Letters on Materials 11 (3), 2021 pp. 244-248 www.lettersonmaterials.com

https://doi.org/10.22226/2410-3535-2021-3-244-248 PACS: 61.46.+w

Assessment and effect of reinforcement of multi-walled carbon nanotubes in Ni-Al_2O_3 and Ni-SiC nanocomposite coatings using pulse reverse electrodeposition technique

K. Venkatesh Raja[†], A. Ranjith Kumar, S. Naren

[†]kvenkateshraja@hotmail.com

Sona College of Technology, Department of Mechanical Engineering, Salem, 636005, Tamil Nadu, India

The nanocomposite coating provides a higher degree of corrosion resistance, microhardness, wear resistance and significantly improves the tribological qualities of the base metal. This research work is aimed at investigating the effect of the proportion of multi walled carbon nanotubes (MWCNT) mixed with Ni-Al_2O_3 and Ni-SiC nanocomposite coatings on a mild steel AISI 1018 specimen against its tribological characteristics through experimental investigation. The pulse reverse electro deposition technique is deployed for coating formulation with optimized coating parameters. The proportions of carbon nanotubes vary in three different ratios ranging from 1:1 to 2:1. Tribological characteristics (microhardness and surface morphology) are assessed using a Vickers microhardness testing machine and a scanning electron microscope (SEM). Nine different coating combinations are considered in this study and their tribological attributes are compared with the un-coated sample. From the results, it can be observed that the samples coated with Al_2O_3 nanoparticles reinforced with carbon nanotubes (CNTs) possess excellent magnitudes of micro-hardness in comparison with the uncoated and SiC-CNT coated samples with an enhancement factor of 2.88 and 1.37, respectively. Moreover, the variation of the CNT proportion in the coating blend has the tleast significant effect and therefore, addition of CNT particles beyond the blend ratio of 1:1 may be avoided to reduce the coating cost of samples significantly. Also, SEM images clearly reveal a uniform coating distribution owing to the application of optimized coating parameters.

Keywords: carbon nanotube, nanocoatings, pulse reverse electro deposition, CNT reinforcement, tribology.

УДК: 538.9

Оценка и влияние армирования многослойных углеродных нанотрубок в нанокомпозитных покрытиях Ni-Al_2O_3 и Ni-SiC с использованием метода импульсного обратного электроосаждения

Венкатеш Раджа К.[†], Ранджит Кумар А., Нарен С.

Технологический колледж Сона, Кафедра машиностроения, Салем, 636005, Тамил Наду, Индия

Нанокомпозитное покрытие обеспечивает более высокую степень коррозионной стойкости, микротвердости, износостойкости и значительно улучшает трибологические свойства основного металла. Данная исследовательская работа направлена на изучение влияния доли многостенных углеродных нанотрубок совместно с нанокомпозитными покрытиями Ni-Al_2O_3 и Ni-SiC на образце из мягкой стали AISI 1018, на его трибологические характеристики путем экспериментального исследования. Метод импульсного обратного электроосаждения используется для получения покрытия с оптимальными параметрами. Пропорции углеродных нанотрубок варьируются в трех различных соотношениях от 1:1 до 2:1. Трибологические характеристики (микротвердость и морфология поверхности) оцениваются с помощью оборудования для определения микротвердости по Виккерсу и растрового электронного микроскопа (РЭМ). В этом исследовании рассматриваются девять различных комбинаций покрытий, и их трибологические характеристики сравниваются с образцом без покрытия. Как видно из полученных результатов, образцы, покрытые наночастицами Al_2O_3, армированными углеродными нанотрубками (УНТ), обладают превосходными значениями микротвердости по сравнению с образцами без покрытия и образцами с покрытием УНТ-SiC с коэффициентом усиления 2.88 и 1.37, соответственно. Более того, изменение доли УНТ в смеси для покрытия имеет наименее значительный эффект, и, следовательно, можно избежать добавления частиц УНТ, превышающих соотношение в смеси 1:1, чтобы значительно снизить стоимость покрытия образцов. Кроме того, РЭМ изображения ясно показывают равномерное распределение покрытия благодаря применению оптимизированных параметров покрытия.

