IOP Conf. Series: Materials Science and Engineering **416** (2018) 012027 doi:10.1088/1757-899X/416/1/012027

Investigations on Dry Sliding Wear and Corrosion Resistance of Thermal Sprayed Molybdenum Coatings

L Păduraru[1], L Nedeloni[1,*], N Kazamer[2,3,*], R Muntean[2], D T Pascal[2], P C Vălean[2,3] and M D Nedeloni[1]

[1]Eftimie Murgu University of Reșița, Faculty of Engineering and Management, Piața Traian Vuia, No. 1-4, 320085, Reșița, Romania
[2]Westphalian University of Applied Sciences Gelsenkirchen, Neidenburger Str. 43, 45897 Gelsenkirchen, Germany
[3]Politehnica University of Timișoara, Department of Materials and Manufacturing Engineering, Piața Victoriei, No. 2, 300006, Timișoara, Romania

*Corresponding author: l.nedeloni@uem.ro; norbert.kazamer@w-hs.de

Abstract. This paper aims to investigate the characteristics of molybdenum thermal sprayed coatings deposited on 1.0570 steel substrate and compare them with the characteristics of the uncoated carbon steel (1.0570), respectively alloyed steels (1.7219 and 1.6582), which are currently used for similar applications, such as parts and structural components used at temperatures down to -100°C, aircraft, terrestrial transportation and other industries. The Mo coating deposition was performed by wire metallization and aimed to increase the wear and corrosion resistance of steels typically applied in railway transportation industry. The microhardness, wear behaviour and corrosion resistance have been investigated for all the presented materials. Molybdenum coatings deposited by wire metallization technique possess superior frictional behaviour due to the formation of an oxide tribo-film. Therefore, the friction coefficient of the presently investigated Mo coatings reached a value of 0.65, correlated with a low wear rate of about $0.65 \cdot 10^{-5}$ mm^3 N^{-1} m^{-1}. The porosity degree of the Mo coatings was found to be around 3.50%, a common value for this type of coatings. Microhardness average value of Mo coating was 480 HV0.3 and the corrosion behaviour was found to be superior in comparison to the other materials, exhibiting an inclination to passivation at around 300 mV.

1. Introduction

Various studies have been carried out lately in order to improve wear behavior of railway vehicle parts [1]. One of the main focus in improving fatigue and wear resistance of railway vehicles main components is to increase the axle size to considerably reduce the stress [2-5]. Another direction relates to the pretreatment of the raw material from which axles are manufactured by different methods or coatings, greatly improving in this way, the wear, fatigue and corrosion behavior [6-12].

The materials use for axles manufacturing are chosen according to the properties to be pursued and the conditions required by an optimal operation, in order to avoid the above-mentioned risks. Carbon steels and also the heat-treated steels are commonly used because they fulfil the resistance conditions, but in exceptional cases, molybdenum, chromium or nickel alloys may also be used [13-20].

Over the last 20 years, most researchers have attempted to replace chemical and electrochemical coatings of steel components using unconventional processes such as thermal spraying of different types of hard particles or superior materials [21-24]. Thermal spraying is an economical and efficient technological process that provides excellent tribological properties, resistance to stress, corrosion and oxidation. It has been shown that molybdenum is a promising candidate for coating various parts which are subjected to corrosion and wear conditions. Also, molybdenum as well and other refractory metals have high melting temperatures, and due to this fact, during the deposition process, the interaction between the substrate and the melted material is very high [25-29].

In this direction, the present study brings a contribution in the field of wear and corrosion resistance coatings which can be applied for railway vehicles main parts. The analyzed steels and molybdenum coating were investigated for microhardness, dry sliding wear and corrosion resistance in 3.5% NaCl solution to compare and highlight their behavior under identical test conditions. The obtained results are reliable compared to other studies [30-36] showing that the Mo coating deposition by wire metallization increases the wear performance and also the corrosion resistance.

