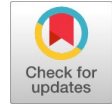


Oxidation Effects on wear Resistance of SS-304 and SS-316 Austenitic Stainless Steels



Jasbir Singh, Sandeep Sharma, Amrinder Pal Singh

Abstract: Present manuscript deals with the sliding wear behaviour of SS-304 and SS-316 with and without oxidation prior to wear test. The dry sliding wear performance of the steel samples was noted in as received conditions and then after oxidizing the sample at 600°C for 6 hours. The variations in hardness of both the steels before and after oxidation were estimated. The dry sliding wear tests were carried out using pin on disk technique at different sliding velocity and different loads, by using hardened steels counter surface. The worn surfaces were characterised by using FE-SEM/EDS analysis to ascertain the mechanism of wear in the samples. From various characterisation results and observations of volume loss, the effect of prior oxidation was analysed for the both stainless steels. It has been found that the oxidation leads to the formation of some protective oxides which leads to increase in the hardness of the samples due to which the wear performance was improved compared to the as received alloys.

Keywords : Sliding wear, Oxidation, Hardness, SEM.

I. INTRODUCTION

Design and fabrication of high strength, high temperature, wear/corrosion resistant materials will offer much benefit in aerospace, automotive, chemical and oil industries to combat the severe service conditions. Wear and tear is a major surface degradation phenomenon which can limit the life and performance of the machine components. The steels having chromium content more than ~12% Cr, are named as stainless steel which resist corrosion, maintain their strength at high temperatures. Nickel favours the rate of formation of passive film when exposed to the high temperature. Sufficient amount Ni in steels also stabilizes the austenite phase. Due to low hardness of the ferritic and austenitic stainless steel, they possess lower wear resistance and hence various methods can be explored from the literature aiming to improve the wear resistance [1-12]. Barcelo et al. [1] studied the hardness and wear resistance for AISI 304 stainless steel subjected low temperature plasma carburizing in the presence of a fixed gas mixture (H₂ and CH₄). A significant improvement in tribological properties after the thermo-chemical treatment was observed. Tassin et al. [5] have employed laser surface alloying method to improve the sliding wear resistance of SS-316 samples by producing,

carbide-hardened surfaces. Various powders i.e. Cr₃C₂, Cr₃C₂+ Cr and Ti +SiC, were used to treat the steel surface using Nd-YAG laser. The micro-hardness of the surface alloy was about 350 HV. Author has optimised the process parameters for both chromium carbide and titanium carbide surface alloying treatments, so that improvement of the sliding wear resistance of AISI 316L stainless steel may occur without any ill effect on high temperature oxidation resistance. Coatings have been used widely to improve the wear resistance of the stainless steels [13-21]. Parthasarathiet. al. [14] have used plasma sprayed NiCrBSiCFe coatings and established that the wear performance of AISI 316 has increased by almost 4-5 times as compared to the bare substrate. In another study, the Cr-C-O composite coatings were developed on AISI 304 stainless steel by using cathodic vacuum arc deposition (CVAD) technique. The tribological behaviour was assessed by using ball-on-disc tests and it was concluded that the Cr-C-O coatings have certainly improved the wear characteristics [17]. From the existing literature, it has been found that the wear resistance of the stainless steels surfaces has been mostly improved by using either coatings or carburizing treatments (case hardening). Present investigation involves the dry sliding wear study of two austenitic stainless steels namely: SS-304 and SS-316. The effect of oxides formation on the wear behaviour of these materials has been explored after exposure to a high temperature environment. This study is particularly important to visualize the amount of wear and effect of oxide layer formed on these steels.

I. EXPERIMENTAL

A. Materials and method:

Commercially available SS-304 and SS-316 were obtained in the form of rectangular bars from the local manufacturer with following composition as shown in table I.

