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Wear and corrosion of niobium carbide coated AISI 52100 bearing steel

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ABSTRACT

Bearing steels must have high hardness, good wear resistance and dimensional stability. In the present work, the AISI 52100 bearing steel was selected as the substrate for a niobium carbide coating produced by a salt-bath thermo-reactive deposition process. The present work addresses the effect of niobium carbide coating on the wear and corrosion resistance of the abovementioned steel. A homogeneous layer composed solely by the cubic niobium carbide (NbC) was produced. The carbide coating yielded average hardness and elastic modulus of 26 GPa and 361 GPa, respectively. No significant decarburization was detected beneath the case by means of hardness fluctuations. Dry wear tests resulted in worn volumes 10 times smaller for the NbC coated steel, comparatively to the untreated substrate, at three different applied loads. Corrosion tests in NaCl solution indicated an improved behavior for the carbide coated bearing steel at applied potentials inferior than 250 mV. At higher potentials, the electrolyte appears to penetrate trough the layer yielding wide corrosion caps.

1. Introduction

Coating of surfaces is one of the most versatile ways to enhance the performance of components with respect to wear and/or corrosion. Hard coatings can be produced by a wide range of processes requiring controlled atmospheres, vacuum and at high costs [1–4]. An alternative and cost-effective method is the thermo-reactive diffusion/deposition (TRD) technique that can be applied to obtain transition metal compound coatings on iron based alloys [1,5]. The process is usually performed in a salt-bath [4–6] or in the solid state [7–9].

During the TRD process the interstitial element (usually C and/or N) diffuse from the bulk towards the surface to meet a carbide/nitride-forming element such as V, Nb, Ti, Ta and Cr. The diffused interstitials react with the carbide/nitride-forming element from the bath/pack to produce a dense and metallurgically bonded coating at the substrate surface [1,5]. Such process is widely known to yield very high hardness, adhesion and a great potential for extreme wear applications [6,10,11].

Niobium carbide (NbC) is an example of a compound that can be obtained by the abovementioned TRD technique in molten borax. The carbide layer forms by the direct combination of carbon in the substrate with the dissolved niobium in the bath. Such formation is feasible due to its lower free energy for carbide formation and higher free energy for oxide formation than boron [12]. This carbide exhibits a number of interesting characteristics for tribological applications [13]. Additionally to high hardness, NbC presents increased toughness and stiffness, an extremely high melting temperature (3873 °C) and chemical stability [14].

The vast majority of the literature deals with the growth kinetics of the carbide layers [15–17], its mechanical [18] and wear properties [10, 13]. Very few studies deal with the electrochemical behavior of carbide coatings produced by the TRD technique. In fact most of the work in the literature is dedicated to boronizing [19,20]. A study on pack chromizing found that protection against corrosion appears to increase with treatment time and temperature [8]. A recent research indicates that percentage of ferro-niobium added to the bath did not influence the corrosion resistance of the NbC layer. However, it is suggested that porosity slightly decreases as the amount of ferro-niobium increase and that porosity favors the corrosion process [21]. Therefore, it is important to understand the electrochemistry of such coatings in order to expand its possible application range.

Wear and corrosion related phenomena are recurrent problems in industry causing material losses that can further lead to a failure. In this respect, the present study focuses on the evaluation of wear properties and additionally the electrochemical response of niobium carbide layers produced by a salt-bath TRD process on a high carbon bearing steel. The selected substrate is the AISI 52100 steel which is one of the most common bearing steel applied in rolling contact and must have high hardness, good wear resistance and dimensional stability [22].

2. Experimental

Initially AISI 52100 square samples with dimensions of 20 × 20 mm and thickness of 3 mm were ground up to 600 mesh emery paper and

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cleaned in ethanol. The AISI 52100 is a bearing steel also known as 100Cr6 and its nominal chemical composition in wt.% is: 0.95–1.10% C, 0.15–0.35% Si, 0.25–0.45% Mn, 0.03% P, 0.025% S, 1.35–1.65% Cr and Fe. Single values represent the maximum percentage of the element.

The salt bath, for depositing the carbide coating, was composed of 5 wt.% ferro-niobium (containing 65 wt.% Nb and particle size > 150 mesh), 3 wt.% aluminum and 92 wt.% sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$).

TRD treatments were performed in an open air pit-type furnace. Firstly, sodium tetraborate (borax) was molten in a steel container then aluminum and ferro-niobium added. Aluminum was applied as a reducing agent and ferro-niobium as the source of niobium [5]. The specimens were hanged in the homogenized melt at 1000 °C for 4 h and quenched in oil directly from the bath. The produced layer was characterized by X-ray diffraction, scanning electron microscopy (SEM), instrumented hardness measurements, micro-abrasive wear and corrosion testing. Prior to the measurements the samples were cleaned in boiling water and gently polished with alumina suspension (1 μm) in order to remove any residue from the salt bath.

Instrumented hardness measurements were performed on a hot mounted cross section of a coated sample applying a *Shimadzu* dynamic ultra micro-hardness tester (DUH-211S), with a *Vickers* indenter. The test load was 50 mN at a loading speed of approximately 3 mN/s. The elastic modulus (E) of the carbide layer and substrate were estimated as well and the indentations repeated at least 5 times. The elastic modulus of the indented specimens were evaluated based on a standardized method initially proposed by Oliver and Pharr [23], considering a fraction of the unloading curves and the Poisson ratio. For phase identification, X-ray diffraction (XRD) was performed on the surface of the samples using the Bragg–Brentano symmetric geometry in a *Rigaku Gergerflex* equipment with scanning angles ranging from 30 to 100°. The analyses were carried out employing copper (Cu) Kα radiation and continuous scanning with a speed of 2°/min.