2. Experimental procedure

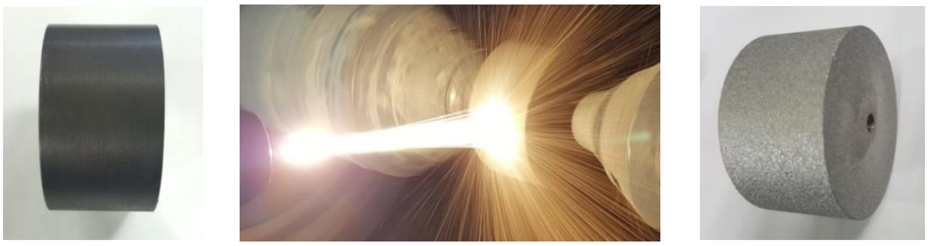
The main steps of this study were deposition of the molybdenum coating through the wire metallization process, morphological and microstructural characterization of the obtained coating by scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM and EDX), Light Microscopy (LM), Laser Scanning Confocal Microscopy (LSCM), microhardness, wear resistance and corrosion behavior for all specimens.

The chemical composition of three types of steel and the Mo coating is shown in table 1.

Table 1. The chemical composition of the specimens (%).

Specimen	C	Si	Mn	Cr	Mo	Ni	P	S
1.0570	≤0.20	≤0.55	≤1.60	-	-	-	≤0.035	≤0.035
1.7219	0.22-0.29	≤0.35	0.50-0.80	0.90-1.20	0.15-0.30	-	≤0.030	≤0.025
1.6582	0.30-0.38	≤0.30	0.50-0.80	1.30-1.70	0.15-0.30	1.30-1.70	≤0.025	≤0.025
Mo coating	-	-	-	-	99.5	-	-	-

The Mo coating was deposited by wire metallization process, using a molybdenum wire of 3.17 mm. During the deposition process, the molybdenum wire was melted by flame produced by the gas mixture combustion used in the process and subsequently the melted particles were finely pulverized on the surface of the specimen. The melting temperature of the molybdenum wire is around 2600°C and the Mo oxides are formed at approx. 700°C. The Mo particles form a fine, microporous coating on the surface of the substrate. This type of coating is considered suitable for various applications which require high wear and corrosion resistance. Figure 1 shows some characteristic images of the specimen before, during and after the Mo deposition.



a) 1.0570 substrate *b) process of the Mo coating* *c) Mo coating*

Figure 1. Characteristic images of the Mo coating specimen and process.

The microstructure, morphology as well as thickness of the obtained Mo coating deposited onto the 1.0570 steel was investigated by SEM. Additionally, the chemical composition of the analyzed coating

IOP Conf. Series: Materials Science and Engineering **416** (2018) 012027 doi:10.1088/1757-899X/416/1/012027

was determined by EDX. The images obtained using LM were further processed using ImageJ software to determine the porosity degree of the Mo coating [37,38].

The microhardness testing was performed with the aid of a Zwick-Roell ZHVμ-S instrument equipped with a known geometry indentor, following the ISO 6507 standard. The applied force was 0.3 kgf and held for 15 seconds for each indentation. The distance between two indentations was set at 0.150 mm for a number of 5 indentations for each specimen, where the final hardness was the average of the measurements.

For the investigations on dry sliding wear, tests were performed using a CSM tribometer according to the Pin-on-Disk method (POD). A 10 N load was applied using a 6 mm 100Cr6 steel ball, with a linear speed of 15 cm s^{-1}, a working radius of 3 mm and a distance of 1500 m at 20°C, in agreement to the ASTM G99-95a standard, in order to determine the friction coefficients and wear rate of the tested system.

Corrosion resistance was investigated by plotting the linear polarization curves with a potentiostat in an electrochemical cell, with three electrodes configuration, where the working electrode consisted of the material to be analyzed, a platinum disk for the counter electrode and saturated calomel electrode (SCE) as reference electrode. Linear polarization curves were recorded from a potential value of -1000 mV to 500 mV, with a scanning rate of 10 mV min^{-1} in neutral 3.5% NaCl solution, following the ISO 13129 standard.

3. Results and discussion

A good wear and corrosion behavior is directly dependent on the quality of the deposited coating, microstructure, compactness and porosity [37]. In this regard, Mo coating was examined on surface and cross-section by SEM, mainly using the BSE detector at 50X to 1000X magnification, in order to analyze the microstructure, thickness, and the quality of the coating/substrate interface (figure 2).

