–C. The compound layer comprises Fe_4N and $Fe_{2-3}N$ after nitriding, and only $Fe_{2-3}N$ after nitrocarburising in both the materials. While the C-alloyed material does not gain any benefit from nitrocarburising with respect to nitriding, an improvement in the wear resistance of the C-free material was observed. In addition, the wear resistance of the nitrocarburised C-free material is similar to that of the nitrided C-alloyed material.

Straffelini et al. [43] studied the dry rolling–sliding wear behaviour of plasma nitrided and heat treated Fe–Mo–C sintered alloys. The heat treated alloy undergoes oxidative wear independently of the load condition and duration of the test investigated whereas the plasma nitrided alloys show distinct wear stages characterised by different wear rates. In particular, while the white layer (constituted by both Fe_4N and $Fe_{2-3}N$ nitrides) is able to remain in place the wear rate is low. After loss of the white layer due to oxidation or microcracking, the wear rate increases because both oxidation and plastic shearing control the wear behaviour.

All these references illustrates that a nitride layer plays an important role on improving the tribological behaviour of PM parts. As already mentioned, the formation of a homogenous mono-phase is more desirable than a mixture of these crystalline structures of iron-nitrogen alloys. This preference for a homogeneous mono-phase is because the different structures and cell parameters of the different crystalline phases can generate stresses into the region, thereby increasing the brittleness of the layer [44].

In this sense, de Mello et al. [20] investigated the effect of the nature of the nitride phase Fe_4N (γ') and $Fe_{2-3}N$ (ε) on the microabrasion behaviour of sintered unalloyed iron. Microabrasive wear tests were carried out in a 'free ball' microabrasion tester using SiC slurries. The microstructures constituted of $Fe_{2-3}N$ (ε) phase presented a superior abrasion resistance. The effect of the nature of the nitride phases on the sliding wear behaviour of plasma nitrided sintered pure iron has not yet been investigated.

In this work, monophasic nitrided layers with the same thickness containing either ε or γ' nitrides were obtained by varying the temperature and the gas mixture in the processing chamber. The main objective of this paper is to evaluate the tribological performance of the two different iron nitride phases applied to sintered unalloyed iron specimens.

2. Material and methods

2.1. Sintering

Samples were produced using atomised Fe powder Ancorsteel 1000B, acquired from Höganäs Brasil Ltda. The powder was mixed with 0.8 wt% of zinc stearate and pressed using a double action