



24th ABCM International Congress of Mechanical Engineering  
December 3-8, 2017, Curitiba, PR, Brazil

COBEM - 2017 - 2328

## Effect of the oxide film on the sliding wear behavior of a CoCrMoSi alloy hardfacing coating

**Jonathan Molina Claros**

*Corporación Mexicana de Investigación en Materiales (COMIMSA), Coahuila, México  
Universidad Pedagógica Nacional Francisco Morazán (UPNFM), Francisco Morazán, Honduras*

**Eduardo Mauro do Nascimento**

*Mechanical Engineering Department, Universidade Tecnológica Federal do Paraná(UTFPR), Curitiba, PR, Brasil*

**Ana Sofia C. M. D'Oliveira**

*Mechanical Engineering Department, Universidade Federal do Paraná(UFPR), Curitiba, PR, Brasil*

**Abstract :** Co-based alloys can be used to protect mechanical parts when wear, temperature and aggressive environment demands are present individually or in association. In the CoCrMoSi alloys the hard  $M_2Si$  Laves phase is the main constituent of their microstructure accounting for the superior properties and performance the alloy can offer. This set of features makes CoCrMoSi alloy very attractive for applications that require good wear performance. In spite of that there are very few studies on the wear performance of this alloys, particularly regarding the effect of the oxide film on the wear behavior. An experimental study was carried out to assess the impact of an oxide film on the sliding wear of CoCrMoSi – T400 hardfacing coatings. Coatings were processed by Plasma Transferred arc on AISI 304 plates and exposed to 450 and 700 °C for 6 h. Sliding wear tests at room temperature, according to ASTM G99-05 standard, used an alumina ball against the CoCrMoSi alloy coatings in the as-deposited condition and after oxidation. Wear tests used an applied force of 5 N, tangential velocity of  $0,1 \text{ ms}^{-1}$  for a total sliding distance of 1000 m. Coatings were characterized by Scanning Electron microscopy (SEM), EDS and X-ray diffraction. Oxides at the surface of coatings after oxidation were identified by Raman spectroscopy. Worn surfaces were analyzed by laser confocal microscopy and scanning electron microscopy. Results showed the wear resistance assessed by the friction coefficient and wear rate depends on the characteristics of the oxides formed at the surface. Coatings oxidized at 450 °C exhibited a small reduction on the wear rate compared to that obtained on as-deposited coatings. However, an enhanced performance (reduction in the wear rate) was gained after oxidation at 700 °C. Surface analysis of the worn track revealed that a continuous oxide film forms during high temperature oxidation, accounting for the superior performance observed in wear tests.

**Keywords:** CoCrMoSi alloy, Pre-oxidation, PTA

### 1 INTRODUCTION

Engineering components that are used at high temperatures need high wear and corrosion resistance. Tribaloy™ alloys, nickel or cobalt based, have been developed for applications where extreme wear is combined with high temperatures and corrosive environments. Its high molybdenum content is responsible for the excellent dry working properties of Tribaloy™ alloys and makes them very suitable for use in case of adhesive wear conditions (metal to metal). The T-400 alloy (CoCrMoSi) exhibits these characteristics, since the Mo and Si elements are added at levels exceeding their solubility limit to induce a large hard volumetric fraction, the Laves intermetallic phase that is distributed in a solid solution matrix of ductile cobalt. The concentration of added Cr is divided around one third in the Laves phase and two thirds in the solid solution, being responsible for the high corrosion resistance of the material (1).

Additionally, the Laves tribolayer oxides phases formed on the surface of metallic components, when subjected to high temperatures, can contribute to the good wear resistance, increasing the useful life of the same. This will depend on the characteristics of the oxide layer for a protective or non-protective action. It is influenced by the chemical composition of the oxides particles that will slide on the surface, by the temperature and by wear parameter, causing the wear loss can decrease or increase (2). The coefficient of friction and wear depend on the mechanical properties of the surfaces that are in contact, as well as the properties of the oxides. A less hard oxide layer can result in a decrease in the coefficients of friction and wear, while a harder and less adherent can act as abrasive particles (3). A thicker oxide layer can contribute to a decrease in the coefficient of friction and increase lubrication at the metal / metal interface (4).

