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Research Article

Investigation of Tribological Properties of TiAlCN Coated Piston Ring

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Abstract

In internal combustion engines (ICE), the friction of parts working in contact affects both engine life and fuel consumption. Piston rings cause a significant portion of friction losses in an ICE. The most effective method to reduce these losses is the surface coating process. The PVD technique draws attention both because it does not pose a problem for the environment and because it enables the coating of complex geometric parts. In this article, the tribological and mechanical properties (microhardness) of TiAlCN ceramic coating and uncoated piston ring coated on the surface of the cast iron piston ring by the cathodic arc PVD technique were investigated. The structural properties of the coated and uncoated samples were investigated by SEM, EDX and the coatings must have XRD methods. As a result of the tribological test, the average friction coefficients of the uncoated and TiAlCN coating under dry conditions were determined as 0.76 and 0.21, respectively. As a result of the reciprocating slip test, the wear rate of the TiAlCN coating was reduced by approximately 97% compared to the uncoated ring. The results showed that the TiAlCN coating exhibited good tribological properties. Besides, wear mechanisms were examined based on the SEM image and EDX analysis taken from the worn surface of the samples.

Keywords: Physical Vapor Deposition (PVD), Piston ring, Wear, TiAlCN

TiAlCN Kaplı Piston Segmanının Tribolojik Özelliklerinin İncelenmesi

Öz

İçten yanmalı motorlarda (ICE) temas halinde çalışan parçaların sürtünmesi hem motorun ömrünü hem de yakıt tüketimini etkiler. Piston segmanları bir ICE de sürtünme kayıplarının önemli bir kısmına neden olmaktadır. Bu kayıpları azaltmak için en etkili yöntem yüzey kaplama işlemidir. PVD tekniği hem çevre için sorun oluşturmaması hem de karmaşık geometrik parçaların kaplanmasına olanak sağlaması nedeniyle dikkat çekmektedir. Bu makalede, katodik ark PVD tekniği ile dökme demir piston segmanı yüzeyine kaplanan TiAlCN seramik kaplama ve kaplanmamış piston segmanının tribolojik ve mekanik özellikleri (mikrosertlik) incelenmiştir. Kaplamalı ve kaplamasız numunelerin yapısal özellikleri SEM, EDX ve XRD yöntemleri ile incelenmiştir. Tribolojik test sonucunda kaplamasız ve TiAlCN kaplamanın kuru koşullar altındaki ortalama sürtünme katsayıları sırasıyla 0.76 ve 0.21 olarak belirlenmiştir. Resiprocating kayma testi sonucu, TiAlCN kaplamanın aşınma oranı kaplanmamış segmana kıyasla yaklaşık %97 oranında azaltılmıştır. Sonuçlar, TiAlCN kaplamanın iyi tribolojik özellikler sergilediğini göstermiştir. Ayrıca, numunelerin aşınmış yüzeyinden alınan SEM görüntüsü ve EDX analizine bağlı olarak aşınma mekanizmaları incelenmiştir.

Anahtar Kelimeler: Fiziksel Buhar Biriktirme (PVD), Segman, Aşınma, TiAlCN.

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1. Introduction

In automotive systems, researches on cost reduction, fuel consumption, and exhaust emission reduction are in progress with innovative technological studies. Reducing environmental problems and ensuring low energy consumption are among the top priorities of automotive manufacturers (Chu et al., 2012; Mehran et al., 2018). This can be avoided by reducing the friction of moving parts in the ICE used as a power source in automobiles (Holmberg et al., 2012; Özkan, 2018).

In ICE, friction losses are the biggest cause of performance losses. Friction losses in the engine adversely affect engine life, engine performance and fuel economy (Nakada, 1994). Friction loss from the piston rings contributes to almost 50% of the total mechanical friction loss in an engine (Dolatabadi et al., 2020; Lin, 2016). Piston rings are located in the combustion chambers of ICE and work in contact with the cylinder surfaces (Silva, 2006). Rings are prone to friction and wear as they move within the cylinder, as they operate under high temperature and heavy load conditions. They are made of wear-resistant materials such as steel or cast iron to reduce wear, and surface coating treatments are applied to increase their wear resistance (Kara et al., 2019; Mehran et al., 2018). It is very important that the coatings have a low coefficient of friction. Because the high coefficient of friction increases the wear rate that affects the performance of the engine (Vinoth et al., 2019). For this reason, it is necessary to know the effects of surface coatings applied to the rings against friction. If the tribological properties of ICE components are improved, the amount of energy consumed by friction and economic losses can be reduced.