Ключевые слова: углеродная нанотрубка, нанопокрытия, импульсное обратное электроосаждение, армирование УНТ, трибология.

1. Introduction and literature review

Surface coating of metals is a proven methodology to enhance the corrosion rate, wear resistance and micro hardness of the metal. Research into the production of nanocomposite coatings by electrolytic co-deposition of fine particles with metal from plating baths has been carried out by numerous investigators [1–3]. Recently, the use of nanocomposite coatings gained significant attention owing to its impressive corrosion resistance, wear resistance and micro hardness [4–6] and such parameters predominantly depends on the composition or percentage of the materials that are to be electro deposited on the metal [7].

The process of electro deposition process helps in uniform reinforcement of particles on the surface of metals. Pulse current electro deposited particles have better tribological characteristics than most other techniques. Various types of nanoparticles with different properties, such as oxides (Al_2O_3, ZrO_2, SiO_2, TiO_2), borides (TiB_2, ZrB_2), carbides (SiC, WC) and multi-wall carbon nanotubes (MWCNT), have been successfully co-deposited with microcrystalline metals and alloy phases to form nanocomposites coatings with outstanding tribological properties [8–13].

Since their discovery, carbon nanotubes (CNTs) are being explored as a reinforcement for polymers, metals, and ceramic matrices due to their extraordinary electrical, mechanical, and thermal properties. The fascinating properties of CNTs have led to a various number of research efforts throughout the world [14–18]. Also, it has been found that CNT-based nanocomposites revealed lower friction coefficient and wear rate in caparison with the pure substrate matrix [17]. CNTs can also withstand repeated bending, buckling, and twisting loading conditions due to its inbuilt stiffness and strength characteristics resulting in higher Young's modulus and tensile strength [19]. The average magnitude of elastic moduli of isolated MWCNTs has been measured to be 1.8 TPa and its bending strength is as high as 14.2 GPa [20]. The value of elastic modulus of CNTs is extremely higher than other rigid materials like carbon fiber (230 GPa) and SiC (414 GPa). However, its density is about one-sixth to one-seventh of steel [21–24].

Moreover, CNTs are believed to be ideal for nanocomposite coatings that can be used to derive excellent surface protection with remarkable performance [25]. In the pulse reverse plating, the current is applied in a non-linear fashion and this facilitates a homogenous coating with fine grains and uniform morphology. The periodic action of the anodic current on the deposited layer of metal, the deposit acquires better protective properties. For several processes, current reversal is a means of achieving smoother and brighter deposits, better current distribution, and less porous deposits with lower internal stresses [26]. Studies on molecular dynamics in aluminium coatings were investigated by Galashev et al [31] and few other works pertaining to coatings techniques and characterization were reported on electro spark deposition and tantalum coatings [32, 33]. Savina et al. [34] investigated the effect tribological characteristics of multi walled CNTs reinforced with aluminium silicon metal matrix composites.

However, to the authors' knowledge, the effect of MWCNT proportion over the magnitude of micro-hardness parameter has not been addressed in detail. Also, the mix of a ductile and brittle nanocomposite powder seems to be interesting area for investigation. Based on the facts, this research work is focused towards assessing the effect of MWCNT percentage through investigation of its microstructure and microhardness phenomenon.

