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TRENDS IN FRICTION AND WEAR BEHAVIOR OF DETONATION AMORPHOUS-CRYSTALLINE Mg-Ti-Si-C COATINGS

The experimental findings in studying wear and the pattern of its relation with sliding velocity when testing coatings with no lubrication have been presented. The amorphous-crystalline composition having high mechanic properties have been found to exhibit considerable wear resistance and to be as good as that of wolfram-based hard alloys of VK15 type, and may be regarded as a promising competitive material in creating tribo-resistant coatings.

The changes in the mechanic properties of the coatings have been investigated according to the quantity of the constituents and their optimal content determined.

The element distributions through the sprayed layer thickness have been studied. The divergences detected in the chemical composition confirm the presence of an unbalanced disperse structure, which is in line with the current concept about the behaviour of amorphous and amorphous-crystalline composites. An amorphous phase amount in the coating is as much as 79%. In addition to the amorphous phase, the coatings are composed of phases localized in some portions of an amorphous matrix, which are characterized by a microcrystalline structure. Their X-ray photographs depict some lines pertaining to an α-Mg lattice,

moreover, in the amorphous matrix are distinguishable some areas full of carbon represented by the ultra-fine inclusions of Mg_2C_3, TiC phases. The $TiSi_2$, TiSi metallide nano-phase structures coherently associated with the matrix have been identified.

The coating surface electron diffraction patterns taken in the initial stage and under friction loading have been analyzed. The formation of the amorphous structure with the increase of sliding velocity have been found to be due to the progressive dissolution of local microcrystalline inclusions, a complete microdifraction pattern being formed by only the amorphous matrix. In friction this is an amorphous layer that aids in decreasing an adhesive component of friction force, and its plastic deformation here does not draw much heat consumption thus contributing to minimize energy losses. The metallographic analysis and strip chart recording of frictional surfaces indicate the absence of noticeable damages to surface layers and confirm that the primary type of wear is mechanical-chemical over the entire range of tests. [dx.doi.org/10.29010/084.4]

Key words: *tribostability; wear intensity; amorphous-crystalline materials; detonation-gaseous spraying.*

Introduction

The achievements in developing new materials to a great extent determine the modern strategy of scientific-technical progress. The development and creation of amorphized structural materials and coatings is nowadays one of the dynamically evolving technologies accompanied by a growing industrial and commercial interest. Being able to produce them with qualitatively and quantatively new operational characteristics makes it possible to persue a fundamentally new level of amorphous-crystalline material properties. The advancements in this area for application purposes are conducive to motivate cognitive activity in studying new logically ranked trends of their structure formation as an objective form in acquiring adequate knowledge for creation of advanced structure material and coatings with amorphous-crystalline structure.

The permanently evolving gas-thermal spraying technology remains to be one of the current approaches to produce the amorphous-crystalline material [1]. The tribotechnical testing of the amorphous coatings of a close phase composition attained by different gas-thermal techniques has shown that the gas detonation sprayed coatings possess the highest wear resistance [2]. In the article [3] are given experimentally derived processing parameters enabling the obtainment of amorphized coatings, emphasis being placed on that the gas detonation spraying not only creates the optimal conditions for formation of near-eutectic compositions in metastable state but affords a number of benefits compared with conventional methods of high-speed cooling.

Problem Formulation

The article aims to summarize the results of the experimental studies on wear resistance of the developed amorphous-crystalline coatings sprayed by the gas-detonation technique using the composite powders based on Mg doped with Ti, Si and C.

Methods

The procedure to test wear resistance of detonation coatings set forth in the work [4] was applied therein. The coatings were deposited using a modified D-gun “Dniepr 3”. The thickness after development testing was measured to be 0,15-0,20 mm at a Ra = 0,63-0,32 roughness. The detonation coatings deposited with a VK15 type wolfram-contained powder and another based on nickel alloyed by chromium, aluminium and boron were investigated to compare with the similar efforts. The wear testing was conducted with a friction apparatus UMT-2 using annular samples made of thermally treated steel 45 (Dxd = 25x17,5) under 8,0 MPa loading in a distributed contact ($К_{вз} \approx 1$) context and a sliding velocity up to 1,5 m/s.