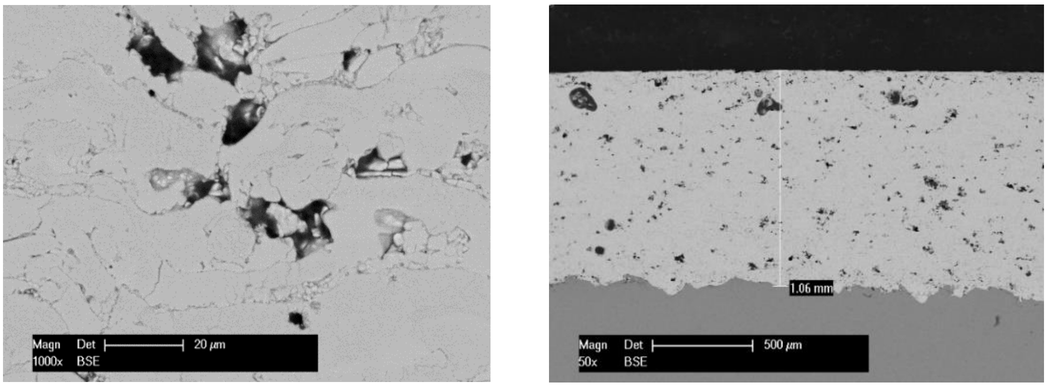


Figure 2. SEM micrographs of the Mo coating on the surface and cross-section.

Cross-section micrograph highlights a coating thickness of 1.06 mm and the interface between the coating and the substrate is clean, free from impurities, pores or cracks, which demonstrates that the adhesion of the coating to the substrate meets the essential requirements (figure 3). A good adhesion to the substrate combined with a compact, non-cracked coating leads to a qualitative coating that fulfills the protective role, especially anticorrosive.

IOP Conf. Series: Materials Science and Engineering **416** (2018) 012027 doi:10.1088/1757-899X/416/1/012027

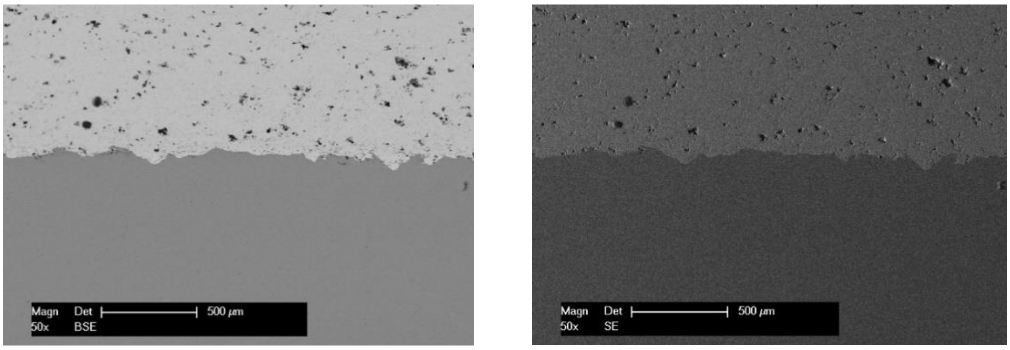


Figure 3. SEM micrographs of Mo coating: with BSE respectively SE detector.

Additionally, EDX analysis revealed the chemical composition of the deposited coating (figure 4).

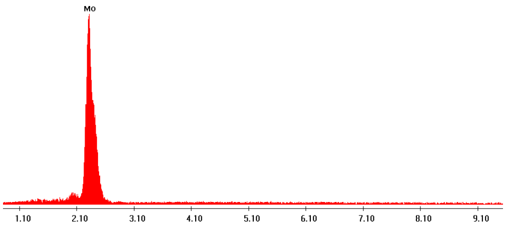


Figure 4. EDX spectrum of Mo coating.

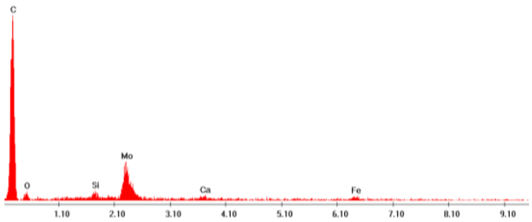
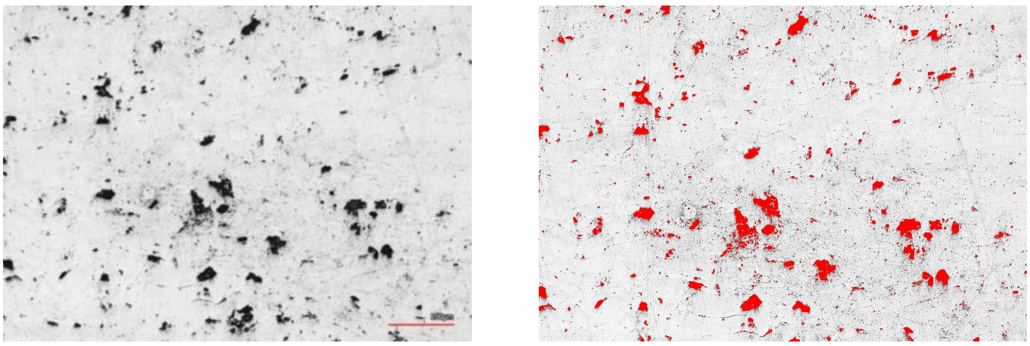