Electron microscopy was applied on the cross section of the NbC coated steel using a scanning electron microscope (SEM), model LEO 440 with a tungsten filament, coupled with an EDS (energy dispersive spectroscopy) detector.

A micro-abrasive wear machine was applied for studying the tribology of coated and uncoated systems. Tests were performed in a fixed-ball machine (described elsewhere [6,11]) without abrasive and using a AISI 52100 steel sphere of 25.4 mm in diameter as a counter-body and hardness of approximately 850 HV. The rotation speed and loads were 500 rpm and 665, 1459 and 1826 g (6.65, 14.59 and 18.26 N), respectively. Mean Hertzian contact stress for an AISI 52100 sphere pressed against a NbC plate was calculated as 360, 470 and 500 MPa, for the three studied loads [24].

Consecutive wear scars were produced for test times of 5, 10, 15, and 20 min in order to obtain the volume loss curve for each applied load. Each test was repeated five times on the substrate and twice on the carbide coated steel. One sphere is used for a series of four tests (5, 10, 15 and 20 min) and the sphere is slightly rotated after each test thereby creating a new circular mark around it at every test duration. The removed volume (V) and the wear depth (h) of each wear crater were calculated according to the following equations [25,26]:

$$V \approx \frac{\pi \times d^4}{64 \times R}, \quad \text{for } d \ll R \tag{1}$$

$$h \approx \sqrt{\frac{V}{\pi \times R}}, \quad \text{for } h \ll R \tag{2}$$

where d is the scar diameter, h the wear depth and R the sphere radius.

Additionally, corrosion tests were performed on coated and uncoated specimens in order to comparatively evaluate the electrochemical response of the systems. Experiments were made by means of potentiodynamic polarization tests. The electrochemical cell used to obtain the polarization curves utilized a saturated calomel reference electrode and a platinum auxiliary electrode. The electrolyte employed was an aqueous solution of NaCl 3.5 wt.%. Prior to the tests the system was led to rest for 15 min and the open-circuit potential (OCP) acquired.

For monitoring the potential and current, an Autolab model PGSTAT-302 potentiostat was applied. The polarization curves were obtained with a scanning speed of 1 mV/s from −1.0 to 1.125 V. Each test was repeated twice and a representative curve is shown. For each experiment, 50 ml of the electrolyte was employed and the area exposed to the saline solution was approximately 0.5 cm^2.

3. Results and interpretation

3.1. Metallography and X-ray diffraction

In the present study, the AISI 52100 bearing steel was quenched in oil directly after the TRD treatment. Fig. 1 shows an electron micrograph and a EDS line scan from the cross section of the carbide coated sample. A continuous layer is observed over the base material, presenting a smooth interface with the substrate. Additionally, a small porosity is detected in the layer.

EDS line scan was performed perpendicularly from the top towards the base material and shows iron (Fe) and niobium (Nb) signals. Qualitatively, the analysis indicates a high niobium content on the layer, which decreases abruptly at the interface, where the iron amount from the substrate is detected. Residual aluminum was not found indicating that it is not incorporated into the carbide layer. The thickness of the layer measured directly on the electron microscope at different locations along the layer was about 6.1 ± 0.1 μm. Moreover, the typical martensitic microstructure is verified below the compound layer which results from oil quenching.

Instrumented hardness was measured on the cross section of a hot mounted carbide coated steel on the diffusion layer and on the quenched substrate. AISI 52100 bearing steel has a hardness of about 64 HRC (850 HV or approximately 8.3 GPa) which results from the usually applied heat treatment conditions. The average value of 27 ± 3 GPa was obtained for the carbide layer, which is more than the double of the substrate hardness (11 ± 1 GPa). By means of hardness measurements on the cross section, no indication of a decarburized sub-surface zone was observed, after the TRD treatment. Such decarburization has been reported to develop as a consequence of carbon consumption to sustain the growth of the carbide layer [27].

The Poisson ratio of NbC as well as of the quenched AISI 52100 steel were taken from the literature as 0.21 [28] and 0.28 [29], respectively. Therefore, average elastic modulus of NbC and quenched AISI 52100 were estimated as 361 ± 35 GPa and 206 ± 14 GPa, respectively.

Specialized literature indicates that elastic modulus of niobium carbide usually ranges from 338 to 580 GPa. Hardness of NbC depends on the metal to carbon ratio and a maximum of 25 GPa is observed for a ratio of 0.8 decreasing to 20 GPa when the ratio reaches the unit [28]. However, these properties are additionally dependent on the fabrication process, presence of impurities, etc. [28]. A study conducted by Orjuela G. and coworkers found hardness values of 26 GPa for niobium carbide coatings produced by TRD on a carbon steel employing nanoindentation [21]. These values are in close agreement with the results of the present work.

In Fig. 2, an X-ray diffraction pattern of the coated AISI 52100 steel is shown. The narrow peaks confirm the presence of a cubic NbC layer on the surface of the substrate, according to ICDD card, number 38-1364. Additionally, ferrite peaks (α-Fe) are detected due to the penetration of the X-rays. These peaks actually correspond to martensite that is obtained after oil quenching the specimens directly from the salt bath after the treatment cycle (1000 °C/4 h). The results are in agreement with previously published research [6,10,11,21].

Niobium carbide layers can be produced in borax salt bath treatment because this transition element has a relatively small free energy of