

PROPERTIES OF THE COATING DEPOSITED WITH THE DIFFUSION OF MO&O₂ OXIDIZED POWDER USING THE APS PROCESS

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Summary:

Powder Mo&O₂ has an important role in the production of coatings with increased resistance to slide in conditions without the use of lubricants. Mo&O₂ coatings have the low coefficient of friction and good abrasion characteristics in mechanical stresses. For the purpose of producing coatings of high hardness, Mo&O₂ powder is plasma deposited with optimal parameters. The surface shape of oxide powder particles and the coating fracture surface are analysed by SEM, and the microstructure of layers is examined by light microscopy. The coating microstructure consists of Mo lamellae and MoO₃ and MoO₂ primary oxide thin films, which surround the Mo lamellae. The analysis of the obtained results showed that the Mo&O₂ coating layers with the diffusion oxidized Mo particles have such a structure and mechanical characteristics which enable its application in working tools under the conditions of wear and sliding friction without lubricants.

Keywords: particles, friction, deposits, property, powders, oxidizers, microstructures, lubrication, coatings.

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Introduction

The MoO₂ coating resistance to wear depends on the oxygen content and the applied kind of technological process of coating production (Mrdak, et al, 2005, pp.235-239), (Salhi, et al, 2005, pp.145–150). Molybdenum powders containing oxygen MoO₂ can attain high hardness values. The content of oxygen in the plasma spray coating essentially depends on the applied gases and applied power devices. After the production of MoO₂ coatings, the layers have sufficient concentration of oxygen which gives to oxides high hardness the values of which exceed 1000HV. Thus deposited coatings can increase fatigue strength to friction up to 120% in working tool surfaces, thus preventing loss of the material by friction. The friction that always occurs between two movable contact surfaces causes damage such as friction wear and friction fatigue. There are many research papers relating to the mechanisms of friction wear and friction fatigue. Modes of friction are standardized and used to study the behavior of different materials regarding the mechanism of friction wear (Vencl, et al, 2011, pp.1281-1288), (Mrdak, 2016a, pp.411-430), (Mrdak, 2016b, pp.949-965). By microscopic examinations, the authors (Chen, et al, 2007, pp.2132-2138), (Yongqing, et al, 2000, pp.231-245) found that Mo lamellae and MoO₂ and MoO₃ primary oxides from powder are present in the MoO₂ coating. Oxides are present in the form of thin films that surround Mo lamellae. The MoO₂ oxide phase increases hardness but also brittleness which negatively affects the cohesive strength of lamellae (Modi, Calla, 2001, pp.480-486). The best structure is found in coatings where oxide films are continuously arranged along the coating and act as a lubricant while preventing metal contact and maintain a low coefficient of friction. The crystal structure of MoO₂ is monoclinic while α-MoO₃ and β-MoO₃ oxides are of orthorhombic and monoclinic structures (Jullien, et al, 1995, p.235). Tests of the MoO₂ coating to wear determined that MoO₂ oxide in the coating reduces the coefficient of friction under 0:15, and MoO₃ oxide to the values in the range of 0.1 to 0.12 which is quite stable (Lyo, et al, 2003, pp.413-421), (Solak, et al, 2003, pp.713-719), (Suszko, et al, 2005, pp.319-324).

The aim of the study was to use atmospheric plasma for depositing MoO₂ powder particles which will form hard slide-resistant coating layers. The paper analyzes the mechanical properties of micro hardness

and the tensile bond strength as well as the microstructure on a light microscope and the morphology of powder particles and the coating fracture surface on the SEM. The analyses of the layers confirm the good mechanical and structural characteristics of Mo&O₂ coatings, which make them reliable in conditions of sliding friction without lubrication.

Materials and experimental details

The Mo&O₂ powder used in the experiment had an oxygen content of 3% made by the Amperite program arising from the HCST production. Figure 1 (SEM) shows the powder particles of sharp and rounded edges, with a range of grains of 5 - 45 μm.