The validity of interrelation between a structure and coating properties to check their quality heavily depends on the selection of research methods and methodology to be applied. A radiography-phase analysis of the coatings was performed with a “Dron-UM1” diffractometer (Co-radiation, voltage 25 кV, current 15 mA). The activation processes in the surface layer were tested using focused electron probe microscopy using a “Camscan” (accelerating voltage 25 кV, beam current 200 mA). The ZAF-L/FLS program was applied for a chemical analysis of the surface structures and the localization areas of their components, as well as the electron diffraction technique to study the state of friction surface. The electron microscope testing was accomplished using an electron microscope JEM-200CX, while the metallographic examination, with a microscope MIM-8 and a microhardnessmeter PMT-3 (0,5H load).

Results and Discussion

The behavior of the developed coating as to their wear resistance was studied using laboratory equipment which had been updated with the view of approaching as much as possible the processes of the physical-chemical mechanics of friction and wear to

Table 1

Mechanical properties of Mg-Ti-Si-C coatings

Component content, %				*E*, H/mm	σ_T, H/mm^2	*m*	HV, MPa
Mg	Ti	Si	C				
74	13	10	3	178800	4140	2,20	1310
68	15	12	5	185300	4540	2,28	1590
63	18	12	7	197200	4890	3,22	1710

the real ones. It should be noted that the components of the coating have a congruent melting and a narrow area of homogeneity. Their advantage lies in that no critical and costly components are involved y they may be found over the Ukraine resource-raw material region [5].

The testing data relating to the physical-mechanical properties of the detonation coatings based on magnium are given in Table 1.

The analysis of the above data shows that the content variation of the coating components causes the change in the physical-mechanical properties of the surface area, and the optimal components content corresponding to the peak values of the surface strength characteristics in friction is (mass %) Mg ~63%, Ti ~18%, Si ~12%, C ~7.

Here, the yield point values (σ_T) estimated for the coatings under testing, Young modulus (*E*) and degrees of strain hardening (*m*) surpass the limiting values for amorphous alloys ($E = 180000$ H/mm^2 and $m = 2{,}5$) [6], which indicate the presence of nanocrystalline phases in the material structure.

The testing data indicating the functional relation between coating wear intensity and velocity and sliding are shown in Table 1.

In studying (Fig. 1) behavior and regularity of structure changes that are responsible for the wear resistence of Mg-Ti-Si-C system coatings (curve *3*), the elements distribution through the thickness of a sprayed layer was examined. The analysis was done with a 2 and 10 μm probe diameter. The results obtained by direct methods revealed a diffused zone of 25 μm available and a section variable concentration of the elements being part of the coating. Here, the comparison of impressions taken by absorbed electrons and X-rays did not allow to unambiguously identify the obtained nanocomposite structure that is characterized by a local inhomogeneity of the chemical elements distribution in depth of the surface layer. The discrepancies in the chemical composition confirm the presence of a nonequilibrium finely dispersed structure, which is in line with the current conception about the nature of amorphous and amorphous-crystalline composites. The amount of amorphous phase in the coating is as much as 79%.

From the X-ray analysis it appears that the coatings composition is different from that of the sprayed powder due to the structural and phase conversion when the components are co-operating under conditions of ultrarapid cooling. While identifying the coating microstructure, a conventional etching agent involving a mixture of nitric and hydrofluoric acid was applied. The coating material has a structure with no grains to eliminate imperfections of crystalline structure (grain boundaries, dislocations, packing defects), however there are inadequate local areas characterized by microcrystalline structure. The X-ray pictures exhibit some lines corresponding to a α-Mg lattice, furthermore, in the amorphous matrix are observable the zones with averaged values up to 0,5-1,5 μm which represent the finely dispersed inclusions of Mg_2C_3, TiC type phases.

Also the presence of the prismatic metallide nanophase structures of $TiSi_2$ type coherently bonded with the matrix has been established.