Table-I: Composition of as received alloys (Wt%)

Alloy	Ni	Cr	Fe	Mn	Si	O
SS-304	8.23	19.7	65.6	0.5	0.1	8.2
SS-316	6.8	11.2	73.2	-	0.8	10.2

The samples were cut and prepared in the form of circular pins (dimensions L=32mm, D=10mm). Some of these samples were then oxidized in furnace at 600°C for 6 hours using laboratory SiC tubular furnace (Digitech, India).

Manuscript published on 30 August 2019.

*Correspondence Author(s)

Jasbir Singh*, Mech. Engg. department, Desh Bhagat University, Mandi Gobindgargh, India. Email: jasbirayam@yahoo.co.in

Sandeep Sharma, Mech. Engg. department, Desh Bhagat University, Mandi Gobindgargh, India.

Amanpal Singh, Mech. Engg. department, Desh Bhagat University, Mandi Gobindgargh, India.

© The Authors. Published by Blue Eyes Intelligence Engineering and Sciences Publication (BEIESP). This is an open access article under the CC-BY-NC-ND license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

Oxidation Effects on wear Resistance of SS-304 and SS-316 Austenitic Stainless Steels

The calibration of the furnace was done by using Platinum/Rhodium thermocouple upto an accuracy of $\pm 5^{\circ}\text{C}$.

A. Pin on disc wear test:

Wear behaviour of the samples was observed by performing test using pin on disc wear and friction monitor manufactured by Ducom Industries Pvt., Ltd, India by using ASTM G-99 standard. Experiments were conducted by using a counter plate of EN-31 steel disk hardened to 60 HRC and keeping track diameter 100mm. The wear graphs and data were processes using Winducom 2010 software. The normal load of 1kg/2kg/2.5kg/3kg was applied on the pin and the wear behaviour was noted at different rotating speeds (200,300, 400rpm). Material removal was determined by weight loss measured at specific intervals of time. Wear tests were carried out for a total sliding time of about 3600 seconds.

Table-II: Composition of the oxidised surfaces (EDX) at same magnification (wt %)

Alloy	Ni	Cr	Fe	Mn	Si	O
SS-304 (Oxi.)	8.1	18.5	63.3	1	1.0	20.5
SS-316 (Oxi.)	7.2	12.3	70.3	-	1.2	22.3

Table -III: Composition of the worn surfaces (EDX) at same magnification (wt %)

Alloy	Ni	Cr	Fe	Mn	Si	O
SS-304	8.23	19.7	65.6	0.5	0.1	8.2
SS-304 (Oxi.)	8.7	20.5	65.3	1	0.5	19.6
SS-316	6.8	11.2	73.2	-	0.8	10.2
SS-316 (Oxi.)	8.1	13.3	68.7	-	0.7	21.3

Commercially available SS-304 and SS-316 were obtained in the form of rectangular bars from the local manufacturer with following composition as shown in table 1.

B. Surface morphology

X-ray diffractometer (Bruker D-8, Cu $K\alpha$ energy) with Ni filter (30mA, 40 kV) was used to analyze the as received and oxidised super alloy samples. The morphology along with chemical composition of the surfaces was investigated using field emission scanning electron microscope (FE-SEM: Carl Zeiss, Germany, ULTRA plus model) with resolution of 0.8 nm and magnifications upto 1,00,000X. The EDAX Genesis Software attached to this instrument was used to calculate the concentration of elements at the particular points and in the specific area. The micro-hardness was measured by using 402MVD (Wilson Instruments). A load of 100 g was applied to the Vicker pyramidal diamond indenter to penetrate in the as deposited coatings. All the reported micro-hardness were

calculated by taking average of five measured values obtained at similar positions on the coatings. The error in the micro-hardness values was ± 10 Hv.

