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Influence of Superficial Titanium Based Ceramic Coating on the Isothermal Oxidation Behavior of High Speed Steels

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ABSTRACT. This work concentrates on the beneficial effects of Titanium-based ceramic coating on the oxidation behavior of high-speed steels. Two types of high-speed steels with varying concentrations of chromium have been investigated by the gravimetric analysis method. Physical Vapour Deposition (PVD) technique was used to coat TiAlN on the steel specimens, and the isothermal oxidation behavior is studied at temperatures, namely 600^{o}C, 700^{o}C, and 800^{o}C. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses were used to analyze the steel specimens' surface before and after the oxidation process. Rapid oxidation is observed at the initial stages of oxidation, and a decrease in oxidation rate was obtained concerning an increase in oxidation time. When the temperature increases, the oxidation resistance decreases. More important chromium content specimen shows improved oxidation resistance. In comparison, a threefold increase in oxidation resistance was observed with specimen coated with TiAlN.

Keywords: Ceramic Coating, PVD, Isothermal Oxidation, High speed steels

1. Introduction

The high-speed steels utilized in cutting applications were subjected to strict real-time parameters such as high temperature and mechanical stress. The steel surface needs an adherent oxide layer with exceptional mechanical to obtain higher efficiency and output. In general, most metals and alloys oxidize faster in the air or air containing water vapor [1, 2]. In recent decades, many research domains have similarities in investigating the oxidation behavior of high-speed steel used in various applications. The oxidation behavior of high-speed steels with varying chromium contents is of interest to determine the effect of chromium on the oxidation behavior and environmental conditions. Also, there have been investigations on the growth kinetics of oxide layer with respect to temperature and time parameters reveal that the temperature and the time of oxidation play a significant role in promoting the formation of oxide scale on the steel's surface from the environmental conditions [3-5]. Most metals and alloys get oxidized at the surface of exposure to the environment [6]. Iron is the primary alloying element in high-speed steels during oxidation at higher temperatures multi-layers of oxide scale form, namely wustite, magnetite, and hematite [7]. The addition of chromium to the steel increases the oxidation resistance by giving rise to the passive chromium oxide layer formation. The patterned oxide layer inhibits the diffusion process by which oxidation takes place at the steel surface. However, when this layer was exposed to severe atmospheric conditions like high temperature and moisture containing air during the operation, there are possibilities for dissociating the passive film leading to further oxidation process. However, the oxidation rate was observed to be lower than in conventional steels [8]. When the passive film breaks, the iron exposes to oxidation leading to multi-layered oxide scale formation. The passive layer's self-healing capabilities have limitations to the temperature and environmental conditions of the operations [9].

Research on Several surface modification techniques of cutting tool materials was carried out to improve the performance of the tool material during real-time application. These researches concentrate on controlling properties such as hardness, wear resistance, oxidation resistance, and thermal resistance [10]. As part of surface modification techniques, cutting tools were coated with hard materials such as TiN, TiC, TiAlN, and TiCN by Chemical Vapour Deposition (CVD) and

Physical Vapour Deposition (PVD) [11 & 12]. The tools with surface coatings have better surface conditions like high hardness, high thermal conductivity, and low thermal expansion coefficient along with good oxidation resistance [13 & 14].

The survey suggests that there is a need for the study of oxidation resistance of the chromium-containing high-speed steels at high temperatures. Also, there is a possibility of surface coating techniques to improve surface properties like hardness and chemical behavior of high-speed steels. Hence this study concentrates on evaluating oxidation behavior high-speed steels at high temperatures with and without PVD TiAlN coating.

2. Materials and Methods

The composition of the High-speed steels considered for the oxidation studies was presented in Table (1).