Surface coatings have found application areas in many branches of industry and the automotive sector in order to improve the wear properties of materials, extend their life, and reduce energy loss. It is known that the piston rings are mostly coated with hard Cr by the electrolytic coating method in the industry (Sharma et al., 2020). However, the harmful chemicals used in this method pose a threat to human health and the environment (Bozyazı et al., 2004; Zhuoa et al., 2000). Therefore, more research should be done to study alternative methods and coatings. In industrial production, Efforts to develop environmentally friendly technologies are increasing day by day. Among them, the PVD method does not pose a problem for human health and the environment (Mehran et al., 2018).

By the PVD (Physical Vapor Deposition) method, advanced technological ceramic film coatings such as wear-resistant hard nitrides (TiN, AlCrN, TiAlN), carbonitride (TiCN), multi-layer coatings can be produced (Bull et al., 2003; Priyan et al., 2016). TiN coating is the oldest and most known coating type among PVD coatings. The TiN coating has become one of the widely used coatings in the industry due to its good tribological properties and especially its low coefficient of friction (Kara et al., 2019; Shan et al., 2013). However, TiN coatings have some disadvantages such as low oxidation resistance (500-600 °C), adhesion and hardness (Hsieh et al., 2006; Kulkarni et al.,2018; Wang et al., 2013). Lately, different elements such as Al or C have been added to the TiN structure to create new systems with improved tribological features and stability (Zeng, 2015). TiAlN coatings are obtained by adding Al to the TiN structure (Larbi et al., 2006; Zhang et al., 2008). The addition of Al provides the formation of a protective aluminum oxide layer (Al2O3) on the coating surface as well as increases the hardness (Paldey and Deevi, 2003; Wang et al., 2017). This layer prevents the diffusion of oxygen atoms to the substrate and increases the oxidation resistance (800-900°C) (Dejun and Haoyuan, 2015; Kulkarni et al., 2018). However, a higher friction coefficient of TiAlN coatings than TiN coating causes poor tribological properties (Tillmann et al., 2020). The addition of C is effective in reducing the coefficient of friction (Zhang et al., 2014; Zhang et al. 2008). Therefore, the new generation quaternary TiAlCN coatings created by adding C to the TiAlN coating system are quite remarkable (Shtansky, 2009; Zeng et al. 2015). This coating exhibits both high thermal resistance and good tribological properties (Zeng et al. 2015; Zhang et al. 2008).

Literature studies on coatings applied to piston rings by the PVD method are summarized below. As a result of the literature review, it was observed that the research on piston rings coating with the PVD method is limited. The researchers observed that the Ti/TiN coating wore 30% less than the cast iron ring (Lyubimov et al., 1992). In another study, TiN, TiAlN and DLC coatings were applied to cast iron rings and their tribological properties were investigated. According to the test results, the best tribological properties were obtained from the DLC coated sample. The worst performance was reported for the TiAlN coated sample (Cho and Lee 2009). Friedrich co-workers deposited CrN coatings on the steel ring and observed that it showed an effective wear reduction of approximately 94% compared to electroplated Cr coated rings (Friedrich et al., 1997). The tribological properties of CrN, DLC, and MoS_2 coated cast iron rings were investigated by Zabala and co-workers by reciprocating wear test. As a result of the test, it was reported that the DLC-coated ring exhibited the best tribological properties (Zabala et al., 2017). In another study, the tribological behavior of CrN and DLC coatings on nitrided stainless steel rings was determined by a reciprocating tribometer. The test results showed that the least wear was on the DLC coating (Tung and Gao 2003). Lin and co-workers worked on the TiSiCN nanocomposite coating, which they developed by adding C to TiSiN on the stainless steel ring surface. Compared to the uncoated ring, the coated ring was found to have 29% lower weight loss (Lin et al., 2016). As a result of the literature review, generally, it was seen that the effects of TiN, CrN and DLC coatings were investigated in the studies of rings coated with the PVD method. However, the TiN coating has low oxidation resistance as described (Hsieh et al., 2006; Kulkarni et al., 2018). The fact that the DLC coating has a low friction coefficient due to the carbon in its structure has attracted the attention of researchers. However, its tendency to show high friction and adhesion at temperatures above 200 °C has been ignored (Banerji et al., 2014). It has been observed that there is no study in the literature in which TiAlCN (Titanium Aluminum Carbonitrid) coating was applied on the cast iron piston ring using the PVD method. In addition, the limited number of TiAlCN studies in the literature makes it difficult to understand their tribological behavior. Therefore, more studies are needed.