Figure 5. EDX spectrum of C inclusions.

Molybdenum is highlighted as a single element, since the wire used in the deposition process had a purity of >99.5%. The possibility of molybdenum to oxidize during the deposition process is also taken into account, since oxidation occurs very strongly at temperatures above 400°C. Once the molten molybdenum reaches the surface of the substrate, oxidation is also possible. The inclusions present in the coating were also analyzed, and the EDX spectrum shown in figure 5, highlights their chemical composition. Some of the inclusions have come from the metallographic processing of the specimen (SiC), metal oxides and other metal impurities.

The CSLM micrographs shown in figure 6 were used to determine porosity of the coating. Figure 6a reveals the micrograph of the Mo coating at 100X magnification, showing that the present pores are closed without interconnection. In figure 6b, the image was further processed using ImageJ, obtaining in this way the porosity degree. By this method, an average porosity value of 3.50% was determined. This value is specific to this type of coating [38].



a) *b)*

Figure 6. CSLM micrographs of the Mo coating and correspondingly processed image.

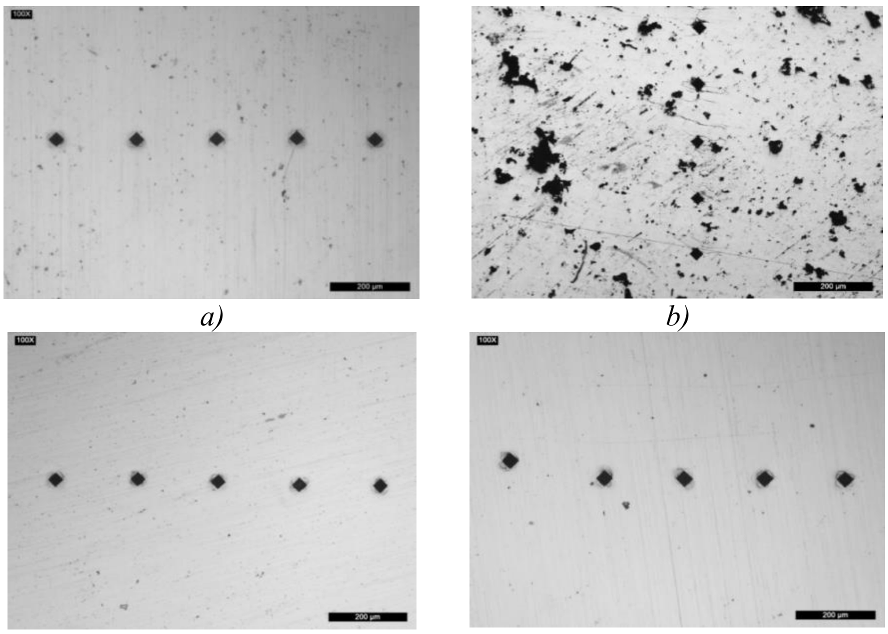
The microhardness was assessed using the Vickers method [21,39] in 5 different areas, on the cross-sectional depth of the molybdenum coating. The final value of the microhardness was calculated as the average of the 5 measurements made on each type of the specimen.

Table 2 presents the minimum and maximum values obtained as well as the calculated mean value of the Mo coating in comparison to the investigated steel materials.

Table 2. Calculated values of HV0.3 microhardness.