Table (1): Chemical composition of the High-speed steels

Specimen	C	Cr	W	V	Mo	Si	Mn	Fe
S1	**1.1**	**3.75**	**1.96**	**4.7**	**2**	**0.2**	**0.1**	**Balance**
S2	**0.8**	**7.5**	**2**	**4**	**2.1**	**0.2**	**0.1**	**Balance**

The specimens of dimensions 20 x 10 x 10 mm were cut from extruded specimens of ratio 1:30 by CNC cutting and prepared for isothermal oxidation testing. The specimens were polished with various grades of SiC papers 80, 120, 220, 320, 600, 800, and 1000 grade, wet polished to 3 µm grit with diamond paste, and degreased in ultrasonic cleaner just before oxidation measurements in a resistance-heating furnace, in which the specimens were stacked in a stainless steel mesh with thin stainless steel wire, and exposed to air at 600, 700, and 800 ^{0}C, respectively, for pre-determined durations of up to 100 hours. The weight of each specimen (in mg) was measured at regular intervals of time to four decimal places using an electronic balance. For each of the temperatures specified, 18 specimens were tested. The first ten specimens were weighed after exposure durations of 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 hours. The next nine specimens were weighed after exposure durations of 20, 30, 40, 50, 60, 70, 80, and 90 hours. At the beginning of the gravimetric analysis, the polished steel surface is fresh, and the oxidation is rapid, and it takes almost a parabolic variation. However, after ten hours of exposure, the oxidation is linear, with not much variation in the oxidation rate. Nevertheless, before 10 hours since the oxidation is rapid, there is a more significant oxidation rate variation. Each specimen was not used again once it was exposed to heat for the specified duration and weighed. Four identical specimens of gross dimensions were tested for each set of test conditions, and the average weight gain used in plotting the graphs to circumvent the effects of experimental error. TiAlN coating deposition was carried out in a pure nitrogen atmosphere under a working pressure of 1.5 Pa. A 1:1 atomic ratio of Ti/Al was achieved for the TiAlN coatings by controlling the direct current (DC) power ratio applied to the two cathodes. A single cathodic target was used in the deposition, and the polished steel specimens were used as substrates. The pre-cleaned substrates were mounted on the substrate holder that rotates at a speed of 8 rpm during deposition. During the deposition, a negative DC bias of −80 V was applied to the substrates, and the deposition temperature was controlled at around 450 °C.

The specimen's topography with and without TiAlN coating before and after Gravimetric experiments was analyzed using the JEOL JSM-6380LA scanning electron microscope. X-Ray analysis of the specimen was done using X-Ray Diffractometer (JEOL JDX – 8P) having copper (30kV, 20mA) target with a Kβ filter. The diffracting angles were set to 20o to 120o with a 2o /min scanning speed and in continuous mode.

3. Results and Discussion

When the steels were subjected to gravimetric analysis as part of oxidation measurements in atmospheric air, above 570 degrees Celsius, the following types of oxides formation took place FeO, Fe3O4 and Fe2O3. Below 570 degrees, Celsius, Fe3O4, and Fe2O3 are thermodynamically stable; Paidassi et al. [19]. The parameters like the temperature of oxidation, time of oxidation, ambient conditions, and the steel's chemical composition influence the oxide scale to grow. First discrete nuclei of oxide layers grow on the matrix and further lead to islands formation. As the exposure time increases, then the crack-bound uniform oxide layer forms over the steel surface.

When the extension of nuclei occurs, mass transportation of ions occurs in a normal direction to the surface.

Further diffusion process takes over as Iron cat ions, and electrons diffuse through the oxide scales. At the gas–oxide interface on the surface, oxygen was reduced to oxygen ions. The growth of the individual iron oxide layers was governed by diffusion. Therefore, temperature, time control the distance the iron atoms can travel, and combining high temperatures with long times will allow the iron atoms to travel far, and the concentration gradient will decrease with time. That will aid the oxide layer's growth since more iron atoms are made available to react with oxygen; G.Béranger et al. and M. H. Davies et al.[20]. The ceramic coating reduces the oxidation of the steel by preventing the steel surface exposure to oxygen.

Figures (1-3) shows the high-speed steels' oxidation behavior with and without TiAlN coating at temperatures, namely 600 0C, 700 0C, and 800 0C. At the initial time of exposure to atmospheric air, rapid oxidation was revealed by the gravimetric analysis graphs. After a few minutes of exposure, the oxidation rate shows a parabolic increase for a few hours, followed by a linear increase.