The present study, it was aimed to investigate the tribological and mechanical features of TiAlCN coating applied to piston ring of cast iron by the Cathodic Arc PVD technique. The tribological properties of the coated and uncoated rings were compared according to the wear test results performed under dry conditions. The tribological properties of the coated and uncoated rings were compared according to the wear test results performed under dry conditions. In addition, according to the SEM photograph and EDX results taken from the wear areas of the samples, the wear mechanisms were investigated.

2. Material and Methods

Piston ring produced of cast iron with dimensions of 4.37x93x3 mm was used as base material. To properly characterize the coating properties, the specimen surfaces must have a smooth structure and the harmful effects such as oxide and dirt on affecting the coating quality must be eliminated. Therefore, firstly specimens were cleaned with ethanol. Secondly, rings were gradually sanded with 60, 120, 240, 400, 600, 800 and 1200 mesh SiC sandpaper. Finally, after polishing the sample surfaces with 1 μm diamond paste, they were cleaned with ethanol again and made ready for coating. The chemical composition of the ring specimen used is shown in Table 1. The ring prepared for the coating and the coated ring is shown in Figure 1.

Table 1. Chemical composition of the base material

Element	**C**	**Si**	**Mn**	**Cu**	**P**	**S**
wt.%	3.48	2.29	0.175	0.72	0.047	0.014

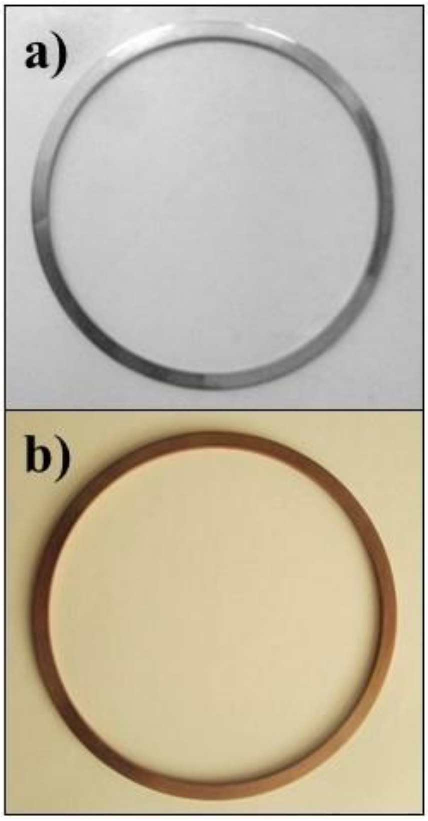

Figure 1. Piston rings a) uncoated and b) TiAlCN coated

The cathodic arc PVD technique was used for the surface coating of the piston ring. (KAPCO coating Co./Turkey) (Figure 2). In the coating process, alloy material ($Al_{67}Ti_{33}$) and pure Ti were used as targets. In the coating production, the applied temperature, cathode current, bias voltage and pressure parameters were 450 ^oC, 55 A, -100 V and $1.5x10^{-2}$ mbar, respectively. The acetylene gas flow rate used as the carbon binder was 20 cm^3/min. Carbonitride compounds were formed on the anode surface by keeping the nitrogen gas flow rate sent into the room at 760 cm^3/min. During the coating process, the ring was rotated around itself (0.5 s^{-1}) and around the carousel center (0.1 s^{-1}) for a homogeneous coating on the piston ring surface. Primarily, the TiN (Titanium nitride) adhesion layer was deposited on the substrate surface for about 5 minutes. Next, the coating was produced by simultaneously powering targets (Ti and AlTi alloy) to deposit TiAlCN on the piston ring.