2. Methodology and Experimental scheme

The nanocomposites (Al_2O_3 + MWCNT, SiC + MWCNT and Al_2O_3 + SiC + MWCNT) are coated on the AISI 1080 steel substrate (10×10×10 mm) by a nickel sulphate bath. The pulse reverse electro deposition technique (PREDT) [29] is utilized for coating all the samples. This technique is selected due to the flexibility in varying the pulse parameters for achieving superior coating characteristics [29]. Based on the data and facts available in the literature, the reverse-pulse parameters are kept constant throughout the study and the percentage of CNTs are varied in this research work. The optimal pulse parameters [30] used in the research work are listed in Table 1 for reference. The base substrate material is used as a cathode and the top layer of the cube shaped sample alone is exposed for coating. The remaining surfaces of the sample are covered with the aid of polyvinyl chloride adhesive layer to ensure proper masking. The surface of the cube is polished with superior grade of abrasive papers in a double disc polishing machine and the surface impurities are completely cleaned with acetone using an ultrasonic cleaning chamber.

Nine different samples are prepared with a unique blend of combinations as listed in Table 1. The proportion of MWCNT varies in three different combinations (5, 7.5 and 10 g) along with Al_2O_3, SiC and Al_2O_3 + SiC (10 g). This unique blend develops three different coating ratios of 1:2, 3:4 and 1:1. The Watts type bath using PREDT is used for electro deposition process. The bath compositions and other optimized parameters considered in this study are clearly listed in Table 1. Dynatronix, USA (Micro star pulse series DPR 20-30-100 power supply) Pulse rectifier is used for experiments and nanocoatings. Each solution is stirred for 8 hours at 400 rpm. The electrodeposition process is carried out in time span of around 15–25 minutes per sample. SDS is used in all the solutions to increase homogenous dispersion [14]. Adding a dispersant in the solution significantly increases the zeta potential of the nanoparticles. The positive zeta potential gives the extra adhesion force between the inert particles and the cathode, resulting in good adhesion between substrate and deposits [15]. A magnetic stirrer bar with a speed of 500–600 rpm is used for coating the samples at a temperature around 55°C. The pH value of the solution is maintained in the range of 4 throughout the process. Fig. 1 exhibits the examples of coated specimens by PREDT.

Table 1. Pulse reverse electro deposition parameters and coating composition.

Pulse Electro Deposition – Bath compositions	
Bath composition	**Quantity (gL^{-1})**
$NiSO_4 \cdot 6H_2O$	300
$NiCl_2 \cdot 6H_2O$	50
H_3BO_3	35
SDS	0.2
Al_2O_3/SiC/Al_2O_3 + SiC	10
MWCNT	5, 7.5 and 10
Pulse Reverse Electro Deposition – parameters	
Anodic current density (ACD) (A cm^{-2})	0.08
Cathodic current density (CCD) (A cm^{-2})	1
Anodic current time (ACT) (s)	0.02
Cathodic current time (CCT) (s)	0.01
Relaxation time (RT) (s)	0.1

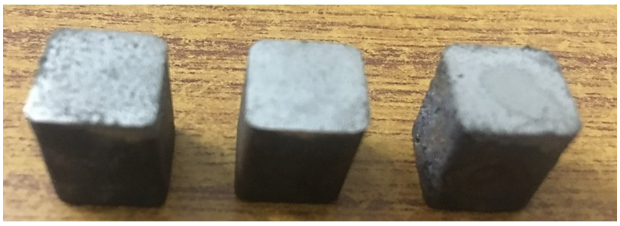

Fig. 1. (Color online) Nanocoated samples.

3. Results and discussion

The microhardness and microstructures of the specimens are carefully examined with the aid of a Vickers microhardness testing machine (Shimadzu tester - HMV 2T intender) and a scanning electron microscope (Carl Zeiss 5.07 Beta-Sigma variant, Germany), respectively. The magnitude of micro hardness is evaluated at six different geometrical locations and the mean is considered for all discussions. A load of about 125 grams is gradually applied on the surface of the coated specimen in a time frame of about 20 seconds.