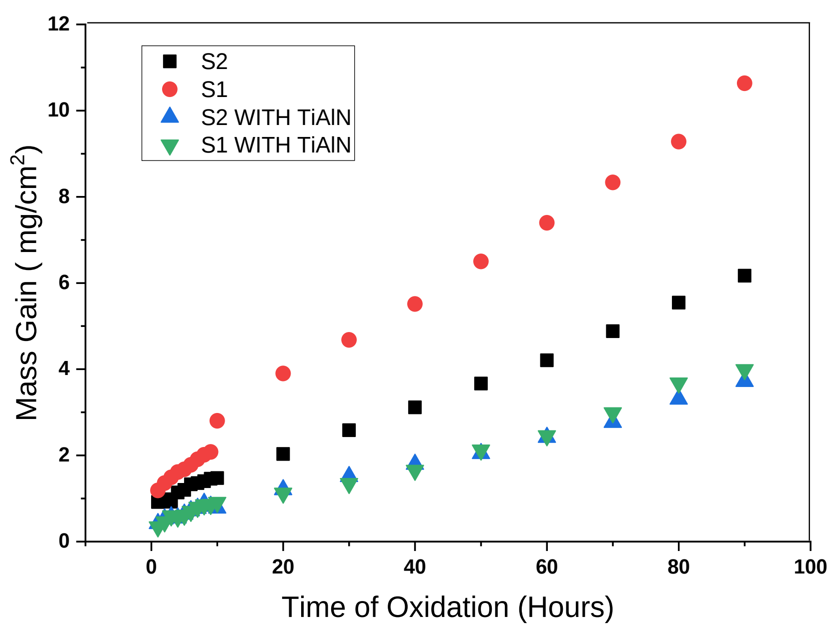


Fig. (1). The oxidation behavior of the steels at 600 ^{0}C.

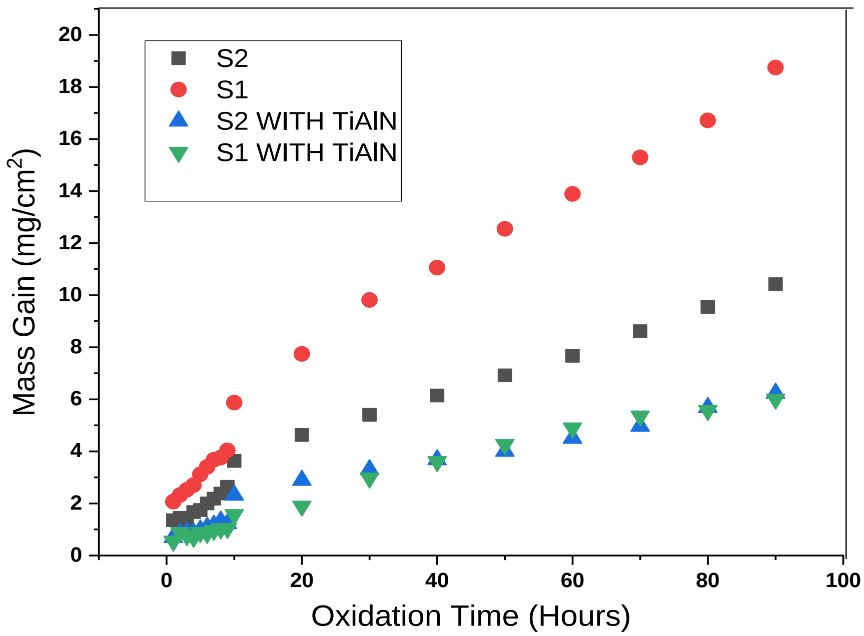


Fig. (2). The oxidation behavior of the steels at 700 ^{0}C.