Plasma Transferred Arc (PTA) is an ideal process for the deposition of coatings. This process produces low dilution values (5, 6), low distortion, small heat affected zone and refined microstructure (6). Many oxides can be formed on the surface of the T-400 alloy, most of which are cobalt and chromium oxides. In the case of coating, the oxides formed are also affected by the dilution with the metal of the substrate, which often is steel.

In this work, the influence of the oxide film formed at temperatures of 450 and 700 °C on the sliding wear behavior of Co-Cr-Mo-Si alloy coatings deposited on an AISI 304 steel substrate by the Plasma Transferred Arc process (PTA) was assessed.

## 2 EXPERIMENTAL PROCEDURE

### 2.1 Material and treatment

Coatings of the CoCrMoSi alloy, known commercially as Tribaloy T-400, processed by Plasma Transferred Arc (PTA) on AISI304 stainless steel plates, were supplied with their top surface machined. The chemical composition of the atomized T-400 alloy, coatings and the substrate is shown in table 1.

Table 1 – Atomized CoCrMoSi alloy composition, coating and substrate.

ALLOY/ELEMENT	Co	Cr	Mo	Si	Ni	Fe
Atomized CoCrMoSi alloy	Bal.	8,5	29,0	2,6	Máx 1,5	Máx 1,5
CoCrMoSi Coating (EDS)	Bal.	10,9 ±0,2	24,0 ±0,2	2,4±0,2	1,9 ±0,06	17,0 ±0,5
AISI 304 Substrate	-----	18,18±0,09	-----	----	8,0±0,08	72,72±0,1

The wear resistance of T-400 was evaluated using a Ball-on-Disc tribometer at room temperature in accordance to the ASTM G99-05 standard. An alumina ball with a diameter of 6 mm was used with the test conditions shown in table 2. To determine the influence of the oxide film, wear tests were performed on as processed and oxidized coatings. Oxidation was carried out at 450 and 700 °C for 6 h in air in a high-temperature furnace with heating and cooling rates of 20 °C.min<sup>-1</sup> and 10 °C.min<sup>-1</sup>.

The tribological behavior was characterized in terms of wear volume, friction coefficient and the morphology of the track and oxide particles (debris). The surface of the wear tracks was analyzed with a confocal laser microscope using profilometry. The volume loss was calculated according to standard G99-05, 16 (sixteen) measurements of the thickness of the wear track were taken along its whole circumference. These measurements were made by confocal laser microscope, and the morphology of the tracks and debris was assessed in a scanning electron microscope - SEM.

Table 2. Ball on disc test parameters

Parameters	Condition
Speed	0.1 m/s
Sliding distance	1000 m
Temperature	Room
Wear track	3 mm radius
Applied load	5 N
Atmosphere	Air

## 3 RESULTS AND DISCUSSION

The CoCrMoSi Tribaloy T-400 alloy coating exhibited an eutectic microstructure, figure 1, due to a higher amount of Mo and Si in relation to the T-401 alloy, which has a hypoeutectic microstructure (6). EDS analysis, table 3, revealed that small variations in composition between the two regions shown in figure 1. The chemical composition of coatings is also expected to differ from that of the atomized alloy due to the ~ 23%, dilution determined by the Fe ratio, in agreement with previous work on Co-based alloys deposited on stainless steel (7). Dilution favors the presence of Fe and Cr, shifting the alloy composition that, together with the oxidation temperature determine the oxides formed at the surface of coatings. As a consequence changes on the wear resistance of coatings are expected.

