Abstract

In this work, Al-doped niobium carbo-nitride coatings were realized on AISI 4140 steel substrate by thermo-reactive diffusion/deposition (TRD) method. The effect of various amounts of aluminum contents on the wear resistance of niobium carbo-nitride coatings was investigated systematically by X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), micro hardness and wear tests. The XRD results showed that the coating layers consist of NbC, NbN, AlN, α-Fe and Fe3N phases. Hardness of the coating layers were obtained ranging from 993.65±106.25 to 2077.58 ± 194.65 HK0.005. Dry wear tests were performed under 2.5, 5 and 10 N applied loads at 0.1 m/s sliding speed against Al2O3 ball. The obtained wear resistance value for the Al-doped niobium–carbo-nitride coating including 1.0 wt. % Al was higher. The wear mechanisms of the coatings were polishing wear.

1. Introduction

Hard and wear resistant coatings are commonly deposited on tools which are used for severe cutting, forming and casting applications, where the conditions typically result in high temperatures, mechanical loads and pronounced wear [1]. Two different deposition technologies are conventionally used, chemical vapour deposition (CVD) and physical vapour deposition (PVD), which, nevertheless present some drawbacks such as the plant investment cost and the need of a vacuum or highly controlled atmosphere [2]. These techniques are limited because their implementation requires the use of complex and costly equipment that must be operated at high-vacuum conditions [3]. Another option for the production of coatings is the thermoreactive deposition process (TRD). This technique was patented by Toyota in Japan and it has been applied successfully for many years at industrial level for producing several types of layers on iron-based alloys [4]. During the TRD process the interstitial element (usually C, N and/ or B) diffuse from the bulk towards the surface to meet a carbide/nitride-forming element (CFE) such as Nb, Cr, V, Ti, Al and Ta. 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. Such process is widely known to yield very high hardness, adhesion and a great potential for extreme wear applications [5]. The TRD technique can be performed with various techniques such as; using molten borax/chloride bath, fluidized bed or pack method [6].

Niobium carbide/nitride coatings have attractive properties such as high hardness, high wear resistance, excellent chemical resistance and high melting point [4] and [6]. Several studies have been performed to investigate the mechanical and wear properties of NbC and NbN coatings produced through TRD technique on steel substrates [5], [8], [9].

Aluminum is added to the transition metal nitrides bath in order to enhancing mechanical properties, wear and oxidation resistance through PVD technique [10], [11]. Differently from this technique, Al is added to coated bath for avoiding the CFE elements from oxidation to the molten borax bath [2]. Unlike the molten borax bath, the pack method is realized with using chlorine gas with the CFE’s. Both elements compose metal-clorine phases which react with interstitial atoms and deposit hard transition metal carbide/nitride based phases on steel substrate. Like this hard phases, Al-based phases can be formed via pack method. In this sense, the aim of this study producing and examining of wear properties of Al-free and Al-added Nb-C-N coating on AISI 4140 steel.

2. Experimental procedure

AISI 4140 steel was selected in the present work as substrate. The substrate material was supplied from Asil Çelik, Turkey in the form of a bar 20 mm in
diameter. The chemical composition of the substrate is reported in Table 1. Slices measuring approximately 5 mm in thickness were cut from the bar and their surfaces were ground up to 1200 grid emery paper and ultrasonically cleaned in ethanol for 15 minutes. For obtaining nitrogen rich layer on the substrates, all samples were nitrided at 803 K for 12 h through the gas nitriding process. The TRD process was carried out on pre-nitrided samples using commercial ferro niobium, ammonium chloride, aluminum (99.5 % purity), alumina and naphthalene at 1000°C for 4h. The amounts of Al in the coating bath were 1.0 wt% and 2.0 wt%, besides Al-free coating.

Table 1. Chemical composition of AISI 4140 steel that used in this study.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass Percentage (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.41</td>
</tr>
<tr>
<td>Si</td>
<td>0.20</td>
</tr>
<tr>
<td>Mn</td>
<td>0.62</td>
</tr>
<tr>
<td>P</td>
<td>0.02</td>
</tr>
<tr>
<td>S</td>
<td>0.02</td>
</tr>
<tr>
<td>Cr</td>
<td>0.96</td>
</tr>
<tr>
<td>Mo</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Phase analyses of the coated samples was realized with the help of a Rigaku diffractometer (Model D/MAX-B/2200/PC, Rigaku Co., Japan) using copper (Cu) K$_\alpha$ radiation, continuous scanning with a speed of 2°/min. and scanning angles ranging from 20° to 80°. Microstructural examinations were carried out using a scanning electron microscopy (Model JEOL JSM-6060, FEI Co., Japan) coupled with energy dispersive X-ray spectroscopy (EDS) on the cross section of the metallographically prepared samples.