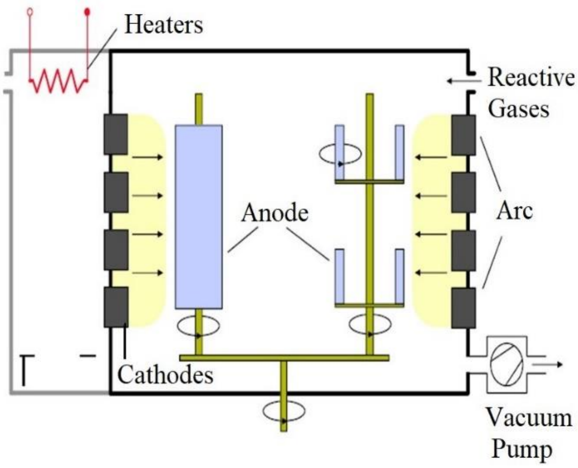

Figure 2. CAPVD system

The coating thickness of the ring, which was applied to the coating process and cut about 1 cm in size, was measured with a Scanning Electron Microscope (SEM, JSM-7001) device. SEM device was used to detect wear marks and wear mechanisms of uncoated and coated test specimens. The identities and percent compositions of the elements in the specimens were determined by Energy Dissipative X-Ray Spectroscopy (EDX, JSM-7001) analysis. The phases formed on the uncoated and coated ring surface were examined using X-Ray Diffraction (XRD, RIGAKU) device. Analysis was performed in Cu-Kα radiation (λ = 1.5405 Å) at a scanning speed of 2^o/min in the scanning range of 2Θ =30-80^o.

The hardness values of the samples were measured with a microhardness tester (SHIMADZU HMV-G20). The hardness test for each sample was carried out under a load of 10 g and a dwell time of 10 s. The measurements were made at five different points and the average hardness values of the samples were determined.

Tribological tests were performed using a reciprocating tribometer (CSM/Anton Paar Instrument) designed according to ASTM G133. As a result of the experiment, the friction coefficients and wear rates of the uncoated and coated samples were determined for a 250 m sliding distance. A profilometer (Veeco Dektak 8 Profilometer) was used to find the wear rates of samples. By using wear profiles of the samples with a surface profilometer, the field of the wear traces was determined. Then, the wear rates were calculated automatically by entering the values into the tribometer software.

3. Results and Discussion

3.1 Structural Characterization

In Figure 3, SEM images of cast iron, TiAlCN coated ring surfaces were given. Fig. 3a shows that the cast iron has a porous structure.

Table 2. Wear test parameters

Parameters	Values
Test type	Ball-on flat
Normal load (N)	10
Velocity (m/s)	0.18
Stroke (mm)	12.5
Ball-type	Alumina (Al_2O_3)
Temperature (^oC)	Room temp. (23±2)
Ambient	Dry

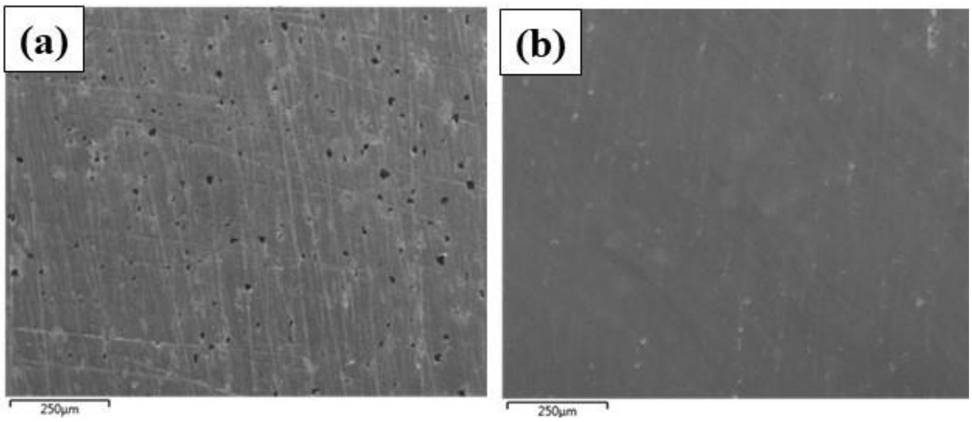

Figure 3. SEM surface morphologies of samples a) uncoated, b) TiAlCN

The presence of pores causes roughness on the surface and therefore a high coefficient of friction. The SEM images provided show that the porous structure is eliminated with the coatings and better surface quality is achieved. The mean thickness was determined as 2.94 µm from the SEM image of the TiAlCN coating (shown in Fig.4). The SEM image shows that the coating is homogeneously coated on the surface.

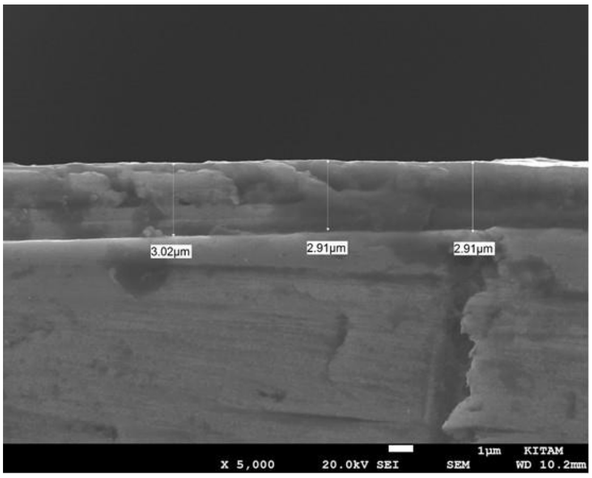

Figure 4. SEM image of the coating TiAlCN

XRD graphics of the samples covered with cast iron base material and ceramic films are given in Figure 5. It was observed that the peaks occurring at 36.19°, 42.58°, 65.12° and 77.8° in the XRD pattern of the TiAlCN coating belong to the planes (111), (200), (220) and (222), respectively. XRD results were found to be compatible with the literature (Klimovich et al., 2018).