II. Results

A. SEM and XRD of as Received and Oxidized Samples

XRD analysis of the as received SS-304, SS-316 and oxidized steel samples has been shown in Figure 1 and Figure 2 respectively. As received stainless steel samples of SS-304 and SS-316 show the peaks of the austenite phase along with some amount of Cr_2C_3 . In case of air oxidation at 600°C of SS-304, the major phases present are Fe_2O_3 , Ni (Fe,Cr) $_2\text{O}_4$ and Cr_2O_3 only. There was no another oxide observed. In case of air oxidation of SS-316 sample, almost same peaks were observed with higher intensity of Fe based oxides.

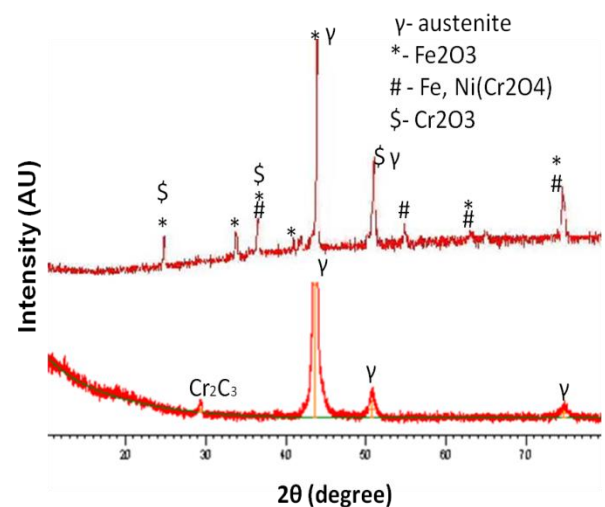


Fig.1. XRD pattern of as received SS-304 steel and oxidized steel at 600°C for 6 hours.

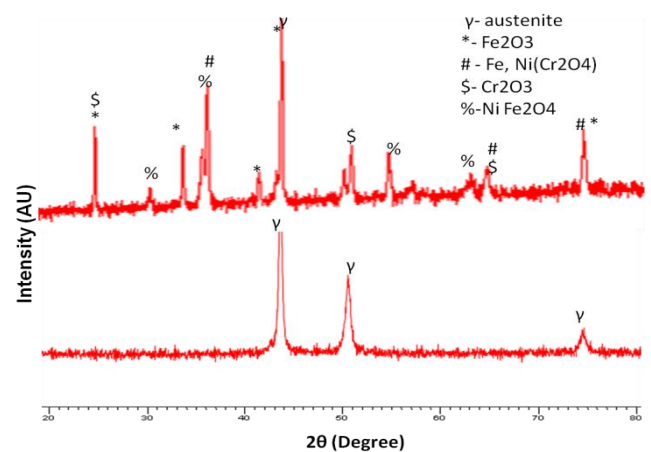


Fig. 2. XRD pattern of as received SS-316 steel and oxidized steel at 600°C for 6 hours.

The surface morphology along with EDS analysis of oxidized steels have been shown in Figure 3 and Figure 4. The lower and higher magnification images of the surfaces of the steels shows that uniform and compact oxides have been formed after oxidation at 600°C for 6 hours.



The main constituents present on the oxidized surface of SS-304 are Fe, Cr, Ni and O (Table 2). Similarly the SS-316 sample shows the major composition of Fe, Cr, Ni and O (Table 2). However, the amount of Fe and O is higher in case of SS-3016 steels.

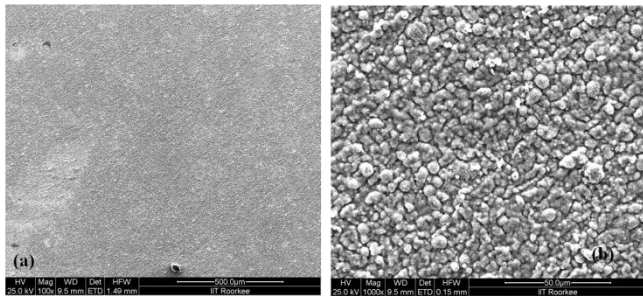


Fig. 3. FE-SEM images of oxidized SS-304 steel samples at 600°C for 2 hours (a) at lower magnification and (b) at high magnification.