3.1. Discussion on micro-hardness

Fig. 2 portrays the disparity in the micro-harness valuesф against three different combinations of MWCNT reinforcement. The ratio of proportion is maintained in such a fashion varied from 1:1 to 1:2. Interestingly, it may be noted that a that the rate of change proportion of MWCNT with all the nanocomposites exhibits only lesser significance over the magnitudes of microhardness value. This is an interesting physical phenomenon and, it can be concluded that lower or equal proportions of MWCNT reinforcement is enough to acquire the best possible hardness factor in the coated specimen. Though, there are limited variations, the maximum percentage is restricted only to a meagre value of 4%. Hence, higher quantity of deposition may not be required for most of the cases and a uniform blending ratio (1:1) can be maintained as the optimal level. The scheme of bonding of the composite coatings is identical in all blending proportions.

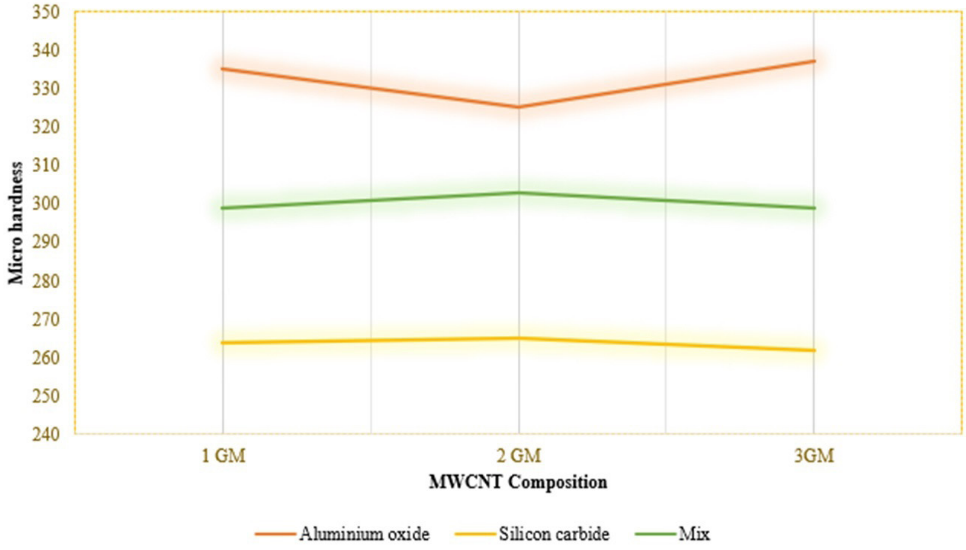

Fig. 2. (Color online) Effect of MWCNT content on microhardness in Al_2O_3-MWCNT solution, SiC-MWCNT solution and Al_2O_3-SiC-MWCNT solution (Mix).