A ball-on disc tribometer which made in accordance with ASTM G133-05 standard was used for the dry sliding wear tests. The tests were all conducted at room conditions with a 10 mm in diameter Al$_2$O$_3$ ball as the counter-body. The sliding speed was selected as 0.1 m/s and the sliding distance was 250 m. The applied loads were 2.5 N, 5.0 N and 10.0 N for the tests. Mean Hertzian contact pressures calculated for Al$_2$O$_3$ ball under the applied loads were 389 N/mm$^2$, 491 N/mm$^2$ and 618 N/mm$^2$, respectively. Wear features of the surfaces were examined using the SEM examinations. Wear rate of the coated samples were measured by making linear height profiles across the wear scar, as shown in Fig. 1, which is a 3D topographic image of a typical wear track. Profiles were made using a stylus profilometer (Model P-7, KLA Tencor, USA). The depth of the wear scar was determined by averaging the lowest point in the center of the three line scans. The calculated debris areas for the three line scans were averaged and used as a surrogate measure of debris volume.

3. Results and Discussion

Fig. 2 shows the typical SEM image of 1 wt. % Al-doped Nb-C-N coatings on AISI 4140 steel. The layer is dense, compact and has a thickness of approximately 6 µm. Any crack or porosity cannot be seen in the coating layer. Coated samples include porosity at low rates at the interface between the coating layer and the substrate. When pre-nitrided substrate is used, generally some porosities and a non-perfectly flat interface can be seen in the diffusion zone of the coated samples [2]. The cooling treatment of the coated samples were done in the coating bath for 1h. Depending on the cooling rate, martensitic transformation cannot be seen on the substrate.
The elemental distributions of the coating layers were investigated means of energy dispersive X-ray spectrometry. Fig. 3 shows that the layer consists of Nb, C, N and Al. The diffusion of iron was not realized to the compound layer. During the TRD coating process, formation of the coating layer is carried out merging into interstitial atoms which contained in the substrate and CFE which comprised in coating bath [6]. Considering the chemical composition of the substrate, there is no any Nb or Al in the substrates of the coated samples according to EDS analysis. In general Nb and Al are strong carbide/nitride forming elements and any free Nb or Al atoms cannot be diffuse in to the steel matrix because of the C/N concentration of the steel.

Aluminum has a significant effect on the hardness of Nb-C-N coatings. The hardness values of the coating layer showed an increase from 994±106 to 2078 ± 195 HK0.005. According to Reiter et al, dissolution of aluminum within the NbN lattice caused to inducing strain in the coating layer, hindering the dislocation movement with the effect of increasing hardness [13].

The XRD patterns of the coated samples were presented in Fig. 3. According to the patterns, the sample which is coated in Al-free bath contains NbC, α-Fe and NbN as major and FeN as minor phases. In chemical composition of the coating layer iron was not found and from this point of view, it can be express as the minor phases are shown in the patterns for containing in the substrate. However, Al addition in the coating bath caused to formation of AlN phase as well as Nb-based phases. In general Nb(C,N) coatings include NbC and NbN phases [12].

The sliding wear test results are presented in Fig. 4 and revealed a relationship between total wear volumes of the tribosystem (ball and disc) and applied load for the coated samples. The higher the applied load caused to increase in the wear rate. As shown from the Fig. 4 that increase in the applied load from 2.5N to 10N caused to 10 times increase of the wear rate of the coating layers against Al2O3 ball. When compared to the bath composition, the least amount of wear was determined in the 1 wt. % Al-doped coating. Al addition in the coating layer resulted to increase of the wear resistance of the NbCN coatings. Archard equation explained that the higher the hardness caused to the higher the wear resistance [13]. However, as shown from the figure that, 1 wt. % Al addition caused to increase in the wear resistance of the layers. In general high content Al addition resulted to increase of the brittleness of the coating layer [14].

Fig. 5 shows typical SEM image of the wear track produced on the 1 wt. % Al-doped coating surface for 10 N loads. The wear tracks have a smooth appearance because of polishing effects of Al2O3 counterpart on the worn surface, gently. With increasing the load was gave rise the polished area. In addition the observation is that any groove or adherence were not found onto the wear tracks. For this reasons, main wear mechanism is polishing.
wear for all loads and all bath compositions. As shown from the figure that under the test conditions, coated layers are withstand.

Figure 4. Wear rate curves of the Al-free and Al-doped Nb-C-N coated AISI 4140 steel with 2.5, 5 and 10 N of applied loads.

Figure 5. SEM image of the wear track produced on the 1 wt. % Al-doped coating surface for 10 N load under dry sliding.

4. Conclusions

In this paper, Al-free, 1 and 2 wt. % Al doped Nb-C-N coatings were produced by the TRD technique at 1000 °C for 2 h on AISI 4140 steel. The Nb-C-N coatings are mainly composed of NbC and NbN phases. With addition of aluminum, AlN phase emerge in the coating. Hardness values of the coating layer showed an increase from 993.65±106.25 to 2077.58 ± 194.65 HK0.005 with aluminum addition. Increasing of the load is increased wear rates for the all coated samples. 1 wt. % Al-doped Nb-C-N coating showed the best wear resistance. Main wear mechanism of the coated samples is polishing wear.

References