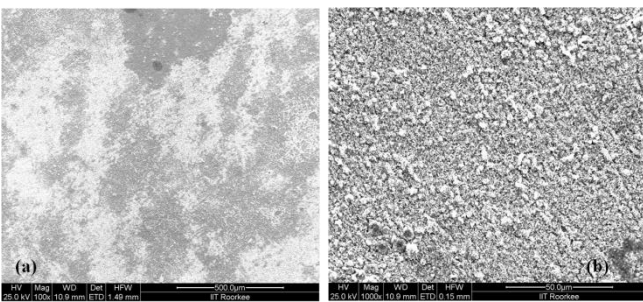


Fig. 4. FE-SEM images of oxidized SS-304 steel samples at 600°C for 6 hours (a) at lower magnification and (b) at high magnification.

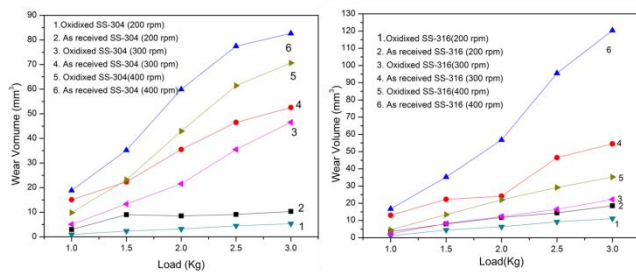


Fig. 5. Variation of wear volume with respect to load at different rpm, (a) for SS-304 and (b) for SS-316.

Both XRD and EDS results confirms the presence of higher amount of Fe based oxides in case of SS-316. Similar observations have been reported by Nomura et. al [22] in their study on analysis of oxide layers on stainless steel (304, and 316) by conversion electron mossbauer spectrometry.

B. Wear Studies

a. Wear loss in case of as received/oxidized steels

The micro-hardness of all the samples in as received and oxidized conditions were noted by taking average of five readings. It has been found that the hardness of both steels has increased after oxidation at 600°C. Micro-hardness of the SS-304 steel has increased by 2.5 times to 600 Hv from 240Hv and that of SS-316 has increased by 2.47 times to 570 Hv from 230Hv.

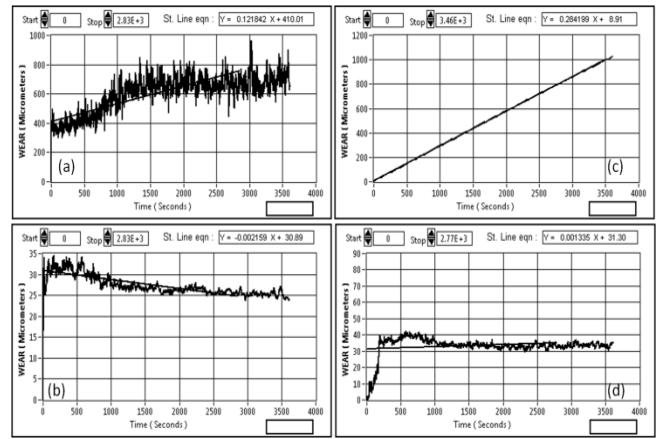


Fig. 6 (a-d). Variation of wear with respect to time upto 1 hour. (a, b) SS-304 without and with oxidation, (c, d) SS-316 without and with oxidation at 600°C for 6 hours.

The wear loss at different speeds and different values of load for both steels has been shown in Fig. 5 (a, b).

All the samples show increase in volume loss as speed and load increases. However, from the curves it can be observed that for the oxidized coatings, the wear loss has been significantly reduced as compared to as received steels in both SS-316 and SS-304 steels.