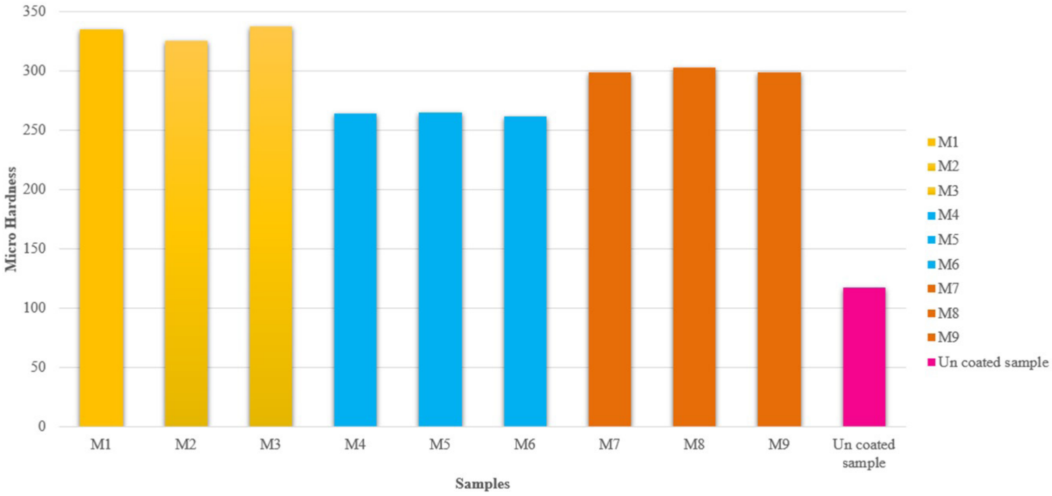

Fig. 3. (Color online) Variation and comparison of microhardness value (M1, M2, M3-Al_2O_3 + MWCNT coatings, M4, M5, M6-SiC + MWCNT coating and M87, M8, M9-Al_2O_3 + SiC + MWCNT).

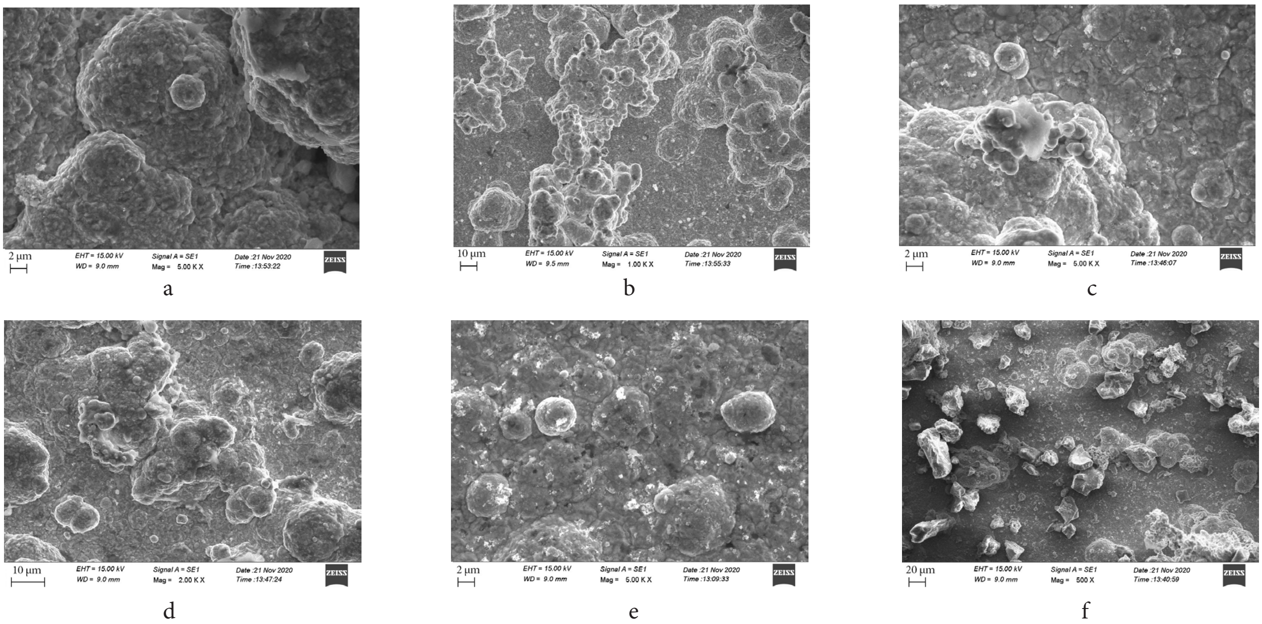

Fig. 4. Microstructure maps of coated samples: Al_2O_3 + MWCNT coating (a), Al_2O_3 + MWCNT coating (b), SiC + MWCNT coating (c), SiC + MWCNT coating (d), Al_2O_3 + SiC + MWCNT coating (mix) (e), Al_2O_3 + SiC + MWCNT coating (mix).