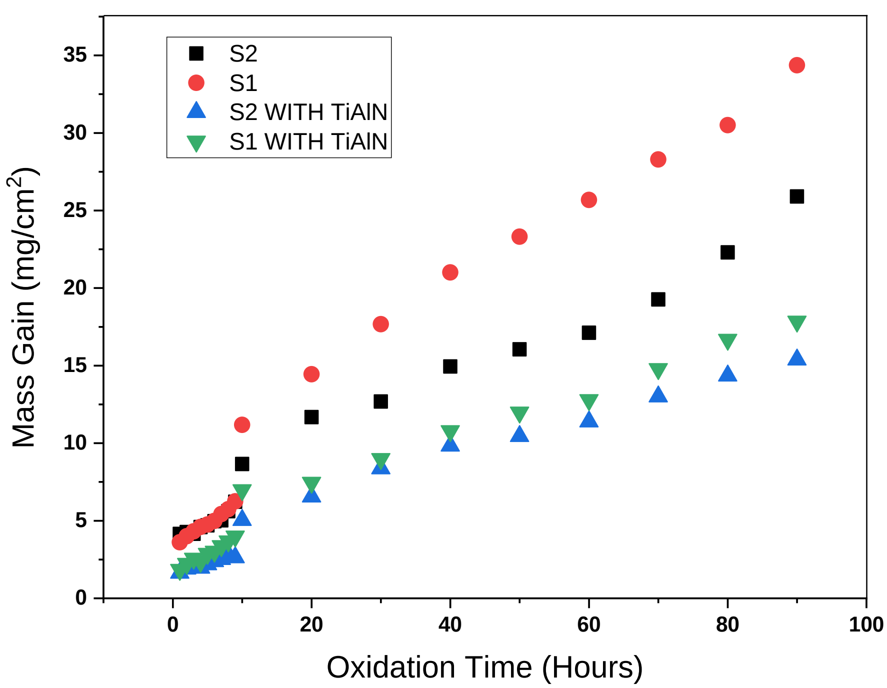


Fig. (3). The oxidation behavior of the steels at 800 ^{0}C

The observed behavior is similar in different categories specimens with a variation of time of exposure. In atmospheric air, most metals and alloys oxidize faster at higher temperatures since the oxidation kinetics depends on the atmospheric air composition and temperature.

At temperatures above 570 ^{0}C, the grown oxide layer contains three phases, namely Wustite (FeO), magnetite (Fe3O4), and hematite (Fe2O3). The growth of Wustite at the interface between the iron and oxide scale. Then the formation of magnetite and hematite takes place in a direction towards the oxide and air interface. At temperatures lower than 570 ^{0}C, the wustite phase is not a thermodynamically stable one when compared to the others. In this order from the metal oxide-interface in direction to the oxide-gas interface [15].

During the oxidation process, the iron is ionized, leading to iron ions and electrons' release. That reduces the magnetite to produce Wustite. The iron ions move across the magnetite layer to form the magnetite phase, further leading to an increased magnetite layer. The ionization of oxygen by released electrons leads to the formation of the hematite phase [15]. Hence, the coexistence of hematite and magnetite phases was observed (Figure (6)).

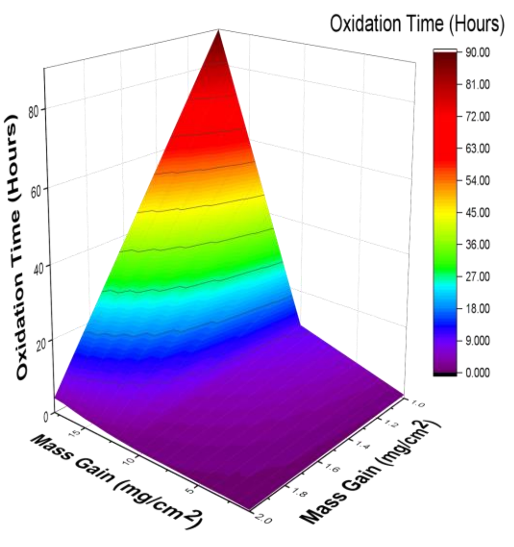


Fig. (4.1). 3D profile of oxidation Behavior of the steel at 600 ^{0}C.

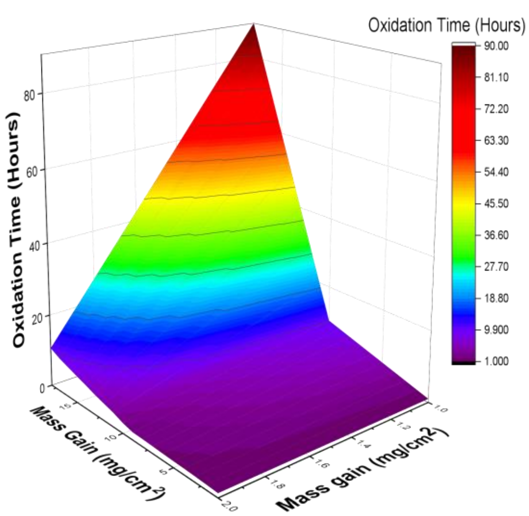


Fig. (4.2). 3D profile of oxidation Behavior of the steel at 800 ^{0}C.