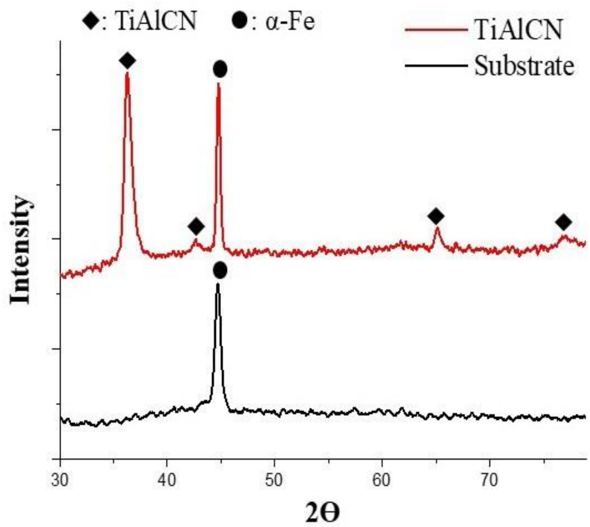

Figure 5. XRD graphics of samples

3.2 Mechanical and Tribological Characterization

One of the aims of PVD coatings is to increase the hardness of the base material. In Figure 6 shows the data from the microhardness test. The hardness value of the base material was measured as 433 ± 34 $HV_{0.01}$ (4.2 GPa). As is known, TiAlCN is obtained by adding C to the TiAlN structure. Thus, it is tried to obtain harder coatings than TiAlN coatings due to the C in the coating structure (Jang et al., 2005; Zhang et al., 2008). The researchers reported that the hardness value of the TiAlCN coating obtained by adding C to its structure with TiAlN applied on the steel substrate increased from 22 GPa to 41 GPa (Jang et al., 2005). In another study, the hardness value of the TiAlCN coating on the steel substrate surface was determined as 33 GPa (Zhang et al., 2014). In our previous study, the hardness value of TiAlN coating on cast iron base mate-rial was measured as 2667 $HV_{0.01}$ (26.1 GPa) (Alışır and Evrensel, 2021). It was observed that the hardness value of the TiAlCN coating produced in this study increased to 3345 ± 0.50 $HV_{0.01}$ (33 GPa) (Figure 6). The results of our studies were found to be compatible with the literature findings.

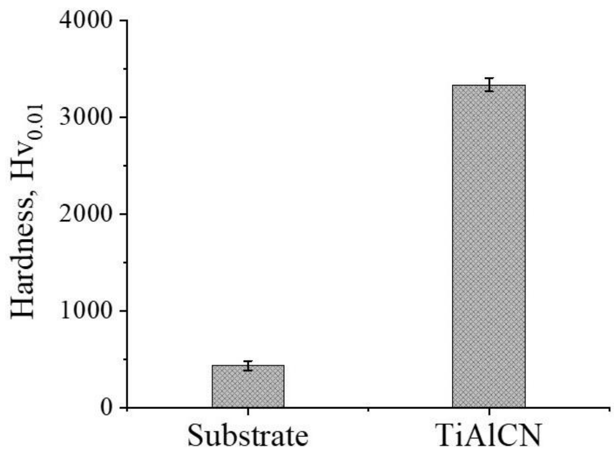

Figure 6. The hardness values of substrate ve TiAlCN coated samples

The graph of the effect of the sliding distance of the uncoated and coated rings on the coefficients of friction (COF) is given in Figure 7. The coefficients of friction for the 250 m sliding distance of uncoated, and TiAlCN coating were determined as 0.76 and 0.21 respectively. As seen in Figure 7, it was determined that the fluctuations were high in the uncoated sample, while the TiAlCN coating exhibited a more stable curve. As the sliding distance increased, the highest COF value was observed in the uncoated sample. It can be said that this is because of the increased iron oxide residues as a result of plastic deformation and the rough surface provides resistance to slipping. Cho and Lee reported in their study that iron oxide formed on metal surfaces causes high friction (Cho and Lee, 2003).