Fig. 3 exhibits the global comparison for all the samples considered in the study along with the uncoated specimen. Al_2O_3 + MWCNT coated samples exhibit a higher rate of micro-hardness than all other combinations. Moreover, Al_2O_3 + Sic + MWCNT coated samples take a reasonable lead when compared with MWCNT + SiC samples. The rate of hardness in the triple mix is diminished due to dominant effect of SiC particles which overrides the significance of Al_2O_3 nanopowders. Also, Al_2O_3 nanopowders seems to be ineffective, and its enhancement effect is partly quashed when its being mixed with SiC particles. Therefore, it is strongly suggested not to mix ductile and soft nanopowders with dominant brittle materials like SiC. From the results, it can be observed that the samples coated with Al_2O_3 nanoparticles reinforced with CNTs possess excellent magnitudes of micro-hardness in comparison with the uncoated and SiC-CNT coated samples with an enhancement factor of 2.88 and 1.37, respectively.

3.2. Surface morphology and analyses of micro-structure

The scanning electron microscopic images of coated and uncoated specimens are clearly illustrated in Fig. 4 for reference. From the SEM images, it can be noted that the nanocomposite coating materials are excellently embedded into the nickel matrix. The nanocomposite powders exhibit a cauliflower shaped crystalline structure in which the MWCNT particles are reinforced. It is essential to assess the dispersion mechanism before performing mechanical testing and therefore, the distribution effect of MWCNTs within the composite matrix has significant effect of the mechanical properties. From Fig. 4 (e and f) it may be noted that, the bonding nature is quite excellent with two different coating materials having diverse characteristics. Hence, relatively higher stability is achieved when compared with SiC coatings (Fig. 4 c, d). Moreover, it may be noted that all the nanocomposites are excellently embedded in the matrix and reinforced well by the MWCNTs.

4. Final outlook and concluding remarks

This research work presents the significant results of Ni-Al_2O_3 and Ni-SiC nanocoatings reinforced with MWCNTs in a mild steel AISI 1018 substrate. Also, the effect of varying the percentage of MWCNT reinforcement is investigated in detail. The micro indentation test is carried out to assess the mechanical performance and microstructure analysis with the aid of SEM analysis. From the results it is evident that, Al_2O_3 coated samples possess excellent tribological characteristics in comparison with SiC and uncoated samples. Moreover, it is evident that the effect of adding the MWCNT composition has less significance and the ratio of 1:1 could be maintained as an optimum level to derive maximum value of microhardness.

Acknowledgements. The Authors would like to express their sincere gratitude to the Management of Sona College of Technology, Salem, Tamil Nadu, India for funding this project work under SEED money scheme. Also, the support from the center for nanomaterials and micro-machining (CNMM), Sona College of Technology is greatly acknowledged.