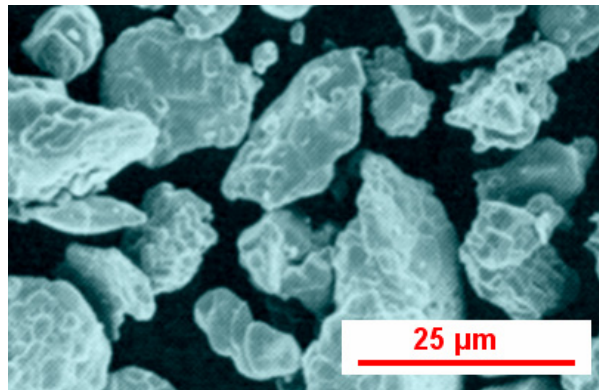


Figure 1 – (SEM) surface shape of Mo&O₂ powder particles
 Рис. 1 – (SEM) Изображение поверхности частиц порошка Mo&O₂
 Слика 1 – (SEM) Облик површине честица праха Mo&O₂

The substrate for deposited coatings was made of steel (X15Cr13 EN10027) according to the standard (Turbojet Engine, 2002). Microhardness was tested using the method of HV_{0.3} with five reading values at the left end of the sample (A) in the middle (B) and at the right end (C) of the sample. The paper presents min. and max. HV_{0.3} values. The bond strength testing was done on five samples by tensile testing at room temperature, and the average values are shown in the paper. The shape of the surface of powder particles and the coating fracture surface were analyzed by SEM. The microstructures of coating layers were analyzed with light microscope and the quantitative analysis of the average pore content in layers was carried out.

Mo&O₂ powder was deposited at atmospheric pressure by a SG-100 plasma gun with the use of a mixture of Ar and He gases and power

up to 40kW. The Mo&O₂ powder disposition parameters are shown in Table 1. The coating was deposited in a thickness from 0.45 to 0.48 mm.

Table 1 – Powder deposition parameters
Таблица 1 – Параметри напыления порошка
Табела 1 – Параметри депозиције праха

Deposition parameters	Values
Plasma current, I (A)	600
Plasma Voltage, U (V)	31
Primary plasma gas flow rate, Ar (l/min)	48
Secondary plasma gas flow rate, He (l/min)	12
Carrier gas flow rate, Ar (l/min)	4.5
Powder feed rate (g/min)	35
Stand-off distance (mm)	100

Results and discussion

Figure 2 shows the values of the Mo&O₂ coating microhardness. At the left end of the sample, the coating microhardness was in the range of 968 - 1260HV_{0.3}, with the average value of 1114HV_{0.3}, the point (A). In the middle of the sample, microhardness is in the range of 972 - 1334 HV_{0.3} with an average value of 1153HV_{0.3}, the point (B). At the point (C) which was located at the right end of the sample, microhardness covers the range of 934-1310 HV_{0.3} with an average value of 1122HV_{0.3}.

The microhardness values were consistent with the oxygen content in the powder and with the primary oxide content in the coating. The microhardness values are quite high in comparison to conventional Mo coatings. Since oxides are present in the coating, the coating microhardness mean values are fairly uniform at all measuring points. This is the first indication that the oxide distribution in the coating layers is uniform (homogeneous). The coating had a mean value of the adhesion strength of 38MPa with a fracture mechanism at the substrate / coating interface.