In the opinion of authors, the presence of the ultracrystalline structure inclusions is due to both the boundary values of cooling rates or to their follow-up formation from amorphous phase as a

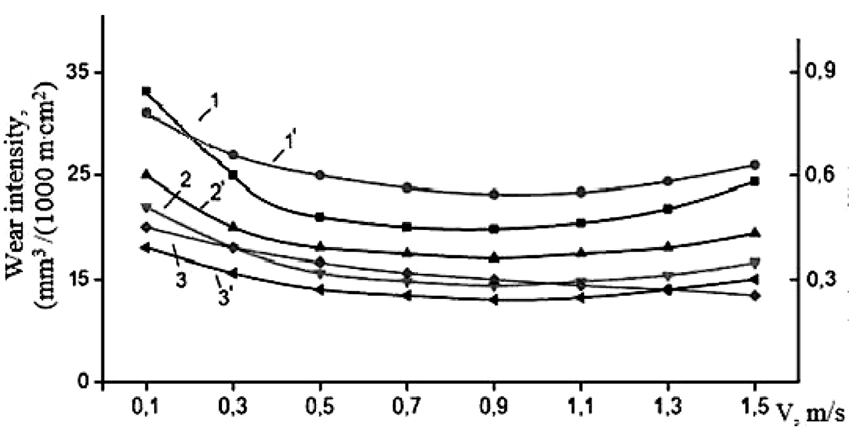
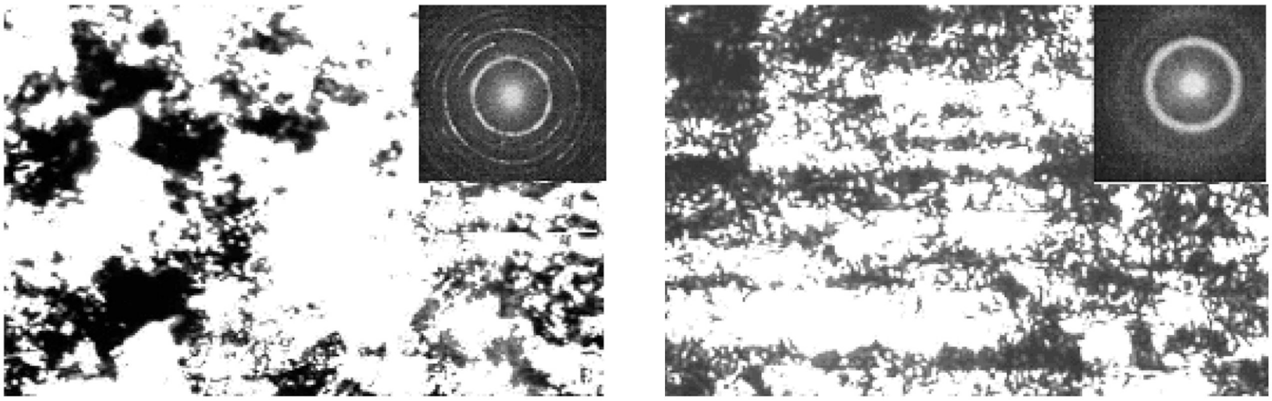


Fig. 1. Dependence of wear intensity (*1*, *2*, *3*) and a coefficient of friction (*1'*, *2'*, *3'*) on the coatings:
sliding velocity: *1*, *1'* – based on Ni (Ni-Cr-Si-B); *2*, *2'* – of VK15 type; *3*, *3'* – of Mg-Ti-Si-C amorphous-crystalline system



a) *б)*

Fig. 2. Electronic photomicrographs of Mg-Ti-Si-C coating surfaces:
a – initial state (x100000); *b* – after testing V = 1,4 м/с (x100000)

result of a local gas flow thermal shock, and to the sprayed detonation spot of the molten particles.

Figure 2 presents the electron-microscopic analysis evidence of the surface layer, which have been obtained by the thin foils method for clearance. It is observable that the friction loading at a sliding velocity up to 1,3 m/s leads to a noticeable change in the structure state of a near-surface layer characterized by the formation of inhomogeneity of about 25-45 nm (Fig. 2*b*).

The comparison of the micro electron diffraction patterns taken both from an initial structure and the surface layer upon friction indicates the presence in the first case of appreciably less width of the first halo (Fig. 2*a*). The behavior of the diffraction picture because of friction is evidence of acquiring mostly amorphous state in the coatings under study.