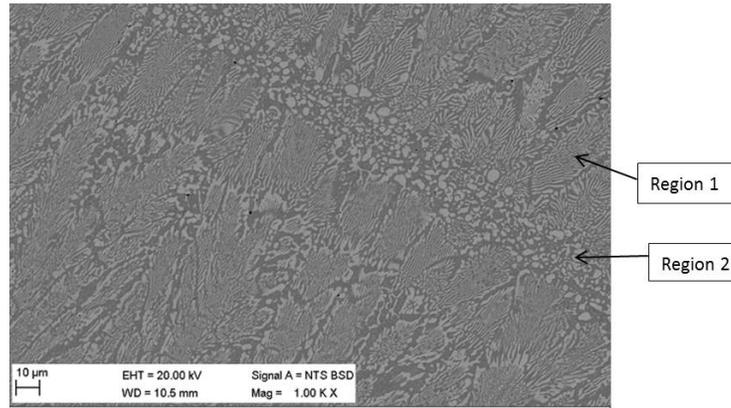


Figure 1. Microstructure of the CoCrMoSi alloy as deposited.

Tabela 3 – Dispersive energy spectroscopy different regions in coatings.

ALLOY/ELEMENT	Co	Cr	Mo	Ni	Fe	Si
Region 1	41,5	11,7	14,2	2,8	24,5	1,51
Region 2	34,82	11,4	20,7	2,7	19,8	1,88

X-ray diffraction analysis of the CoCrMoSi alloy coating in the deposited condition confirmed the presence of Laves phase CoMoSi and Co<sub>3</sub>Mo<sub>2</sub>Si, and other intermetallic compounds, figure 2.

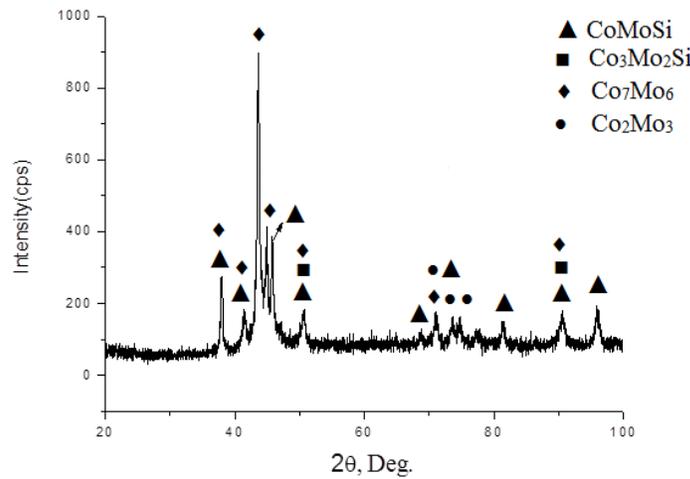


Figure 2. X-ray diffraction showing the phases of Laves and Co / Mo intermetallic in the coating before oxidation.

Previous work showed that for a given set of parameters, the oxides formed at the surface of CoCrMoSi coatings strongly depend on the oxidation temperature (7). The temperature influences the type of oxide formed as authors identified by raman spectroscopy, Figure 3 (7). Oxidation at 450 °C resulted in the formation of Co<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> oxides. However, at temperatures of 700 °C, oxides with low thermal stability such as Fe<sub>3</sub>O<sub>4</sub> are not observed giving rise to oxides with higher thermal stability like Cr<sub>2</sub>O<sub>3</sub>.

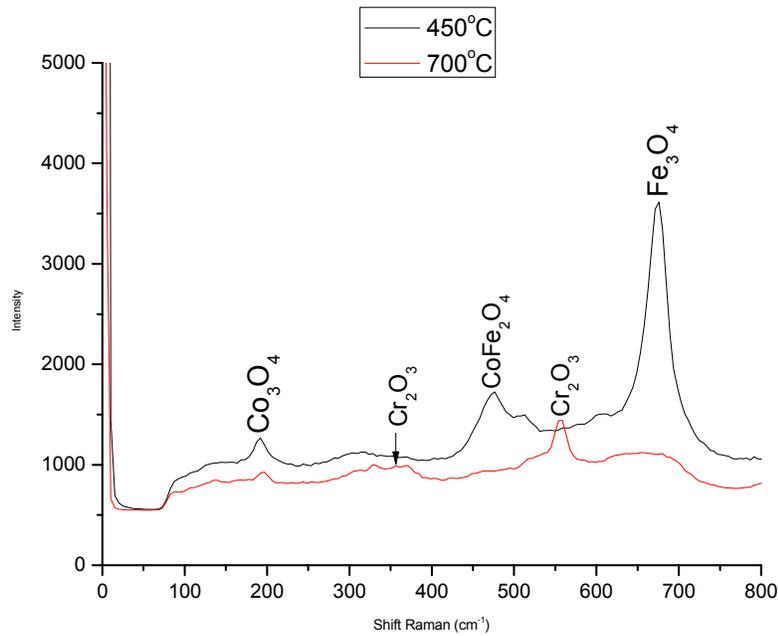


Figure 3. Raman spectroscopy at 450 and 700 °C (7)