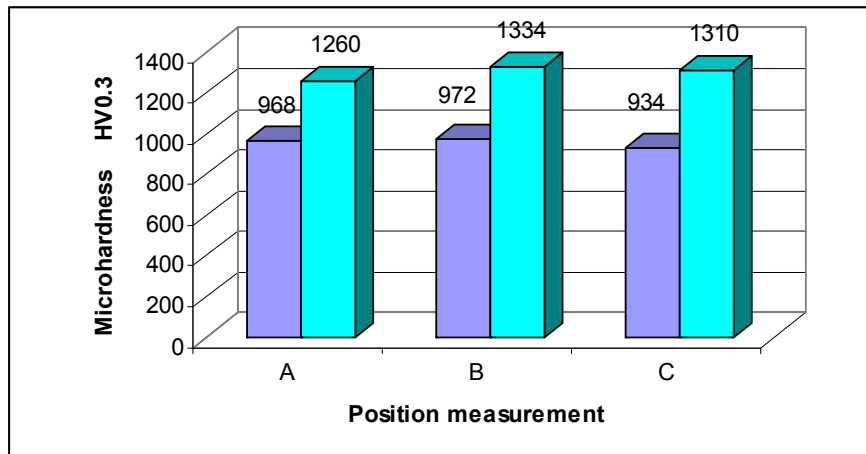


Figure 2 – The microhardness of the Mo&O₂ coating, the measurement positions
 Рус. 2 – Микротвердость покрытия Mo&O₂ в точках измерения
 Слика 2 – Микротврдоће превлаке Mo&O₂ на позицијама мерења

Figure 3 shows the microstructure of the plasma spray Mo&O₂ coating recorded on a light microscope. At the substrate / coating interface, there are not any abnormalities that would reduce the impact on the coating adhesion strength. Light Mo lamellae are seen and between them dark and thin films of primary oxides are precipitated. At the inter-lamellar boundaries, there are black micro pores smaller than 10µm with a medium content in the coating of up to 3%.

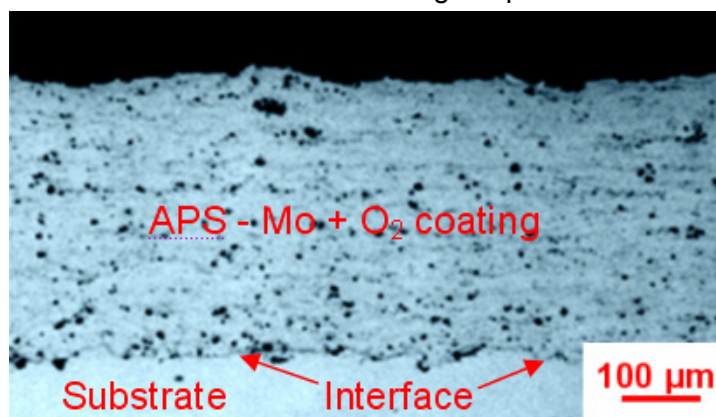


Figure 3 – Microstructure of Mo&O₂ coatings
 Рус. 3 – Микроструктура Mo&O₂ покрытия
 Слика 3 – Микроструктура превлаке Mo&O₂

Figure 4 shows the microstructure of Mo&O₂ coatings at a higher magnification for the purpose of analysing the microstructure more clearly. The structure is the same as in Figure 3, except that dark oxide films can be more clearly noticed and that there are precipitates in the structure as a product of collisions of drops of molten powder particles with the substrate. There are neither cracks nor unmolten particles which could reduce the cohesive strength and coating resistance to friction fatigue. The coating primary phase is Mo with a centered cubic lattice in which are present the phases of MoO₂ oxide with the monoclinic lattice and MoO₃ oxide with the orthorhombic and monoclinic lattice (Chen, et al, 2007, pp.2132-2138), (Yongqing, et al, 2000, pp.231-245).

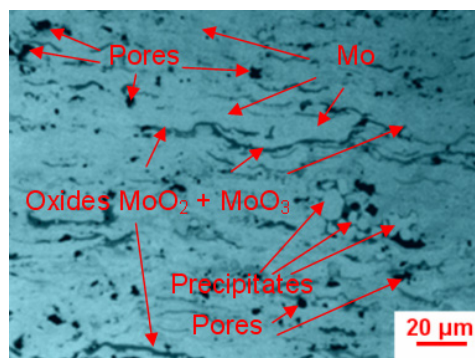


Figure 4 – Microstructure of Mo&O₂ coatings
 Рис. 4 – Микроструктура Mo&O₂ покрытия
 Слика 4 – Микроструктура Mo&O₂ преваке

Figure 5 shows the Mo&O₂ coating surface recorded by electron microscope (SEM).