The gradual dissolution of the local micro crystalline inclusions with the rise of temperature seems to take place, and this is only the amorphous matrix that forms a complete microdiffractional model. Energetically, the transformation involved may be regarded as an adequate mechanism for the self-organization and self-regulation of the processes of destruction and regeneration of the surface structures in the process of adaptability. It is authors' opinion that in these conditions the friction factor value is not only the function of normal loading, but the function of tribophysical processes resulting from the additive combination of load, sliding velocity, temperature, and generalized vector of friction parameters (material, environment, conditions and so forth).

Thus, the surface layer is conducive to diminishing the adhesive component of the frictional force, and its plastic deformation here does not involve much heat consumption and makes for minimizing expenditure of energy. The behavior of the friction factor versus the testing speed is in close agreement with the specific wearing pattern determined by the surface structure properties while its stability is the evidence of a high coatings performance.

Figure 3 shows a portion of the coating surface with a digital map of chemical compound distribution.

The frictional surfaces of the coatings tested at sliding velocities of 0,5 m/s and 1,3 m/s respectively are apparent in Fig. 4. The working coatings surfaces are remarkable by a developed submicrorelief with no cracks and scuffing's, which is characteristic of theoretically inevitable and practically conceivable mechanochemical wear.

The profilograms of frictional surfaces with increase in sliding velocity bear witness to the change of the surface microrelief in forming equilibrium roughness compared to the initial one which is indicated by diminishing of Ra values that are 0,08-0,10 in this range. In this manner, a stationary wear process is characterized by equilibrium roughness.

The submicrorelief variables were qualitatively taken by electronic fractography, it could be noted that as the sliding velocity increases there occurs smoothing of the working surface which is basically due to the elimination of asperities and aids in forming continuous surface structures films.

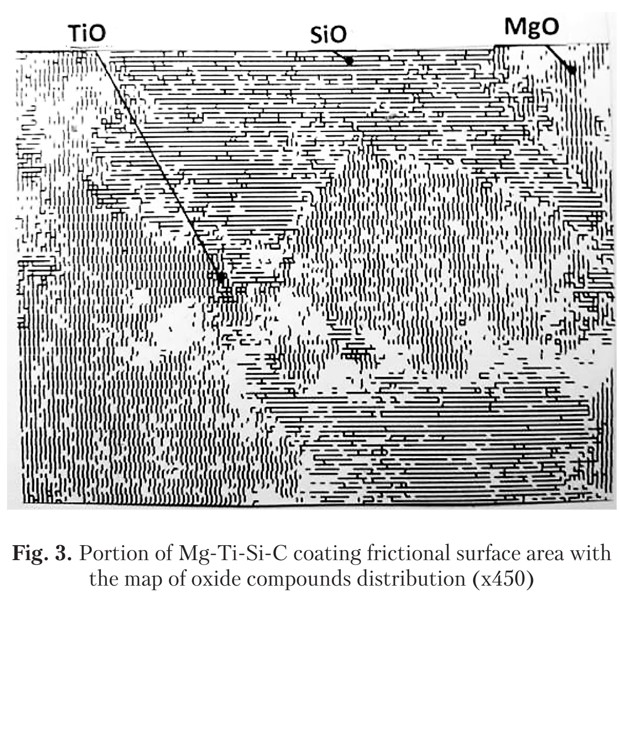
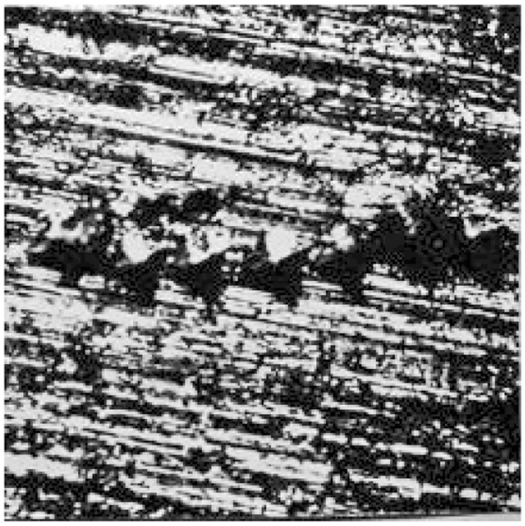
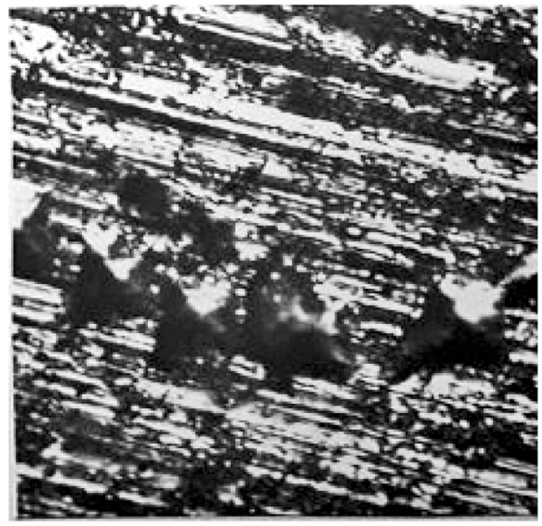