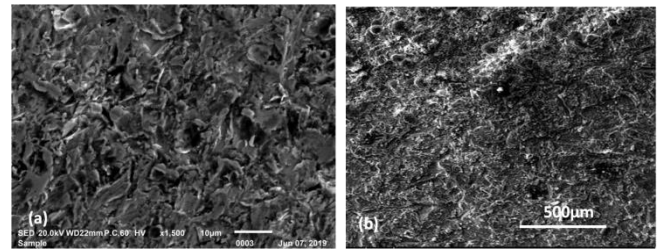


Fig. 7. SEM micrographs of SS-304 after wear at 4kg at 400 rpm for 1 hour, (a) as received SS-304 and (b) Oxidized SS-304 at 600°C for 6 hours. The variation of wear with respect to time (1 hour) for all four samples has been shown in Fig. 6 (a-d). From the graph it is clear that the oxidized coatings have shown initial sharp increase in wear rate which ultimately slows down as the process proceed further. The as received steel samples have shown a smoother variation in wear as compared to the oxidised samples. However in steady state behaviour, the slope of the wear curve for the as received steels becomes higher and that of oxidized steels becomes almost constant.

b. Characterisation of worn surfaces

The SEM micrographs of worn surfaces of as received samples have been shown in Fig. 8 (a, b) and Fig. 9(a,b). Both SS-304 and SS-316 have shown the characteristics morphology corresponding to the adhesive wear. The composition of worn surfaces has been also shown in Table 3. The worn surfaces of both the steels after oxidation have shown the delamination and brittle fracture marks during wear.

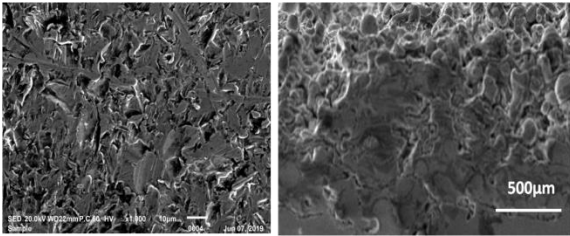


Fig. 8: SEM micrographs of SS-316 after wear at 4kg at 400 rpm for 1 hour, (a) as received SS-316 and (b) Oxidized SS-316 at 600°C for 6 hours.

III. DISCUSSION

The oxidation of steel samples in the presence of air at 600°C resulted in the formation of various oxides on the surface which have uniform and compact morphologies as indicated by the XRD and SEM results. The formation of the oxides Fe_2O_3 , Cr_2O_3 and spinels can be explained on the basis of the oxygen affinities of the various elements. Fe has highest affinities than Cr and Ni resulting in formation of initial stages the oxides of Fe in larger quantities. Cr formed beneath the Fe_2O_3 layer by diffusion of the oxygen through the spinels and Fe_2O_3 layer. These results are within agreement of already existing literature [23-25]. The protective oxides can be also indicated by their compact and uniform morphology and thickness which directly affect the adherence of the oxides to the substrate [26-27].

The formation of protective oxides with no sign of cracking and spalling in present case can also understood by the fact that the steels have exposed for 6 hours at 600°C. In this time duration the main mechanism of oxidation was chemical reaction between oxygen and metal atoms. The cracking or spalling predominately occurs when the oxidation occurs at oxide/metal interface by inward diffusion of oxygen. In such case the thermal mismatch exists at the metal/oxide interface and scale adhesion become poor. However when atoms diffuse outward and react at oxide/air interface then mismatch do not exist.

The increase in micro-hardness after oxidation is attributed to the formation of oxides which ultimately increased the surface hardness. The oxide phases are well known to possess high hardness as compared to their counter metallic components. The SEM images of the SS-304 and SS-316 both shows the presence of adhesive wear as indicated by the unique morphology. The metal to metal contact causes the development of shear stress on the contacting surface resulting in deformation of the asperities which ultimately ruptures causing the mass loss. It has been also seen that worn surfaces have some oxygen content causing a little oxidation of the steel surfaces during dry wear test. These types of observations have been also made by author et al. [28-29] in their study.