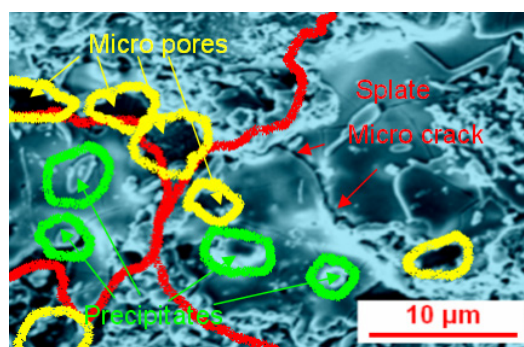


Figure 5 – (SEM) Surface of the Mo&O₂ coating
 Рис. 5 – (SEM) поверхность Mo&O₂ покрытия
 Слика 5 – (SEM) површина Mo&O₂ преваке

On the surface it is possible to see two flattened disc-shaped particles, created by the collision of drops of molten powder particles with the substrate and by their subsequent cooling to the surface temperature. These discs are separated by red lines. This kind of deformation of liquid droplets in a collision with the substrate and solidification is an indicator of good inter-lamellar cohesive strength. On the formed discs, there are visibly noticeable micro cracks caused by the solidification of liquid drops. They cannot gather since the substrate was exposed to spreading due to the increase in temperature caused by the amount of heat carried liquid drops and transferred to the substrate. At the interface between the discs (lamellae), there are black micro-pores of less than $10\mu\text{m}$ in diameter. Micro pores of irregular shapes are highlighted in yellow. Fine deposits on the surface of the discs and the discs boundaries are marked in green.

Figure 6 shows the surface of an Mo & O₂ coating fracture recorded on the SEM. Thin lamellae with clearly distinguished interfaces can be seen on the coating fracture. The morphologies of micro pores and precipitates are also clearly visible.

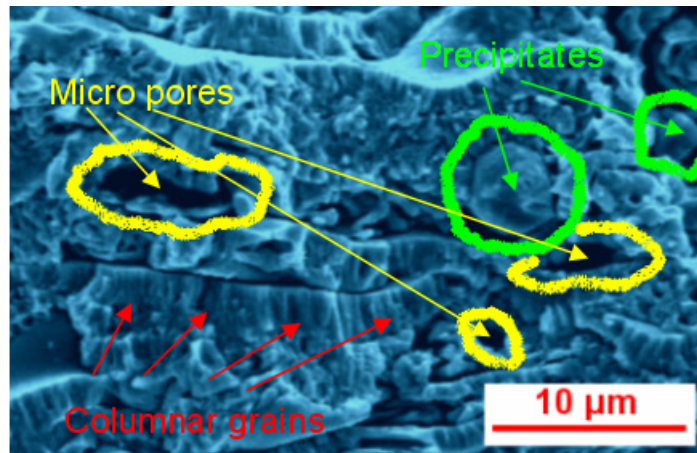


Figure 6 – SEM fracture of the Mo&O₂ coating surface
 Рис. 6 – (SEM) Поврежденная поверхность покрытия Mo&O₂
 Слика 6 – (SEM) површина лома превлаке Mo&O₂

The initial micro cracks occur in places with the highest stress. These places are interlamellar pores and interlamellar boundaries. Under the action of fracture forces on the substrate surface, initial micro cracks spread rapidly into macro cracks propagating vertically from the substrate surface through lamellae and micro pores up to the coating surface. The fracture shows clearly Mo lamellae with columnar grains

directed normally to the metal substrate. Columnar metal grains originate from and are formed on the surfaces of the previously deposited drops of melted particles cooled to the temperature of the substrate with deposited layers (Vardelle, et al, 1994, pp.50–58). The fracture image shows precipitates and micro pores smaller than 10 μm . The coating fracture is brittle due to present oxides.

Conclusion

The paper presents the results of the analysis of the atmospheric plasma spray deposited Mo&O₂ coating with a thickness from 0.45 to 0.48 mm. Based on the analysis of the layers, the following conclusions have been derived.