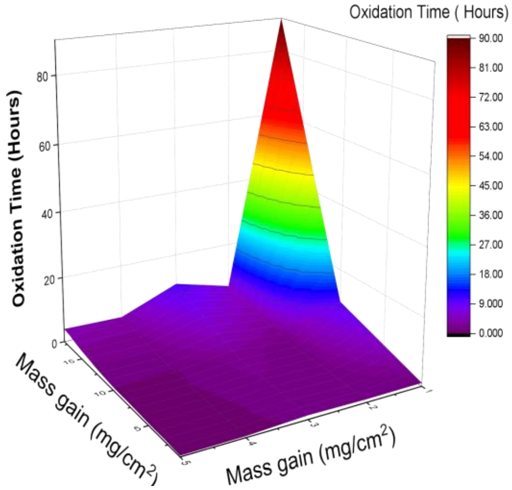


Fig. (4.3). 3D profile of oxidation Behavior of the steel with TiAlN at 600 ^{0}C.

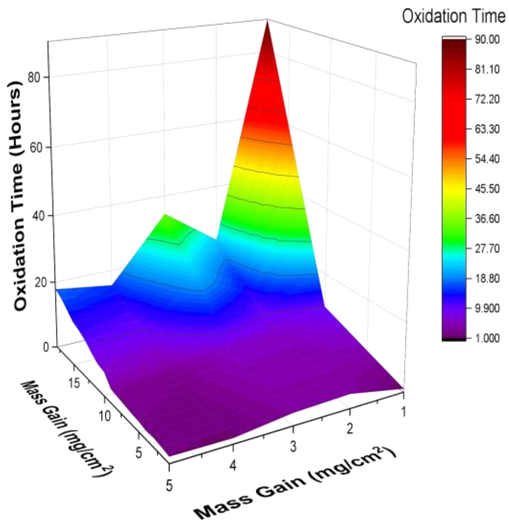


Fig. (4.4). 3D profile of oxidation Behavior of the steel with TiAlN at 800 ^{0}C.

The water vapor in the air influences the oxidation kinetics to no small extent. The water vapor provides a second source of oxygen needed for the oxidation reactions, apart from the fraction of oxygen that was already contained in the dry air. The following reactions occur during the oxidation of steel at high temperatures in atmospheric air [15].

$$3\,Fe + 2O_2 \rightarrow Fe_3O_4$$

$$4\,Fe + 3\,O_2 \rightarrow 2\,Fe_2O_3$$

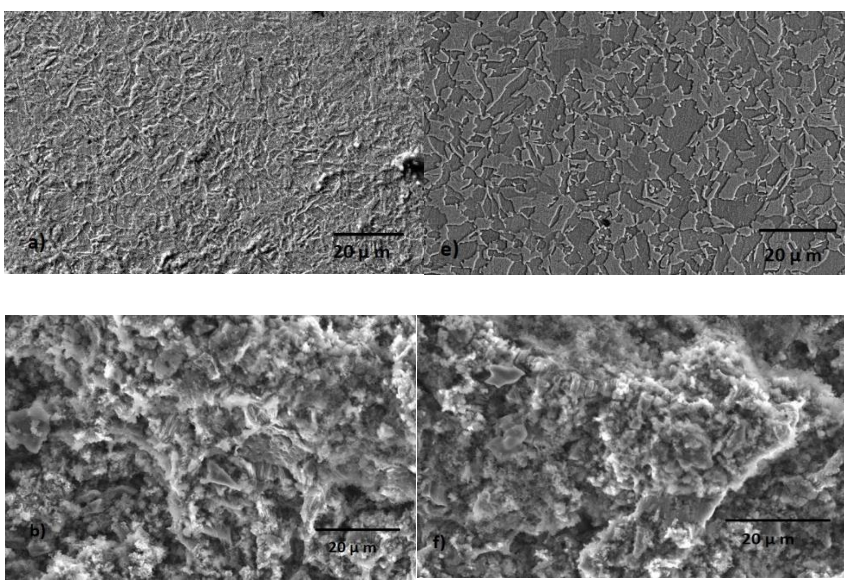
Another reaction of the oxidation process is as follows.