The analysis of the tribological behavior of the T-400 alloy suggest that there is no significant difference between the coefficient of friction of the samples under the different test conditions studied. As shown in Figure 4, coatings exposed to oxidation at 450°C ( $\mu \approx 0.59$ ) exhibited a slightly lower coefficient of friction than those oxidized at 700°C ( $\mu \approx 0.69$ ), the latter having a similar performance to the as-processed CoCrMoSi alloy coatings ( $\mu \approx 0.68$ ). However, it is evident that there is an unstable behavior of the coatings exposed to oxidation at 450°C before the wear test.

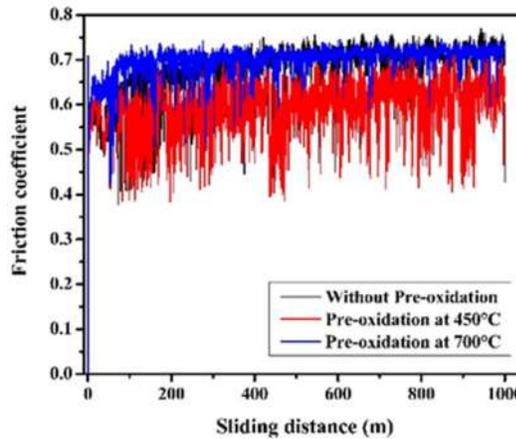


Figure 4. Friction coefficient curves for T-400 coating with and without pre-oxidation.

This behavior can be attributed to a non continuous oxide film with poor adhesion expected for the oxides formed at 450 °C, figure 7. Consequently, particles may detach from the film and act as abrasives destabilizing the behavior of the coating in the wear test but may also have a lubricant character that decreases the coefficient of friction. On the other hand, after the initial ajustement, the behavior of coatings exposed to oxidation at 700 °C before the sliding wear tests was more stable, partially due to the formation of a more adherent and continuous oxide layer that decreased the detachment of particles and also to the poor contribution to the lubrication of the surfaces in contact (coatings and alumina ball), thus explaining the results of the coefficient of friction. These results are an evidence that in a tribological process there are many factors that modify the test conditions, the frictional force is associated with the evolution of the wear, and the detached particles can alter that interaction between surfaces and as a consequence the values of coefficients of friction. [8, 9, 10].

The performance of coatings exposed to different oxidation conditions was also evaluated comparing the volume loss due to wear. Volume loss was calculated in accordance to the ASTM G99-05 standard. Figure 5 shows a decreasing trend in the volume loss during wear and oxidation temperatures used prior to the wear test, which is confirmed by data in the literature [11]. Results suggest that the presence of the oxid film, even if non-continuous have a positive contribution to wear resistance since the volume loss of the as-processed coatings was higher than the that of oxidized surfaces.

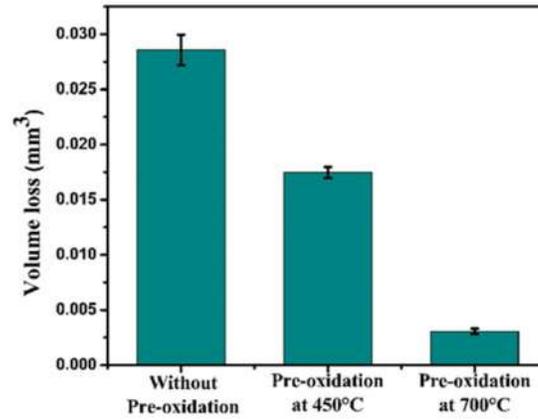


Figure 5. Wear volume losses of T-400 under Pin on Disc wear test.