The Mo&O₂ coating had a high average value of microhardness 1114 to 1153HV_{0.3} and the adhesive bond strength of 38MPa due to the presence of oxide phases in the structure. The tensile testing showed the adhesive fracture mechanism.

The structure of the Mo&O₂ coating is lamellar, consisting of Mo lamellae and thin films of MoO₂ and MoO₃ primary oxides between the Mo lamellae. Among the Mo lamellae, there are micro pores of irregular shape up to 3%, and precipitates of less than 10 μm in size.

With its mechanical and structural characteristics, the Mo&O₂ coating can significantly increase the resistance of working surfaces exposed to dry sliding friction, which is what they are intended for.

References

Chen, D., Jordan, E., & Gell, M., 2007. Effect of solution concentration on splat formation and coating microstructure using the solution precursor plasma spray process. *Surface & Coatings Technology*, 202, pp.2132-2138. Available at: <http://dx.doi.org/10.1016/j.surfcoat.2007.08.077>.

Jullien, C., Khelifa, A., Hussain, O.M. and Nazri, G.A., 1995. Synthesis and characterization of flash-evaporated MoO₃ thin films. *Journal of Crystal Growth*, 156(3), p.235. Available at: [http://dx.doi.org/10.1016/0022-0248\(95\)00269-3](http://dx.doi.org/10.1016/0022-0248(95)00269-3).

Lyo, I.W., Ahn, H.S., Lim, D.S., 2003. Microstructure and tribological properties of plasmasprayed chromium oxide-molybdenum oxide composite coatings. *Surface & Coatings Technology* 163, pp.413-421. Available at: [http://dx.doi.org/10.1016/S0257-8972\(02\)00613-8](http://dx.doi.org/10.1016/S0257-8972(02)00613-8).

Modi, S.C., Calla, E., 2001. A study of high-velocity combustion wire molybdenum coatings. *Journal of Thermal spray technology*, 2001, 10(3), pp. 480-486. Available at: <http://dx.doi.org/10.1361/105996301770349259>.

Mrdak, M., Kakaš, D., Pović, Đ., 2005. *Characterisation of APS-Mo wear resistant coatings*, pp.235-239. In: BALKANTRIB '05, 5th International conference on tribology, Serbia, Kragujevac, 15-18.

Mrdak, M., 2016a. *Properties of the ZrO₂MgO/MgZrO₃NiCr/NiCr triple-layer thermal barrier coating deposited by the atmospheric plasma spray process*. *Vojnotehnički glasnik / Military Technical Courier*, 64(2), pp.411-430. Available at: <http://dx.doi.org/10.5937/vojtehg64-9612>.

Mrdak, M.R., 2016b. *Characterization of Cu10wt.%Al intermetallic coatings applied by the atmospheric plasma spraying process*. *Vojnotehnički glasnik / Military Technical Courier*, 64(4), pp. 949-965. Available at: <http://dx.doi.org/10.5937/vojtehg64-10688>.

Salhi, Z., Klein, D., Gougeon, P., Coddet, C., 2005. Development of coating by thermal plasma spraying under very low-pressure condition <1 mbar. *Vacuum*, 77(2), pp.145-150. Available at: <http://dx.doi.org/10.1016/j.vacuum.2004.08.013>.

Solak, N., Ustel, F., Urgan, M., Aydin, S., Cakir, A.F., 2003. Oxidation behavior of molybdenum nitride coatings, *Surface & Coatings Technology* 174, pp.713-719. Available at: [http://dx.doi.org/10.1016/S0257-8972\(03\)00702-3](http://dx.doi.org/10.1016/S0257-8972(03)00702-3).

Suszko, T., Gulbinski, W., Jagielski, J., 2005. The role of surface oxidation in friction processes on molybdenum nitride thin films. *Surface & Coatings Technology*, 194(2-3), pp.319-324. Available at: <http://dx.doi.org/10.1016/j.surfcoat.2004.07.119>.