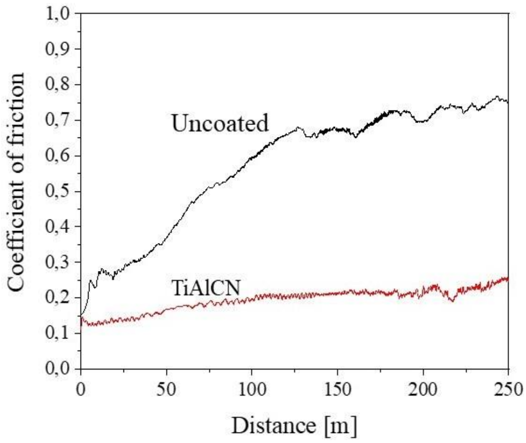

Figure 7. Coefficients of friction of uncoated and coated piston rings

After the wear test, SEM/EDX analyzes from the wear zone of the uncoated specimen showed that oxidation residues were formed (Fig. 8a and Fig. 8b). In the obtained SEM image, it was observed that the base material underwent high plastic deformation (Fig. 8a). In addition, as the friction continued, iron oxide residues formed by adhesive wear revealed abrasive wear, which caused the wear to increase further. The separation of deep wear lines and layers in the SEM image shows that the wear mechanism was abrasive and delamination wear.

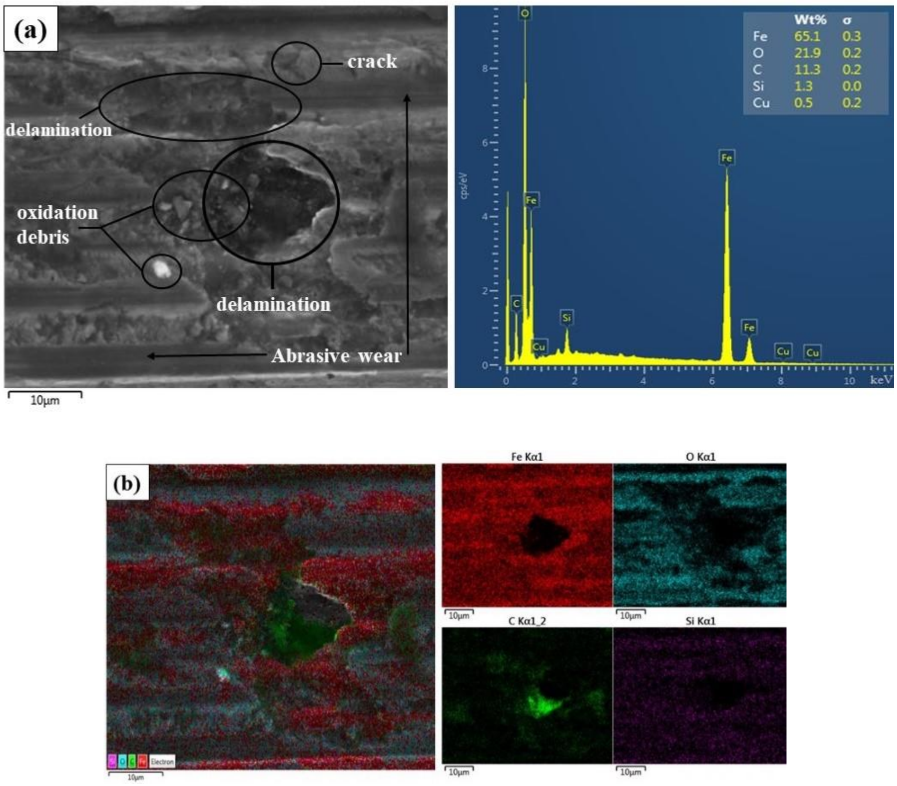

Figure 8. Taken from the wear area of the uncoated sample; a) SEM image and EDX analysis and b) EDX map results

As seen on the EDX map, ın the wear test carried out in dry conditions, oxidized aluminum due to its contact with air formed an aluminum oxide (Al_2O_3) layer on the surface of the coating (Figure 9b). This Aluminum oxide layer helps to form an additional protective layer on the worn surface, thus increasing their abrasion resistance (Ananthakumar et al., 2012). When looking at the EDX map taken from the slip zone of the TiAlCN coating, it is seen that the protective oxide layer is not destroyed and the coating elements (C, O, Ti, N, Al) are properly spread on the surface (Fig. 9b). The obtained SEM image and EDX data show that the ball does not descend into the base material, and the coating protects the base material surface (in Fig. 9a and 9b). The fact that the Fe element signal is very low in the EDX analysis and the absence of other elements belonging to the base material supports this situation.