Specimen	HV0.3 min.	HV0.3 max.	HV0.3 mean
1.0570	187	196	191
1.7219	321	326	323
1.6582	381	393	387
Mo coating	302	657	480

It can be noticed that the Mo coating has the highest value of microhardness (480 HV0.3). This is attributed to the high molybdenum hardness as property of the material as well as to the coating's compactness. The absence of large and interconnected pores leads also to a higher value of hardness. The heat-treated stainless steel 1.6582 has also high hardness (387 HV0.3), compared to 1.7219 and 1.0570 used as substrate for the Mo coating. Figure 7 shows LM micrographs of the microhardness indentations for each specimen.



a) *b)* *c)* *d)*

Figure 7. LM micrographs of the microhardness indentations: a) 1.6582, b) Mo coating, c) 1.0570 respectively d) 1.7219.

Regarding the dry sliding wear behavior, the friction coefficient and the wear rate was obtained. Therefore, the friction coefficient was monitored with the integrated software and the wear rate was represented by volume loss depending on the counterpart, applied load and the distance on the specimen surface.

The obtained results presented in figure 8 and 9 respectively table 3 reveal a superior behavior of the Mo coating. Even if the average value of the friction coefficient is lower for the 1.0570 steel substrate compared to the Mo coating, the Mo coating show a lower value of wear rate.

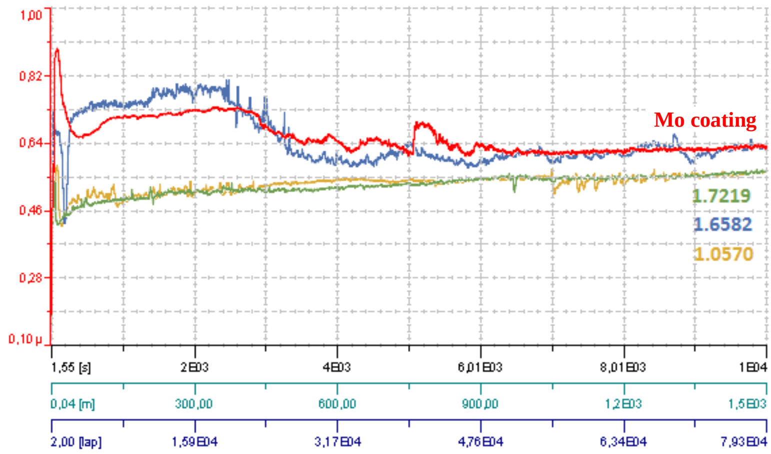
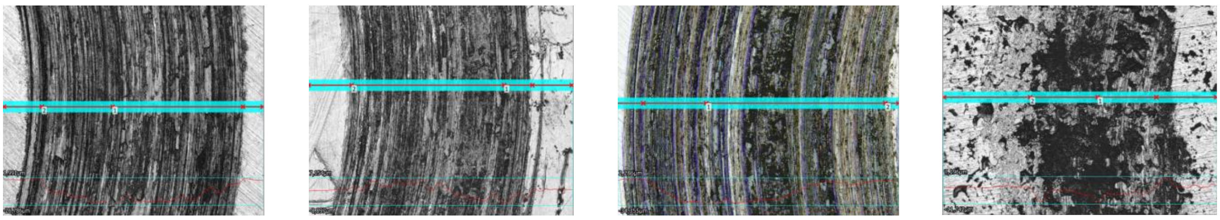


Figure 8. Evolution of friction coefficients for the investigated specimens.



a) 1.0570 *b) 1.7219* *c) 1.6582* *d) Mo coating*

Figure 9. Wear track profiles for a) 1.0570, b) 1.7219, c) 1.6582 and d) Mo coating.

Table 3. Values of the wear rate.

Specimen	h (μm)	s (μm)	A (μm^2)	W_v (mm^3)	k ($mm^3N^{-1}m^{-1}$)
1.0570	27.15	1089.56	19730	0.3719	$2.48 \cdot 10^{-5}$
1.7219	9.41	966.44	6063	0.1143	$0.76 \cdot 10^{-5}$
1.6582	34.30	1218.42	27877	0.5255	$3.50 \cdot 10^{-5}$
Mo coating	12.02	653.50	5238	0.0987	$0.65 \cdot 10^{-5}$

The plots presented in figure 10, show the logarithmic form of the polarization curves of the investigated specimens in 3.5% NaCl solution. The values of the corrosion current as well as the corrosion potential was determined by Tafel slope method and are presented in table 4.