Fig. 3. Portion of Mg-Ti-Si-C coating frictional surface area with the map of oxide compounds distribution (x450)



а)



б)

Fig. 4. Frictional surfaces of Mg-Ti-Si-C coating tested at:
a – *V* = 0,5 m/s; *b* – *V* = 1,3 m/s (x240)

According to the micro X-ray spectroscopic analysis the supra-surface layer of the coating is composed of both single oxides of MgO, TiO_2, SiO_2 type and the complex ones of Mg_2SiO_4, $TiSiO_3$.

The wear resistance of amorphous coatings (Fig. 1, curve *3*) within practically the entire range approaches the values commensurate with those of the resistance wear of the VK15 coating (Fig. 1, curve *2*). High wear resistance, in authors' opinion, is due to the passivation on account of the properties of both the oxide structures formed and the physical-mechanical characteristics of the surface layer.

In compliance with the structure-energy principles of friction the surface film developed due to structure adaptability, represents an oriented metastable structure characterized by clearly manifesting high plasticity and strength within wide and stable structure-time range. With the foregoing as background, it can be claimed that if the surface coating structure may adapt under given frictional conditions thus blocking an adhesion interaction, it is certainly bound to occur or, to be more exact, if there exist any microsurface structures distribution suitable to the adaptability state, the system will adapt and the friction profiles will be minimal.

Conclusions

Thus, upon the analysis of the observations relating to the coatings whose structure contains the amorphous and crystalline phases, it may be asserted that the amorphous and crystalline composition with an optimal combination of its constituents exhibits high surface strength, wear resistance, and satisfactory working capacity in the entire test range.

In closing, it should be noted that the further testing of the amorphous and crystalline coatings developed on the basis of domestic raw materials are aimed at the thorough study of their strength and antifriction properties, at the feasibility to apply the coatings under extreme friction conditions for the solution of the theoretical and engineering problems as to the identification of their technological and economic restrictions as well as the implementation of their performance properties in finished products.

References

[1] Babak, V. P. Wear resistance of amorphous-crystalline detonation coatings with solid lubricant additive in vacuum / V. P. Babak, V. V. Shchepetov, E. A. Astahov, S. D. Nedaiborshch // Journal of Friction and Wear. – 2017. – Vol. 38., Issues 1. – P. 32-40.

[2] Cavaleiro A., Hosson Jeff T. de (Eds.). Nanostructured Coatings. Series: Nanostructure Science and Technology 1st Edition. – 2006. – 648 p.

[3] Kamata, S.Y. Ultrahigh-temperature tensile creep of TiC-reinforced Mo-Si-B-based alloy / Shiho Yamamoto Kamata, Daiki Kanekon, Yuanyuan Lu, Nobuaki Sekido, Kouichi Maruyama, Gunther Eggeler & Kyosuke Yoshimi // Scientific Reports – 2018. – P. 2-13.

[4] Popov, V.L. Mechanics of Contact Interaction and Physics of Friction. From nanotribology to earthquake dynamics – M.: FIZMATLIT, 2013. – 352 p.

[5] Patent 114047 Ukraine, Wear-resistant amorphous-crystalline material / Babak V.P., Shchepetov V.V., Mirnenko V.I., Yakovleva M.S.; Applicant and patent holder Institute of Engineering Thermophysics of the National Academy of Sciences of Ukraine. – published Apr 10, 2017, Bull. No. 7

[6] Pinchuk V.G., Korotkevich S.V. Kinetics of hardening and destruction of the surface layer of metals under friction. – Saarbrucken: LAP. – 2012. – 188 p.