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

The specimens S1 and S2 show appreciable differences in mass gain variation since the S2 contains a higher chromium percentage. The passive layer of chromium oxide can self-heal itself so that the oxide layer is stable at various environmental conditions. Figure (4.1) to (4.4) shows the 3d oxidation profile of the steels with and without coating. They clearly show that the oxidation at the initial stage is rapid and uniform. The higher oxidation rate was observed up to a few hours, and then it decreases gradually with an increase in time. At 800 0C, the higher oxidation rate was obtained for a longer duration, followed by a decreasing trend. Another significant observation of the 3d profile is that the coated specimen shows a much lower oxidation rate than the uncoated specimen.

The oxidation behavior of the two types of coated specimens shows a similar trend, revealing that the coating has improved the steels' oxidation resistance to a greater extent. The oxidation of the coating is due to the only formation of the Al2O3 phase transformed form AlN. The complete transformation of TiN to TiO2 occurs at higher temperatures around 1000 0C [16-18]. Hence the coated specimens show threefold improvement in oxidation resistance.

Concerning the increase in temperature, the steels' oxidation resistance with and without coating was observed to be decreasing. The gravimetric analysis shows that as the temperature increases, the mass gain also increases. At higher temperatures, the energy available for the diffusion process by which the oxidation occurs is more leading to greater oxidation. However, as the ceramic coating, the TiAlN shows better oxidation resistance at higher temperatures than that of uncoated steel specimens, which was evident in the analysis of the 3D oxidation profiles.



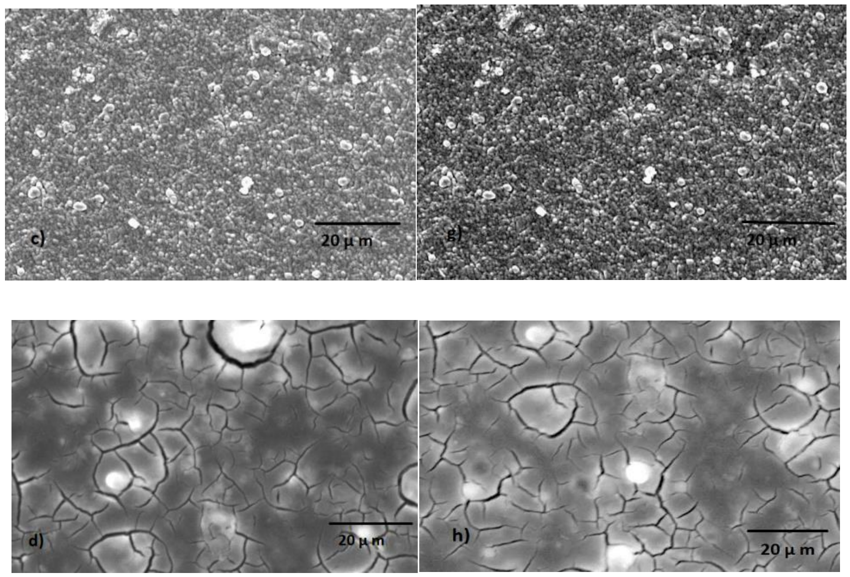


Fig. (5). SEM pictures of a) S_1, b) S_1 after exposure to 800 ^{0}C, c) S_1 with TiAlN coating, d) S_1 with TiAlN after exposure to 800 ^{0}C, e) S_2 f) S_2 after exposure to 800 ^{0}C, g) S_2 with TiAlN coating, and h) S_2 with TiAlN coating after exposure to 800 ^{0}C.

The XRD analysis clearly realizes that the steel surface after subjected to an oxidation test contains a combination of oxides, namely Fe_2O_3 and Fe_3O_4. As the oxidation test temperature increases, the Iron peaks intensity is decreasing, whereas the peak intensity of Fe2O3 and Fe3O4 are increasing, and the XRD profiles of the high-speed steels that were subjected to oxidation tests can be observed. Interestingly the peak intensity of Fe_2O_3 increases as the temperature of isothermal treatment increases compared to that of Fe_3O_4. It indicates that the transformation of Fe_3O_4 into Fe_2O_3 takes place at high temperatures, Khanna A.S [15].

The SEM microstructures of the steel surface subjected to oxidation tests reveal an oxide scale, as indicated by the XRD analysis. The TiAlN coating surface contains a uniform layer of AlN and TiN, as indicated by the XRD analysis. When subjected to heat treatment, the coating becomes a crack-bound but uniform intact layer on the steel's surface. When subjected to oxidation at high temperatures, the TiO_2 and Al_2O_3 formation occur but to a smaller extent. Hence the oxidation resistance of the high-speed steel is greatly enhanced by the presence of TiAlN coating.