The volume loss of the coatings oxidized at 700°C was 89% lower than of the as-processed coatings. Likewise, oxidation at 450 °C resulted in a reduction in the volume loss of ~ 39%.

Worn tracks confirmed the different response to wear of coatings depending on the characteristics of the surface. Figure 6 shows the worn track in the as-processed coatings (Figure 6a) the deterioration of the surface of the track by abrasive wear is evident.

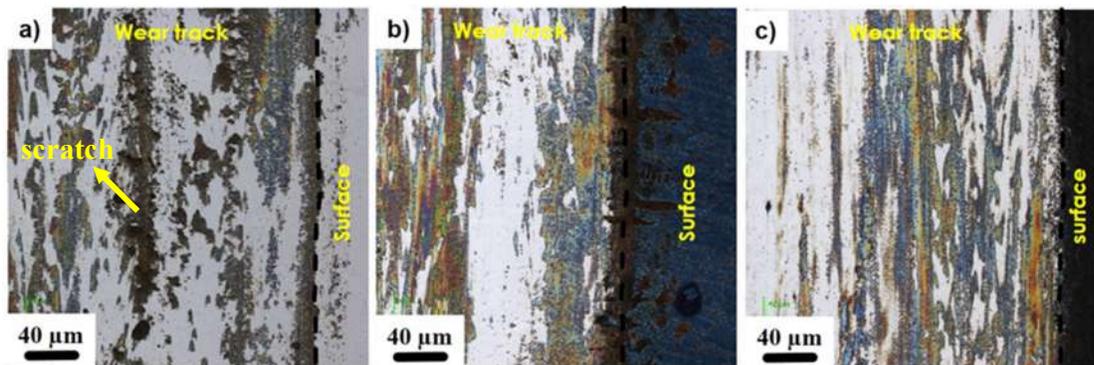


Figure 6. Confocal image of wear track of T-400 alloys coatings: a) as-processed, b) oxidation at 450°C and c) oxidation at 700°C.

Oxides were identified in the worn tracks regardless of the starting condition of coatings, the presence of regions of oxides even in sample without preoxidation that is corroborated in the analysis by SEM EDX (Figure 7). The formation of this oxide film is due to the increase in temperature due to the friction between the ball and the surface of the coating, which is a characteristic behavior of this type of cobalt base alloy susceptible to changes in temperature as has been reported in other studies [12, 13]. No debris were identified on the surface of the alumina ball, the counter surface in the wear test.

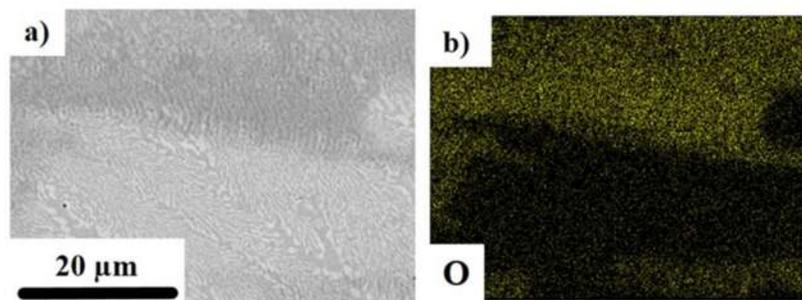


Figure 7. a) SEM image of wear scar of as-processed coatings, b) elemental mapping of Oxygen of wear scar (SEM-EDX) that support the oxide presence outside the track and removal of oxide after the wear.

Although this film is not expected to modify the behavior of the tribological pair since it is a thin film easily removed or broken [14]. Oxidation at 450 °C and 700 °C resulted on similar wear scars (Figure 6b and 6c, respectively), inspite of the difference in the volume loss. This behavior can be related to the thickness of the oxide layer formed, which depends on the heating history of the samples [15,16]. The oxide film that forms at 700 °C is thicker than that expected after oxidation at 450 °C