The corrosion currents are of the same order of magnitude for all the investigated specimens and there are no major differences, but the corrosion potential for the Mo coating is shifted to more positive values, due to the chemical composition of the coating.

The curve corresponding to the Mo coating presents a passivation tendency around 300 mV and its anodic branch is characterized by lower current densities compared to the other steels. The better corrosion behavior among the three types of steel is represented by the 1.6582 steel, which can be assigned to the higher Cr and Ni content in its chemical composition, favoring the passivation phenomenon.

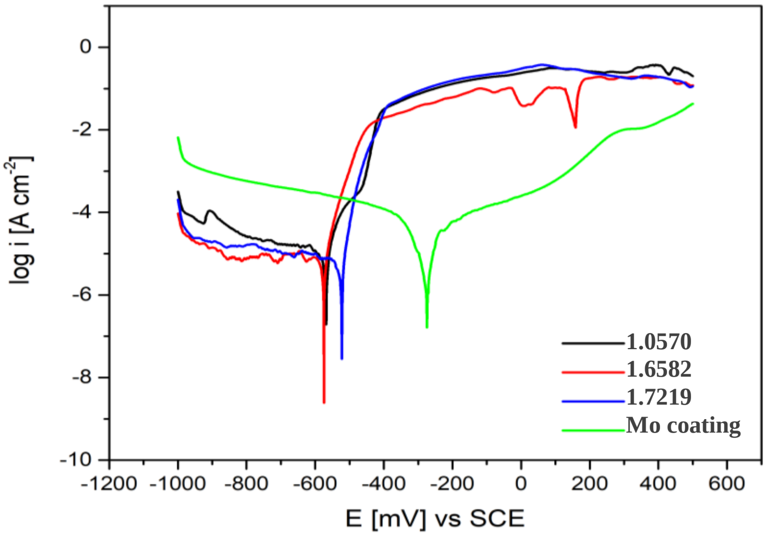


Figure 10. Logarithm representation of corrosion curves.

Table 4. Values of potentials and corrosion currents.

Specimen	E_{corr} [mV] vs. SCE	i_{corr} [A cm^{-2}]
1.0570	-577	$1{,}23\cdot10^{-5}$
1.7219	-534	$1{,}17\cdot10^{-5}$
1.6582	-587	$1{,}34\cdot10^{-5}$
Mo coating	-275	$3{,}38\cdot10^{-5}$

4. Conclusions

The investigated Mo coating possess superior characteristics, in comparison to the three analyzed steels, fact that makes it suitable for various applications. The interface between the Mo coating and the substrate was clean, without inclusions, leading to a good adhesion of the coating. CSLM micrographs reveal the presence of pores, which do not affect the structure and the resistance of the coating because they are closed and with no cracks. The average porosity was assessed to 3.50%, this value being specific to this type of wire deposition. From the other tested materials, the Mo coating showed the highest microhardness value. The friction coefficient and the wear rate were determined through POD method and the profiles were analyzed using the CSLM laser microscope.

The results showed a superior wear behavior of the molybdenum coating, with a lower friction coefficient and wear rate. The superior corrosion resistance of the Mo coating confirms the effectiveness of depositing this type of coating in order to extend the life of the railway vehicles components.

5. References

[1] Smith R A 2008 *Ironmaking and Steelmaking* **35**(7) 505-13
[2] Olofsson U and Nilsson R 2002 *J. of Rail and Rapid Transit* **216**(4) 249-64
[3] Olofsson U and Telliskivi T 2003 *Wear* **254** 80-93
[4] Sebesan I, Făinuş L and Zaharia N L 2013 *Mater Plast* **50**(4) 253-6
[5] Făinuş L, Zaharia N L, Tudose D I and Hadăr A 2016 *UPB Scientific Bulletin, Series D: Mechanical Engineering* **78**(3) 107-18
[6] Jin G, Xu B, Wang H, Li Q, Wei S 2007 *Surf Coat Tech* **201**(15) 6678-80