Turbojet Engine – Standard Practices Manual PN 582005, 2002. Pratt & Whitney, East Hartford, USA.

Vardelle, M., Vardelle, A. and Leger, A.C., 1994. Influence of particle parameters at impact on splat formation and solidification in plasma spraying processes. *Journal Thermal Spray Technology*, 4, pp.50-58. Available at: <http://dx.doi.org/10.1007/BF02648528>.

Vencl, A., Arostegui, S., Favaro, G., Zivic, F., Mrdak, M., Mitrović, S., Popovic, V., 2011. *Evaluation of adhesion/cohesion bond strength of the thick plasma spray coatings by scratch testing on coatings cross-sections*. *Tribology International*, 44(11), pp.1281-1288. Available at: <http://dx.doi.org/10.1016/j.triboint.2011.04.002>.

Yongqing, F., Jun, W., Andrew, W., 2000. Some considerations on the mitigation of fretting damage by the application of surface-modification technologies. *Journal of Materials Processing Technology*, 99(1-3), pp.231-245. Available at: [http://dx.doi.org/10.1016/S0924-0136\(99\)00429-X](http://dx.doi.org/10.1016/S0924-0136(99)00429-X).

СВОЙСТВА ПОКРЫТИЯ, НАНЕСЕННОГО ДИФфуЗИОННЫМ ОКСИДНЫМ ПОРОШКОМ Mo&O₂ МЕТОДОМ APS

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ВИД СТАТЬИ: оригинальная научная статья

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Резюме:

Применение порошка Mo&O₂ играет важную роль в процессе нанесения покрытия с повышенной устойчивостью к скольжению в бесшмазочных условиях. Покрытия Mo&O₂ обладают низким коэффициентом трения и высоким пределом прочности при механическом напряжении. В целях достижения наибольшей прочности покрытия, порошок Mo&O₂ наносится методом плазменного напыления, с учетом оптимальных параметров. Характеристики состояния поверхности частиц оксидного порошка и поверхности излома покрытия установлены SEM методом. А микроструктура слоев нанесенного покрытия испытана методом световой микроскопии. Микроструктура покрытия состоит из ламелей Mo и тонких оксидных прослоек MoO₂ и MoO₃ вокруг ламелей Mo. Анализ полученных результатов доказал, что слои покрытия Mo&O₂ с диффузионными оксидными частицами Mo обладают структурой и механическими характеристиками, позволяющими нанесение данного покрытия на поверхности рабочих участков в условиях износа и скольжения при бесшмазочном трении.

Ключевые слова: частицы, трение, нанесение, свойства, порошок, оксидаторы, микроструктуры, смазка, покрытие.

СВОЙСТВА ПРЕВЛАКЕ ДЕПОНОВАНЕ ДИФфуЗИОНО ОКСИДИРАНИМ ПРАХОМ Mo&O₂ ПРИМЕНОМ APS ПРОЦЕСА

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ВРСТА ЧЛАНКА: оригинални научни чланак

ЈЕЗИК ЧЛАНКА: енглески

Сажетак:

Прах Mo&O₂ има значајну улогу у производњи превлака са повишеном отпорношћу на клизање у условима без примене

мазива. Превлаке MoO_2 имају мали коефицијент фрикције и добре карактеристике на хабање при механичким напрезањима. Ради производње превлака високе тврдоће, прах MoO_2 је депонован плазмом са оптималним параметрима. Карактеризација облика површине честица оксидног праха и површине прелома превлаке изведена је методом SEM, а микроструктура слојева применом светлосне микроскопије. Микроструктура превлаке састоји се од ламела Mo и танких филмова примарних оксида MoO_2 и MoO_3 које окружују ламеле Mo . Анализа добијених резултата показала је да слојеви превлаке MoO_2 са дифузионо оксидираним честицама Mo имају структуру и механичке карактеристике које омогућују њену примену на површинама радних делова у условима хабања и клизања трењем без мазива.

Кључне речи: честице, трење, депозити, својства, прах, оксидатори, микроструктуре, подмазивање, превлаке.

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