The topographical analysis (Figure (5a, b, e, & f)) reveals that both S_1 and S_2, when exposed to higher temperatures, get oxidized to a more considerable extent. The oxide scale formed on the surface contain the combination of Magnetite and Hematite. The XRD analysis (Figure (6&7)) proves the presence of two types of oxides on the oxide scale formed during the exposure to 800 ^{0}C for 90 hours. 5 (c, d, and g, h) show that there exists a uniform TiAlN coating on type S_1 and S_2 when exposed to 800 ^{0}C for 90 hours' duration; the topography becomes crack bound and intact.

The XRD spectrum (Figure (6)) suggests that the S2 has higher oxidation resistance when compared to that of S1, due to the fact that S2 has higher chromium content than S1. The analysis of the peaks in Figure (6), show that the high-speed steels oxidize more as the temperature of exposure was increased.

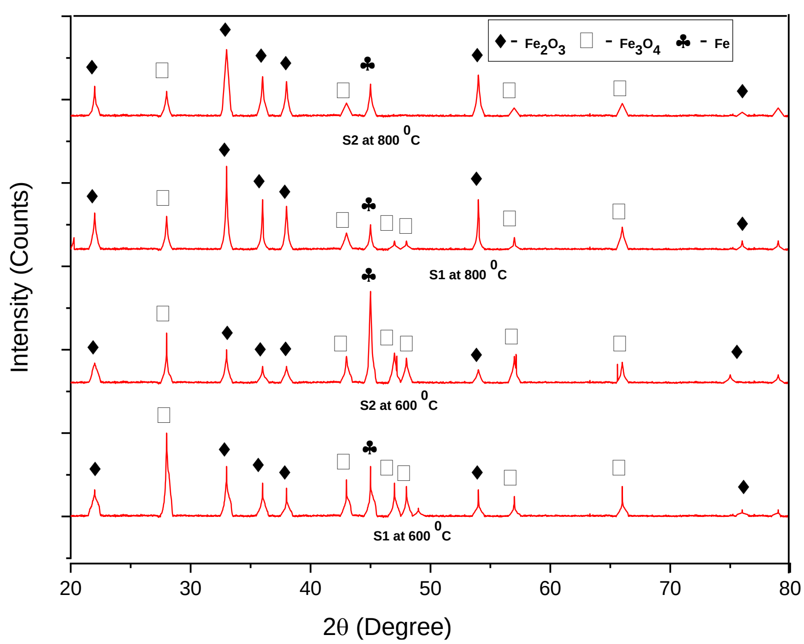


Fig. (6). XR-D analysis of S1 and S2 after oxidation measurements at 600 ^{0}C and 800 ^{0}C.