[7] Kazamer N, Pascal D T, Marginean G, Serban V A, Brandl W and Valean P C 2016 NANOCON pp 383-8
[8] Secosan E R, Marginean G, Ciubotariu R C, Frunzaverde D and Campian V 2015 *Annals of the „Eftimie Murgu" University of Resita* **22**(1) 385-96
[9] Davis J R 2001 Introduction to Surface Engineering for Corrosion and Wear Resistance *Surface Engineering for Corrosion and Wear Resistance* ASM International chapter 1, pp 1-10
[10] Lazar P, Bejinariu C, Sandu A V, Cazac A M, Corbu O, Sandu I G and Perju M C 2017 IOP Conference Series: Materials Science and Engineering, Romania, May 25-26, pp 1-5
[11] Lyphout C, Sato K, Houdkova S, Smazalova E, Lusvarghi L, Bolelli G and Sassatelli P 2016 *J Therm Spray Techn* 2**5**(1-2) 331-45
[12] Lungu M V et al. 2018 BALTTRIB'2017, pp 27-33
[13] Ivan A, Ivan M and Both I 2010 *WSEAS Transactions on Applied and Theoretical Mechanics* **5**(3) 187-96
[14] Pascal D T, Muntean R, Kazamer N, Marginean G, Brandl W and Serban V A 2016 NANOCON pp 775-80
[15] Hulka I, Şerban V A, Secoşan I, Vuoristo P and Niemi K 2012 *Surf Coat Tech* **210** 15-20
[16] Modi S C and Calla E 2001 *J Therm Spray Techn* **10**(3) 480-6
[17] Dumitrascu V, Benea L and Danaila E 2017 IOP Conference Series: Materials Science and Engineering, Iasi, Romania, May 25-26, pp 1-8
[18] Budai A M, Campian V C, Frunzaverde D, Miclosina C and Pepa D 2017 *Technical Gazette* **24**(2) 271-7
[19] Cîndea L, Haţiegan C, Pop N, Negrea R, Răduca E, Gillich G R, Dănuţ M, Nedeloni M D 2016 *Appl Therm Eng* **103** 1164-75
[20] Lungu M V et al. 2017 Conference Series: Materials Science and Engineering, Iasi, Romania, May 25-26 pp 1-11
[21] Kazamer N, Pascal D T, Marginean G, Serban V A, Codrean C and Utu I D 2016 *Sol St Phen* **254** 71-6
[22] Rigou I V, Mărginean G, Frunzăverde D and Câmpian C V 2011 TAM '11, Greece, July 14-16, pp 219-22
[23] Zajchowski P and Crapo H B 1996 *J Therm Spray Techn* **5**(4) 457-62
[24] Cojocaru V, Frunzaverde D, Campian C V, Marginean G, Ciubotariu R and Pittner A M 2010 EMESEG '10, Greece, July 22-24, pp 177-80
[25] Ozdemir I, Tekmen C, Okumus S C and Celik E 2003 *Surf Coat Tech* **174** 1964-69
[26] Wayne S F, Sampath S and Anand V 1994 *Tribol T* **37**(3) 636-40
[27] Laribi M, Vannes A B, Treheux D 2006 *Wear* **262**(11-12) 1330-36
[28] Ahn J, Hwang B and Lee S 2005 *J Therm Spray Techn* **14**(2) 251-7
[29] Ciubotariu C R, Frunzaverde D, Secosan E, Marginean G and Campian V 2016 *Stroj Vestn-J Mech E* **62**(3) 154-62
[30] Sampath S and Wayne S F 1994 *J Therm Spray Techn* **3**(3) 282-8
[31] Chi W, Sampath S and Wang H 2006 *J Therm Spray Techn* **15**(4) 773-8
[32] Wang Y, Wang D, Yan J and Sun A 2013 *Appl Surf Sci* **284** 881-8
[33] Zhao X B and Ye Z H 2013 *Surf Coat Tech* **228** 266-70
[34] Yan J, He Z, Wang Y, Qiu J and Wang Y 2016 *J Therm Spray Techn* **25**(7) 1322-29
[35] Paraschiv A, Matache G, Puscasu C and Grigorescu M 2018 MATEC Web of Conferences, Bulgaria, September 6-10, pp 1-9
[36] Yan J, Guo Y, Wang Y, Zhou P and Qiu J 2018 *Lubricants* **6**(48) 1-11
[37] Oksa M, Turunen E, Suhonen T, Varis T and Hannula S P 2011 *Coatings* **1** 17-52
[38] Tailor S, Modi A and Modi S C 2018 *J Therm Spray Techn* **27** 757-68
[39] Mendes V B and Leta F R 2003 Proceedings, XVII IMEKO World Congress, Croatia, July 22-27, pp 992-5