C [7], which can also be related to the difference in the wear test results. Yao et al. [17] suggests that at higher temperatures the wear is influenced by the speed of recovery of the oxide films and the applied load, if the a small applied load is used the wear rate will be reduced because the worn track is shallower allowing the oxide film to regenerate easily. However, at room temperature the behavior of this tribological pair is different, the temperature generated by the friction is not enough to form a continuous oxide layer during the wear. Coatings exposed to oxidation before the sliding wear test, revealed hat the wear resistance is influenced by the thickness of the oxide layer and its adhesion to the surface. The oxide layer can be brittle and break at any time due to mechanical action. The detached oxide particles may act as abrasive particles which accelerate surface wear or may form a tribolayer, decreasing direct contact between the tribological pair and increasing the wear resistance of the surface [18, 19]. Costa et al. [9] reported that the size of the oxide debris has a significant influence on the role of the oxides particles in the resistance to wear. Small particles act as abrasives, whereas large particles participate actively in the formation of a protective tribolayer.

To understand the acting wear mechanisms in the tested surfaces, wear tracks were analyzed by scanning electron microscopy. Figure 8a and 8b show in detail the worn surface of coatings exposed to oxidation at 450 °C and 700 °C, respectively. The wear mechanism in both samples is adhesive wear whereas in the as-processed coating (Figure 6a) a combination of abrasive and adhesion wear mechanism is observed, attributed to the action of abrasive particles detached from the oxides formed due to the flash temperature (increase in temperature due to friction between the surface and the ball).

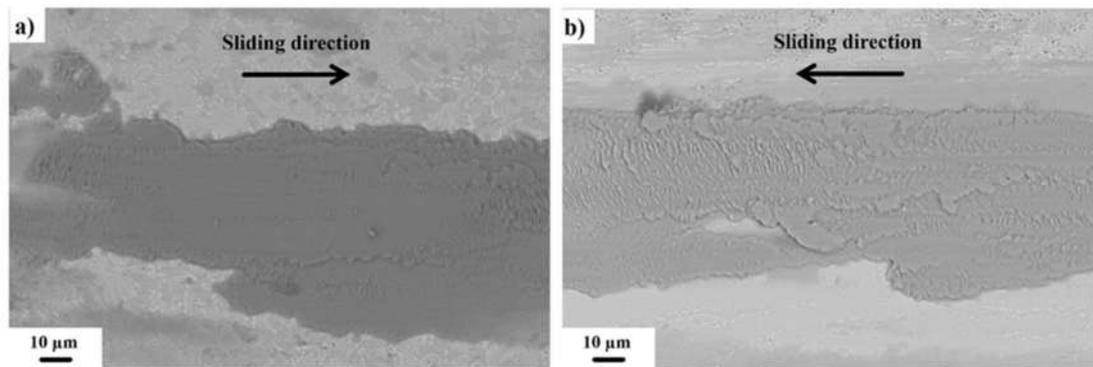


Figure 8. SEM image of wear track: a) coatings oxidized at 450 °C before the wear test and b) coatings oxidized at 700 °C before the wear test.

#### 4. CONCLUSIONS

Under the conditions tested in this study regarding the effect of oxides in the wear performance of CoCrMoSi coatings in the as-processed condition and after oxidation at different temperatures it is possible to conclude that:

The oxidation temperature determined the characteristics of the oxides formed at the surface of coatings. Sliding wear at room temperature showed that coatings exhibited a reduction in wear resistance compared to coatings that were oxidized before the wear test.

Oxidation at 450 °C decreased the volume loss compared to that of as-processed coatings. Oxide debris act as sources of abrasive agents, causing a rapid degradation when submitted to the ball-on-Disc test.

The T-400 alloy deposited by PTA oxidized at 700 °C before testing showed a continuous layer of chromium oxide that offers a better protection against sliding wear, shown by the reduced volume loss.