The worn surfaces of the SS-304 and SS-316 both have oxide layer of certain thickness which was generated on the entire surface during oxidation at 600°C. The improvement in the wear can be seen for all loads and at all speeds upto 400 rpm. This improvement may be attributed to the increased hardness of the surface which resist for further material removal during dry sliding wear test. Similar observations have been also found in literature in case of oxidative wear resistance of TiAl alloys. In this study the coating of ceramic

material (oxides) was deposited on the alloy by using electric arc method. Suitable electrolytes were used to obtain the desired composition of the coating consisting of oxide layers of Al_2TiO_5 and TiO_2 . These layers were found to possess high hardness as compared to the substrate alloy and showed about 10 times reduction in wear volume [19]. Moreover this oxide layer prevented the metal to metal contact and hence adhesion between the steel surfaces. Most of metals and alloys are prone to oxidation as they come in contact with atmosphere and form a thin layer of oxide. These oxides may be removed when two metal surfaces come into contact with each other as asperities on both surfaces interact with each other (adhesive wear). This interaction caused removal of oxide layer and fresh surface come into contact with atmosphere and process repeats. But in present case there is no sign of adhesive wear was seen [30-32]. The SEM morphology of the worn surfaces is also showing the sign of delamination of the oxide layer which is characteristics of the fatigue mechanism. This type of behaviour of the stainless steels has been also observed by Wel. Et. al. [28] and Quinn, et al. [29] on their wear study of steels at higher temperature. They have referred this wear as typical oxidative mild wear and hence the lowest wear rate was explained. However in present case the oxides were already formed before the wear test and a compact and crack free oxide scale was developed. The pre formed oxides and their beneficial effect has been also reported by Jin et al. [18] on their study on characterization of wear-resistant coatings on SS-304 fabricated by rapid surface hardening technology named cathodic plasma electrolytic oxidation.

IV. CONCLUSIONS

From the above discussions and results the following conclusions have been made:

1. The pre oxidation of the of SS-316 and SS-304 samples at 600° C for 6 hours resulted in the formation of oxides of Fe, Ni and Cr. The formation of these oxides resulted in the increase in surface hardness of the steel samples.
2. Both steels developed a compact and adherent surface scale when oxidised for 6 hours at 600°C.
3. Wear resistance of the SS-316 and SS-304 changes significantly after oxidizing the steels at 600°C in presence of air before wear test. This change in wear rate was found to exist for all speeds of 200, 300 and 400 rpm and for all loads from 1 kg to 3 kg.
4. The inherent nature of stainless steel to form protective oxide scale proves beneficial for improving wear resistance of SS-316 and SS-304 steels. The oxides formed on the surfaces of the steels acted as barrier between metal to metal contacts and hence the adhesive wear of the metallic surface was prevented.
5. The pre oxidized samples showed the sign of abrasive wear resulted by fatigue failure.
6. The wear mechanism changes from adhesive wear to abrasive wear as oxide layer prevented the metal to metal contact. The oxides of Fe, Cr and Ni increases the surface hardness which could be the probable reason for improved wear resistance.