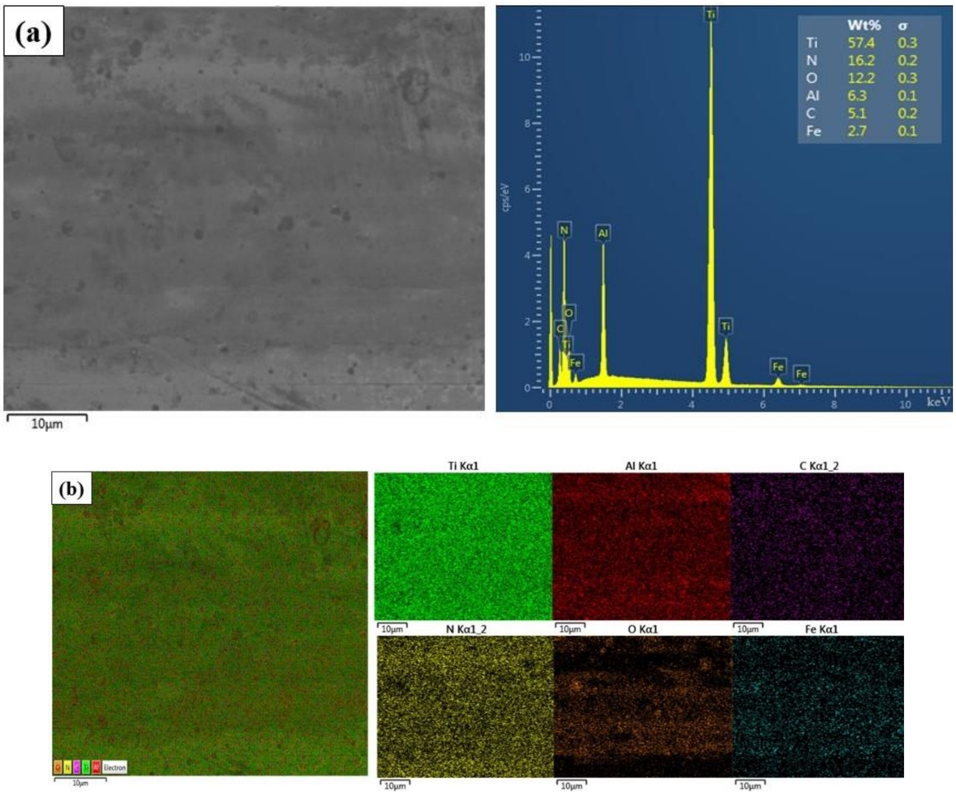

Figure 9. Taken from the wear area of the TiAlCN coated sample; a) SEM image and EDX analysis and b) EDX map results

In Figure 10, SEM pictures of the wear scars occurring on the surface of the samples as a result of the wear tests are shown. When the obtained images were examined, the widest wear scar was seen on the uncoated sample. The narrowest wear scar was detected in the TAlCN coated sample.