References

1. M. Ghouse, M. Viswanathan, E.G. Ramachandran. Met. Finish. 78 (8), 57 (1980).
2. M. Ghouse, M. Viswanathan, E.G. Ramachandran. Met. Finish. 78, 44 (1980).
3. M. Ghouse, E.G. Ramachandran. Met. Finish. 79(6), 85 (1981).
4. M.R. Vaezi, S.K. Sadrnezhaad, L. Nikzad. Colloids Surf. A. 315, 176 (2008). Crossref
5. E.A. Pavlatou, M. Stroumbouli, P. Gyftou, N. Spyrellis. J. Appl. Electrochem. 36, 385 (2006). Crossref
6. A.C. Ciubotariu, L. Benea, M. Lakatos-Varsanyi, V. Dragan. Electrochim. Acta. 53, 4557 (2008). Crossref
7. S. Mirzamohammadi, R. Kiarasi, M.K. Aliov, A.R. Sabur, A. Hassanzadeh-Tabrizi. Trans. IMF. 88, 93 (2010). Crossref
8. Z. An, M. Toda, T.Ono. Compos. Part B.Eng. 95, 137 (2016). Crossref
9. S.R. Yu, Y. Liu, W. Li, J.A. Liu, D.S. Yuan. Compos. Part B.Eng. 43, 1070 (2012). Crossref
10. K.H. Hou, Y.C. Chen. Appl. Surf. Sci. 257, 6340 (2011). Crossref
11. H. Goldasteh, S. Rastegari. Surf. Coat. Technol. 259, 393 (2014). Crossref
12. H. Li, Y. He, Y. Fan, W. Xu, Q.B. Yang. RSC Adv. 5, 68890 (2015). Crossref
13. M. Yousefpour, A. Rahimi. Mater. Des. 54, 382 (2014). Crossref
14. H. Cai, F.Y. Yuan, Q.J. Xue. Mater. Sci. Eng., A Struct. Mater. 364, 94 (2004).
15. W.X. Chen, F. Li, G. Han, J.B. Xia, L.Y. Wang, J.P. Tu, Z.D. Xu. Tribol. Lett. 15, 275 (2003). Crossref
16. Z. Yang, B. Dong, Y. Huang, L. Liu, F.Y. Yan, H.L. Li. Mater. Chem. Phys. 94, 109 (2005). Crossref
17. Z. Yang, B. Dong, Y. Huang, L. Liu, F.-Y. Yan, H.-L. Li. Mater. Lett. 59, 2128 (2005). Crossref
18. B. Dong, Z. Yang, Y. Huang, H.-L. Li. Tribol. Lett. 20, 251 (2005). Crossref
19. E.W. Wong, P.E. Sheehan. Science. 277, 1971 (1997). Crossref
20. M.M. J. Treacy, T.W. Ebbesen, J.M. Gibson. Nature. 381, 678 (1996). Crossref
21. J.P. Lu. Phys. Rev. Lett. 79, 1297 (1977).
22. E.W. Wong, P.E. Sheehan, C.M. Lieber. Science. 277 (5334), 1971 (1977). Crossref
23. H.W. Zhu, C.L. Xu, D.H. Wu, B.Q. Wei, R. Vajtai, P.M. Ajayan. Science. 296, 884 (2002). Crossref
24. K.T. Kashyap, R.G. Patil. Bull. Mater. Sci. 31, 185 (2008). Crossref
25. C. Wang, B. Dong, G.Y. Gao, M.W. Xu, H.L. Li. Mater. Sci. Eng. A. 478(1-2), 314 (2008). Crossref
26. N.V. Mandich. Met. Finish. 100, Supplement 1, 359 (2002). Crossref
27. E. Bełtowska-Lehman, A. Goral, P. Indyka. Arch. Metall. Mater. 56, 919 (2011). Crossref
28. S. Sangeetha, G.P. Kalaignan. Ceram. Int. 41, 10415 (2015). Crossref
29. M.S. Chandrasekar, M. Pushpavanam. Electrochim. Acta. 53 (8), 3313 (2008). Crossref
30. J.S. Shathish Kumar, A. Jegan. Mater. Res. Express. 7 (5), 055012 (2020). Crossref
31. A.Y. Galashev, O.R. Rakhmanova, V.A. Kovrov, Y.P. Zaikov. Lett. Mater. 9 (4), 436 (2019). Crossref
32. A.A. Burkov, M.A. Kulik. Lett. Mater. 9 (2), 243 (2019). (in Russian) [А.А. Бурков, М.А. Кулик. Письма о материалах. 9 (2), 243 (2019).] Crossref
33. I.V. Sapegina, O.Y. Goncharov, V.I. Lad'yanov, L.H. Baldaev. Lett. Mater. 9 (1), 22 (2019). (in Russain) [И.В. Сапегина, О.Ю. Гончаров, В.И. Ладьянов, Л.Х. Балдаев. Письма о материалах. 9 (1), 22 (2019).] Crossref
34. J.P. Savina, B.V. Raghavendra, D. Rangappa. Lett. Mater. 11 (1) , 73 (2021). Crossref