REFERENCES

- M.A. Barcelos, M.V. Barcelos, J.desarujjo, A.R. Franco Jr., E.A. Vieira, "Wear resistance of AISI 304 stainless steel submitted to low temperature plasma carburizing", *REM - Int. Eng. J.*, vol. 70, 2017, pp. 293-298.
- T. Kumar, P. Jambulingam, M. Gopal and A. Rajadurai, "Surface hardening of AISI 304, 316, 304L and 316L SS using cyanide free salt bath nitriding process", *International Symposium of Research Students on Materials Science and Engineering*, December 2002-04 Chennai India.
- S.G.Sapate1, Amit Kumar, R.K.Khatirkar, S.Chandel, "Abrasive Wear Properties of Plasma Nitrided H11 Steel", *Proc. of Int. Conf. on Advances in Mechanical Engineering 2012*
- R. Goyal, K. Singh, S. Singla, "Wear Behaviour of Thermal Spray Coating Process on Carbon Steel", *IJRMET* Vol. 4, Issue 2, Spl- 2 May - October 2014.
- C. Tassin, F. Laroudie, M. Pons, L. Lelait, "Improvement of the wear resistance of 316L stainless steel by laser surface alloying", *Surface and Coatings Technology* 80(1), pp. 207-210.
- E. Wen, R. Song, W. Xiong, "Effect of Tempering Temperature on Microstructures and Wear Behavior of a 500 HB Grade Wear-Resistant Steel", *Metals*, 9, 2019, pp.45-52;
- L.H. Paijan, M.N. Berhan, M.S. Adenan, N.F.M. Yusof, E. Haruman, "Structural Development of Expanded Austenite on Duplex Stainless Steel by Low Temperature Thermo chemical Nitriding Process", *Adv. Mater. Res.* Vol.576, 2012, pp. 260-263.
- D. Oliveira, W.R. Kurelo, B.C.E.S. Ditzel, D.G. Serbena, F.C. Foerster, C.E.de Souza, "On the S-phase formation and the balanced plasma nitriding of austenitic-ferritic super duplex stainless steel", *Appl. Surf. Sci.*, vol. 434, 2018, pp. 1161-1174.
- Y. Sun, X. Li, T. Bell, "Structural characteristics of low temperature plasma carburised austenitic stainless steel", *Mater. Sci. Technol.*, vol. 15, 1999, pp. 1171-1178.
- N. Mingolo, T. Schiptschin, A.P. Pinedo, "On the formation of expanded austenite during plasma nitriding of an AISI 316L austenitic stainless steel" *Surf. Coat. Technol.* vol. 006, 2012, pp. 4215-4218
- F. Borgioli, A. Fossati, E. Galvanetto, T. Bacci, "Glow-discharge nitriding of AISI 316L austenitic stainless steel: Influence of treatment temperature", *Surf. Coat. Technol.* VOL. 200, 2005, pp. 2474-2480
- M.P. Fewell, D.R.G. Mitchell, J.M. Priest, K.T.Short, G.A. Collins, "The nature of expanded austenite", *Surf. Coat. Technol.* vol.131, 2000, pp. 300-306.
- A. Recco, D. Lopez, A.F. Bevilacqua, F. Silva, A.P. Tschiptschin, "Improvement of the slurry erosion resistance of an austenitic stainless steel with combination of surface treatment: nitriding and TiN coating", *Surf. Coat. Technol.* vol. 202, 2007, pp. 993-997.
- N. L. Parthasarathi, M. Duraiselvam, "Improvement of High Temperature Wear Resistance of AISI 316 ASS through NiCrBSiCFe Plasma Spray Coating", *Journal of Minerals & Materials Characterization & Engineering*, vol. 9, No.7, 2010, pp.653-670..
- L. Bourithis, G. Papadimitriou, "Three body abrasion wear of low carbon steel modified surfaces", *Wear*, vol.258, 2005, pp. 1775-1786.
- S.Das, "Processing and Characterization of Plasma Sprayed Ceramic Coatings on Steel Substrate: Part I. On Coating Characteristics", *Metallurgical and Materials Transactions A*, vol. 34 (9), 2003; pp. 1909 - 1918.
- Cheng-HsunHsu ; Wei-Che Huang ; Chi-Yu Chang ,Improvement on wear resistance of 304 stainless steel via Cr-C-O Arc-coatings, 2017 International Conference on Applied System Innovation (ICASI).