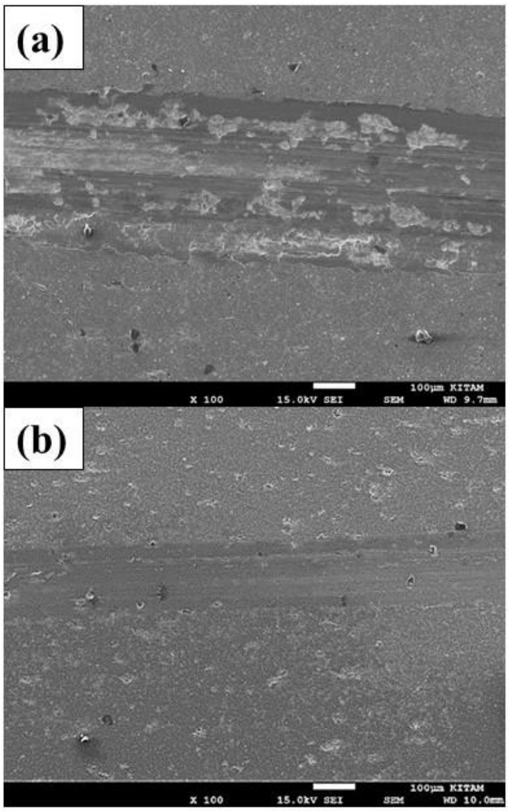

Figure 10. SEM images of wear scars a) Uncoated and b) TiAlCN

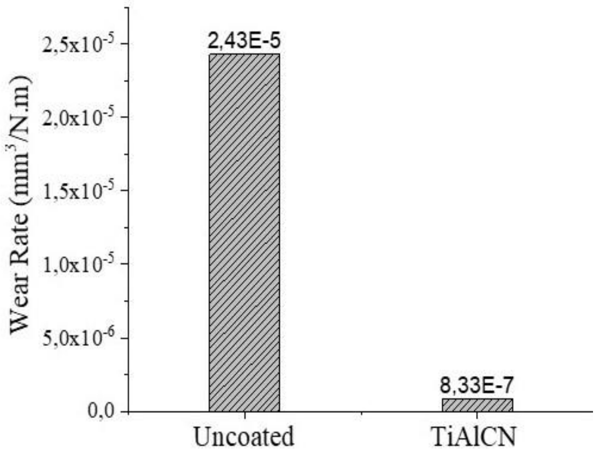

Figure 11. Wear rates of uncoated and TiAlCN coated samples

When the SEM images in Figure 10 were examined, it was seen that there was a parallelism between the wear scars and the wear rates (Fig. 11). As a result, the highest wear rate was obtained from the uncoated ring ($2.38x10^{-5}$ mm^3/N.m). Compared to the untreated specimen, a 97% reduction in the wear rate of the TiAlCN coated ring was detected. In the results obtained, it can be said that the reason for the highest wear in the uncoated sample is that both its hardness is low and the iron oxide particles formed by friction heat cause high friction and reduce the strength. The better wear resistance of the sample coated with the ceramic film was attributed to the aluminum oxide layer formed, high hardness and low friction coefficients. As it is known, another purpose of adding C to the TiAlN structure is to reduce the friction coefficient. Accordingly, while the friction coefficient of TiAlN coating was 0.60 in our previous study, it was observed that the friction coefficient decreased to 0.21 with the addition of C (Alışır and Evrensel, 2021). Therefore, this situation also affects the wear rate. In short, it is expected that the sample with a lower friction coefficient will wear less. The results show that the wear rates of the TiAlN and TiAlCN coating compared to the uncoated ring were reduced by 63.9% and 97%, respectively. Lackner et al. have reached similar results in their studies. In their study, it was reported that the TiAlCN (μ=0.20) coated sample, which has a low friction coefficient, wears less than TiAlN (μ=0.70) (Lackner et al., 2004).

4. Conclusions

Increasing environmental awareness and ensuring low energy consumption is very important for automobile manufacturing companies. This can be provided by improving the wear and friction of engine parts. In this paper, the piston ring which causes a significant part of the energy loss in internal combustion engines to surface improvement was aimed with TiAlCN coating. For this purpose, the morphological properties, microhardness, friction coefficient, wear rates and wear mechanisms of the rings were also investigated. The results supported by experimental data are given below;

- XRD analysis data shows that TiAlCN coating was successfully obtained on the surface of cast iron base material by cathodic arc physical vapor deposition technique.
- The hardness test results showed an 8 times increase in the hardness of the TiAlCN coated ring (3345 $HV_{0.01}$) compared to the uncoated specimen (433 $HV_{0.01}$).
- According to the friction test results of the untreated and TiAlCN coated ring, the lowest COF value was obtained for the TiAlCN coated ring (μ=0.21).
- When the wear rates were examined, the highest wear rate was found for the uncoated sample. It can be said that The reason for this is that both its hardness is low and the iron oxide residues formed by friction heat reduce the strength. It was observed that the wear rate of the TiAlCN coated piston ring decreased by ≌97 according to the untreated ring.
- When the wear scars were examined, a parallelism with the wear rate was obtained. As a result, the largest wear scar was obtained for the uncoated sample. A significant reduction in the scar width of the TiAlCN coating was observed.

- When the wear mechanisms were evaluated, it was determined that dominant abrasive wear and delamination occurred in the uncoated sample. Experimental findings from the wear zone of the TiAlCN coating showed that the surface was quite even. It was determined that the TiAlCN coating on the surface was preserved, while almost no wear was observed.
- As a result, the surface properties of the ring coated with TiAlCN were improved.
- ❖ The PVD system is an environmentally friendly technique. For this reason, the evaluation of the tribological effects of the new generation coatings to be produced with the PVD system on the rings will contribute to the literature.

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Author contribution statement

The contribution of both authors is equal in this study.

Ethics in Publishing

There are no ethical issues regarding the publication of this study.

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