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ТРЕНДЫ ПОВЕДЕНИЯ ТРЕНИЯ И ИЗНОСА ДЕТОНАЦИОННЫХ АМОРФНО-КРИСТАЛЛИЧЕСКИХ Mg-Ti-Si-C ПОКРЫТИЙ

Представленные экспериментальные результаты исследования износа и его закономерности от скорости скольжения при испытании покрытий без смазки. Выявлено, что аморфно-кристаллический композит обладает высокими механическими свойствами и износостойкостью, которая не хуже, чем в твердых сплавах на основе вольфрама типа ВК15, и может рассматриваться как перспективный конкурентный материал для создания трибопокрытий.

Изменения механических свойств покрытий были исследованы в зависимости от количества составляющих и их оптимального содержания.

Изучено распределение элементов по толщине напыленного слоя. Расхождения, выявленные в химическом составе, подтверждающих наличие несбалансированной дисперсной структуры, отвечающей современной концепции поведения аморфных и аморфно-кристаллических композитов. Количество аморфной фазы в покрытии составляет 79%. Также аморфные фазы покрытия состоят из фаз, локализованы в некоторых частях аморфной матрицы и характеризуются микрокристаллической структурой. На рентгеновских снимках некоторые линии, относящиеся к решетке -Mg, причем в аморфной матрице выделяются некоторые области, наполненные углеродом, и представлены сверхтонкими включениями фаз Mg_2C_3, TiC. Были идентифицированы металлоидные наноструктуры $TiSi_2$, TiSi, взаимоувязанные с матрицей.

Проанализированы дифрактограммы поверхности покрытия в начальной стадии при нагрузке трением. Установлено, что образование аморфной структуры с увеличением скорости скольжения связано с постепенным растворением локальных микрокристаллических включений, причем полная картина микродифракции формируется только аморфной матрицей. При трении указанный аморфный слой помогает уменьшить адгезионную составляющую силы трения, а его пластическая деформация не дает большого расхода тепла, способствует минимизации потерь энергии. Металлографический анализ и полученные зависимости указывают на отсутствие заметных повреждений поверхностных слоев и подтверждают наличие механохимического износа во всем диапазоне испытаний. [dx.doi.org/10.29010/084.4]

Ключевые слова: *трибостабильность; интенсивность износа; аморфно-кристаллические материалы; детонационно-газовое напыление.*

Литература

[1] Бабак В. П. Износостойкость аморфно-кристаллических детонационных покрытий с твердой смазывающей добавкой в вакууме / В. П. Бабак, В. В. Шепетов, Э. А. Астахов, С. Д. Недайборщ. // Трение и износ. – 2017. – т. 38., № 1. – С. 32-40.

[2] Кавалейро А., Хоссон Джефф Т. де (Ред.). Наноструктурированные покрытия. Серия: Наноструктурные науки и технологии 1-е издание. - 2006. - 648 с.

[3] Kamata, S. Y. Сверхвысокотемпературная предел прочности на растяжение TiC-армированного сплава Mo-Si-B / Shiho Yamamoto Kamata, Daiki Kanekon, Yuanyuan Lu, Nobuaki Sekido, Kouichi Maruyama, Gunther Eggeler & Kyosuke Yoshimi // Научные доклады – 2018. – С. 2-13.

[4] Попов В. Л. Механика контактного взаимодействия и физика трения. От динамики нанотрибологии до землетрясений - М .: ФИЗМАТЛИТ, 2013. – 352 с.

[5] Патент 114047 Украина, Износостойкий аморфно-кристаллический материал / Бабак В. П., Щепетов В. В., Мирненко В. И., Яковлева М. С.; заявитель и патентообладатель Институт технической теплофизики Национальной академии наук Украины. – a201601800 ; опубл. 10.04.17, Бюл. № 7.

[6] Пинчук В. Г., Короткевич С. В. Кинетика упрочнения и разрушения поверхностного слоя металлов при трении. – Саарбрюккен: LAP. – 2012. – 188 с.