## 5. REFERENCES

- [1] Cameron, C. B., Hoffman R. A. and Positt R. W., 1975, Tribology intermetallic alloy compositions- new materials or additives for wear resistant applications, *Prog. Powd. Metall.* Vol 31, p. 42-51.
- [2] F. H. Stott., 1998, The role of oxidation in the wear of alloys, *Tribology International*, Vol 13, p. 61-71.
- [3] Miln, J. C. G., Carvalho, M. A., Xavier, R. R., Franco, S. D. and Mello, J. D. B. de., 2005, Effect of temperature, normal load and pre oxidation on the sliding wear of multi-component ferrous alloys, *Wear*. Vol 259, p. 412-4123.
- [4] Munther, P. A., Lenard, J. G., 1981, The effect of scaling on interfacial friction in hot rolling of steels, *Journal of Materials Processing Technology*. Vol 88, p. 105-113.
- [5] Yao, M. X., Wu, J. B. C., Liu, R., 2005, Microstructural characteristics and corrosion resistance in molten Zn-Al bath of CoMoCrSi alloys, *Materials Science & Engineering A*. 407 (299-305).
- [6] Scheid, A., D'Oliveira, A. S. C. M., 2013, Effect of processing on microstructure and properties of CoCrMoSi alloy, *Materials Research*. Vol 16, p. 1325-1330.
- [7] Nascimento, E. M. do, Amaral, L. M., D'Oliveira, A.S.C.M., 2017, Characterization and wear of oxides formed on CoCrMoSi alloy coatings", *Surface & Coating Technology*. <https://doi.org/10.1-16/j.surfco.2017.07.081>.
- [8] Gómez Botero, M. A., 2005, Caracterización de las propiedades tribológicas de los recubrimientos duros, tesis doctora, Universitat de Barcelona, Barcelona..
- [9] Costa, H. L., Junior, M. M. O., and Mello, J. D. B. De, 2017, Effect of debris size on the reciprocating sliding wear of aluminium," *Wear*. Vol 376–377, p. 1399–1410.
- [10] Korashy, A., Attia, H., Thomson, V., and Oskoei, S., 2015, Characterization of fretting wear of cobalt-based superalloys at high temperature for aero-engine combustor components", *Wear*. Vol 330 – 331, p. 327–337.
- [11] Liu, Y.L., Zhou, H.B., Zhang, Y., and Duan, C., 2012, Point defect concentrations of impurity carbon in tungsten," *Comput. Mater. Sci.* Vol 62, p. 282–284.
- [12] Jiang, K.. 2013 Effects of Heat Treatment on Microstructure and Wear Resistance of Stainless Steels and Superalloys.,” PhD thesis, Ottawa University.
- [13] Falqueto, L. E., Butkus, D. J., Mello, J. D. B. De, Bozzi, A. C. and Scandian, C., 2017, Sliding wear of cobalt-based alloys used in rolling seamless tubes," *Wear*. Vol 376–377, p. 1739–1746.
- [14] Navas, C., Cadenas, M., Cuetos, J. M., and Damborenea, J. de, 2006, Microstructure and sliding wear behaviour of Triballoy T-800 coatings deposited by laser cladding", *Wear*. Vol 260, p. 838–846.
- [15] Sun, W., Tieu, A. K., Jiang, Z., and Lu, C., 2004, High temperature oxide scale characteristics of low carbon steel in hot rolling", *Journal of Materials Processing Technology*. Vol 156, p. 1307–1312.
- [16] Varga, M., Rojacz, H., Winkelmann, H., Mayer H. and Badisch, E., 2013, Wear reducing effects and temperature dependence of tribolayer formation in harsh environment," *Tribology Int.* Vol 65, p. 190–199.
- [17] Yao, M.X., Wu, J.B.C., Yick, S., Xie, Y. and Liu, R., 2006, High temperature wear and corrosion resistance of a Laves phase strengthened Co – Mo – Cr – Si alloy, *Materials Science and Engineering A*. Vol 436, p. 78–83.
- [18] Nsoesie, S., Liu, R., Jiang, K. and Liang, M., 2013, High temperature Hardness and Wear Resistance of Cobalt based Triballoy Alloys, *International Journal of Material and Mechanical Engineering*. Vol 2, p. 48–56.
- [19] Huang, C., Zou, B., Guo, P., Liu, Y., Huang, C. and Wang, J., 2016, Sliding behavior and wear mechanism of iron and cobalt-based high temperature alloys against WC and SiC balls, *International Journal of Refractory Metals and Hard Materials*. Vol 59, p. 40-55.

## 6. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.