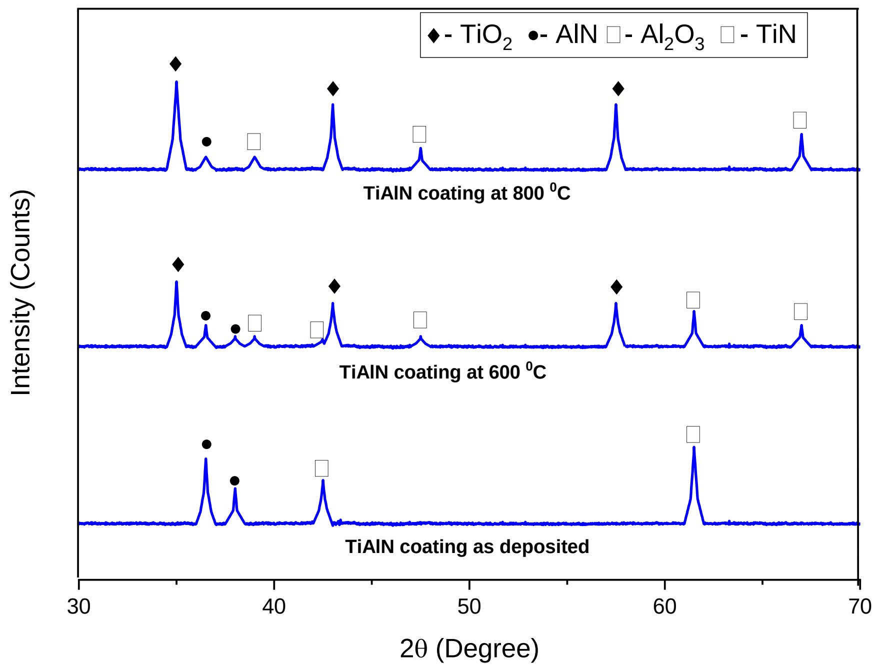


Fig. (7). XR-D analysis of TiAlN coated on HSS before and after oxidation measurements at 600 ^{0}C and 800 ^{0}C.

Also, at lower temperatures, both hematite and magnetite present approximately in equal quantities, whereas at higher temperatures, part of the magnetite phase transforms into hematite. Generally, the high-speed steel oxidation behavior involves the initiation of oxidation at the interface between the carbides and the matrix then extended to the matrix itself [15] since TiAlN coating works as a uniform coating covering the matrix, carbides and the interface between them from the exposure to atmosphere the oxidation resistance of the steel increases to a greater extent. XR-D spectrum (Figure (7)) of the TiAlN coating before and after exposure to atmosphere at 600 0C and 800 0C show presence AlN and TiN phases before exposure. After exposure to 600 0C there are distant peaks of Titania and Alumina. When exposed at 800 0C the Titania peaks are of higher intensity level compared to that of alumina, revealing that Titanium's transformation into Titania is severe only at higher temperatures. Hence the TiAlN coating can increase the oxidation resistance of the steel to a threefold level.

4. Conclusions

The beneficial effects of Titanium-based ceramic coating on the oxidation behavior of two types of high-speed steels were carried out using the gravimetric analysis method. The steel specimens were coated by the Physical Vapour Deposition (PVD) technique, and the isothermal oxidation behavior was studied at different temperatures.

The gravimetric analysis carried out in isothermal oxidation test of the two types S_1, and shows that they get oxidized when exposed to the atmosphere at temperatures range of 600 to 800 ^{0}C. Also, the oxidation rate of the steels gets increased as the temperature of isothermal treatment is increasing.

The high-speed steel with higher chromium content (S_2 type) shows better oxidation resistance than type S_1. The microstructural analysis shows that TiAlN ceramic coating is uniform throughout the specimen's surface, preventing the oxidation processes of the steel surface.

The gravimetric analysis and XRD analysis show that the TiAlN coating on both types and high-speed steels proves that the steel's oxidation resistance was increased to almost the threefold level.

5. Acknowledgement

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5. References

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تأثير طلاء الخزف السطحي بالتيتانيوم على سلوك الأكسدة متساوي الحرارة للفولاذ عالي السرعة

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(قدم للنشر في 2020/5/3 وقبل للنشر في 2020/8/10)

ملخص البحث. يركز هذا البحث على التأثير الإيجابي باستخدام طلاء السيراميك القائم على التيتانيوم على سلوك عملية الأكسدة للفولاذ عالي السرعة. تم فحص نوعين من الفولاذ عالي السرعة بتركيزات متفاوتة من الكروم بواسطة طريقة تحليل الجاذبية. ودُرس سلوك الأكسدة على عينات الصلب **TiAlN**، استخدمت تقنية الترسيب البخاري الفيزيائي لطلاء المتساوي متساوي الحرارة عند درجات حرارة معينة، وهي 600 درجة مئوية ، 700 درجة مئوية ، و 800 درجة مئوية**.** طبق لتحليل سطح عينات الفولا **(XRD)** وتحليل حيود الأشعة السينية **(SEM)** تحليل الفحص المجهري الإلكتروني قبل وبعد عملية الأكسدة. لوحظ حدوث أكسدة سريعة في المراحل الأولى من الأكسدة كما وأنه تزامن انخفاض في معدل الأكسدة كلما زاد وقت تعرض العينات للأكسدة. عندما تزداد درجة الحرارة ، تقل مقاومة العينة للأكسدة. ايضاً, تُظهر العينة ذات محتوى الكروم المعتبر تحسن في مقاومة العينة للأكسدة. بالمقارنة ، لوحظت زيادة بمقدار ثلاثة أضعاف في مقاومة العينة للأكسدة عندما يتم طلاءها بال **TiAlN.**