- XiaoyueJin, BinWang, WenbinXue*, Jiancheng Du, Xiaoling Wu, Jie Wu, "Characterization of wear-resistant coatings on 304 stainless steel fabricated by cathodic plasma electrolytic oxidation, *Surface and Coatings Technology*, Volume 236, 15 December 2013, Pages 22-28.
- Engineering Coatings—Design and Application, 2nd ed., S. Grainger and J. Blunt, Ed., Woodhead Publishing Ltd., 1999, p 7.
- D. L. Duan, S. Li, X. H. Duan, S. Z. Li (2005) "Wear behavior of thermally sprayed coatings under different loading conditions", *Tribology Transactions*, vol. 48 issue 1, pp. 45-50.
- Y. N. V. Sai Ram, Syed Kammaluddin, Shabana, Deva Raj and P. MastanRao, *International Journal of Advanced Science and Technology*, vol.93 (2016), pp.45-54.
- K. Nomura, Y. Ujihira, "Analysis of oxide layers on stainless steel (304, and 316) by conversion electron faussbauer spectrometry", *Journal Of Materials Science* vol. 25, 1990, pp.1745-1750.
- H. Hooshyar, T. Jonsson, J. Hall, J. E. Svensson, L. G. Johansson, J. Liske, "The Effect of H2 and H2O on the oxidation of 304L- stainless steel at 600°C", *General behavior (part I)" Oxidation of Metals*, 2015, pp 1-22.
- R. Guillaumet, J. Lopitiaux, B. Hannoyer and M. Lenglet, "Oxidation of stainless steels (AISI 304 and 316) at high temperature. Influence on the metallic substratum", *Journal de Physique IV Colloque* vol. 03 (C9), 1993, pp.C9-349-356.
- T. Ujiro, K. Yoshioka, R. W. Staehle, "Differences in Corrosion Behavior of Ferritic and Austenitic Stainless Steels", *Corrosion*. 1994;50(12):953-962.
- W.N. Liu, X. Sun, E. Stephens, M.A. Khaleel, "Life prediction of coated and uncoated metallic interconnect for solid oxide fuel cell applications", *J. Power Sources* vol. 189, 2009, pp. 1044-1050.
- D.J.Young, "High temperature oxidation and corrosion of metals", *Corrosion Series, ed. T. Burstein*. vol. 1. 2008, Elsevier Science.
- M.X. Wel, S.Q. Wang, J. Wang, X.H. Cui, "Wear and friction characteristics of a selected stainless steel", *Tribology Transactions*, vol. 54, 2011, pp. 840-848.
- T. F. J.Quinn, J. L. Sullivan, D. M. Rowson, "Developments in the Oxidational Theory of Mild Wear," *Tribol. Int.*, 13, 1980, pp 153-158.
- R. C. Dante, *Handbook of Friction Materials and their applications* Woodhead Publisher, 2016, pp. 123-134.
- S.Q. Wang, M.X. Wei, F. Wang, "Transition of Mild Wear to Severe Wear in Oxidative Wear of H21 Steel", *Tribol Lett* 32, 2008, pp. 67-72.
- H.So, D.S.Yu, C.Y. Chuang, "Formation and wear mechanism of tribo-oxides and the regime of oxidational wear of steel", *Wear* vol. 253, 2002, pp.1004-1015 .
- G.A. Fontalvo, C. Mitterer, "The effect of oxide-forming alloying elements on the high temperature wear of a hot work steel", *Wear* 258, 2005, pp. 1491-1499.

AUTHORS PROFILE



Jasbir Singh research scholar pursuing Ph.D in Mechanical Engineering from Desh Bhagat University, Mandi Gobindgarh. He had published 3 research papers in reputed international Journal



Dr. Sandeep Sharma working as HOD in the department of Mechanical engineering at Desh Bhagat university, Mandi Gobindgarh. He had published several research papers in reputed refereed international Journals.



Dr. A.P. Singh working as Professor in the department of Mechanical Engineering at UIET, Chandigarh. He had published several research papers in reputed international journals.

