Basic concept of tribocrystallochemistry of composition antifriction coatings

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Abstract. The article considers a possibility of introducing a new term, ‘tribocrystallochemistry of composite antifriction coatings’, which can be used in scientific terminology to explain friction and wear processes, modeling processes in the chemical nanoconstituent of composite antifriction coatings, modifiers and surfaces in contact with a composite antifriction coating, as well as technological aspects of receiving composites. The developed concept is based on the scientific knowledge of crystal chemistry, tribology, physical chemistry, tribochemistry, materials science, as well as theoretical and experimental research of the author.

1. Introduction
Modern technical systems and machines contain many components and mechanisms that require increased reliability and durability. [1,2]. To extend their service life, coatings of various types and compositions are used, which have different physical and mechanical properties, unique application technology, etc. [1,2]. In order to increase the efficiency of the coating, it is necessary to take into account, in addition to wear resistance, its possible multifunctionality, such as: antifriction, corrosion resistance, heat resistance, cold resistance, etc.

2. Discussion and experimental results
Let us recall some well-known terms on which we will rely in the future:
- tribology - science that studies friction and the processes that accompany friction (‘tribos’ - friction; ‘logos’ - science) [3];
- tribotechnology - a practical application of tribology knowledge in the design, manufacture, testing and operation of tribosystems (friction units of machines, instruments, apparatuses and tools in technological production) [3];
- crystal chemistry is science of the atomic structure of crystals and its effect on the physicochemical properties of crystalline substances [4];
- tribochemistry is a field of chemistry that studies chemical and physicochemical changes in solids under the influence of mechanical energy [5];
- composite coating is a coating formed by a volume combination of chemically heterogeneous components with a clear interface between them;
- antifriction coating is a coating applied to parts operating in friction conditions.
From literary sources it is known that composite coatings modified by fillers can increase durability of mechanisms. Various materials are used as filler: aluminum oxide, silicon carbide, boron nitride, molybdenum disulfide, graphite, etc. [6].

Depending on the type of components included in the composite coating system, various systems can be formed, such as: heterogeneous systems (solid phase mixtures - chemical compounds, element mixtures, mixtures with different chemical bonds); homogeneous systems (phases of variable composition - solid solutions); chemical compounds and intermetallic compounds are phases of constant composition [1,6,7].

The physicomechanical properties of composite coatings used in friction units often depend on the size of the phases, their shape, size and quantity, chemical composition and structure, as well as presence or absence of various elements between the phases, etc.

Knowing the structure and characteristics of the phases included in the coating, in the substrate (base) on which the coating is applied, in the surface with which the coating is in contact, it is possible to create composite coatings with previously known, and possibly unique properties. Since the composite coating thickness can be small, for example, 1-2 μm, this allows to nanoconstruct them both when creating and when working in the friction unit [7]:

- with phases, often not quite classical: unstable, stable polymorphic, metastable, applied, etc.;
- with chemical compounds having different chemical bonds (metal, ionic, covalent);
- with several layers having different connections, etc.

To date, the possibilities of developing composite coatings for friction-units have not been exhausted, since many options for the internal structure of materials allow you to vary their properties.

In accordance with the research by I.V. Kragelskiy (molecular theory of friction) friction surfaces interact in a tribological contact, there are changes in the surface layer and destruction of surfaces. Moreover, these phenomena are unstable (not regular) in order and time, and in dynamic motion affect each other [8].

B.I. Kostetskiy in his works notes that the surface layer in a friction contact undergoes a change in structure and it becomes active. With his students, he formulated a definition of such a phenomenon as ‘structural adaptability’, which is realized by friction of any materials depending on loads and speeds of mutual displacement [9].

The surfaces involved in friction are ‘open’, exchanging both energy and matter. All this contributes to the interaction between phases (particles/components) in the friction system and organization of surface structures that contribute to the weakening of friction forces [9–11] due to the occurrence of physicochemical processes where external normal friction is realized.

External friction can be represented as \( A = E_0 + \Delta E_i + \Delta E_S + E_e + E_c \), which, in accordance with the first law of thermodynamics, is mainly spent on the formation of released energy and internal energy of solids. Internal energy contributes to the flow of certain mechano-physico-chemical processes occurring in the surface layer [12].

V.D. Kuznetsov and G.P. Shpenkov believed that the process of friction and wear is quite complicated, it is necessary to consider one of its sides, with the aim of further substantiating the wear process [11].

Thus, for example, for a long time, theoretical studies of Novocherkassk scientist V.V. Ivanov made it possible to lay the foundations for predicting the specified properties of antifriction and wear-resistant materials, as well as modeling their structural states [13]. In the joint work of I.N. Shcherbakov and V.V. Ivanov developments in the field of composite coatings modeling operating in friction-units based on the phenomenon of a phase-disordered state in the volume and surface layers of coatings are reviewed [7, 14].

The author has developed and investigated composite antifriction coatings [6,14-17] based on scientific and technical developments in the field of tribological materials science, crystal chemistry studies of the structural states of various substances that predetermine the phenomenon of self-organization in dissipative self-adjusting systems and prediction of processes in the friction zone [7,17]. A new term has been introduced – ‘tribocrystallochemistry’ [18,19].
This term was introduced to explain the processes occurring during mechanical work, as well as to more efficiently create composite antifriction coatings that work in friction units.

Let us consider what tribocrystallochemistry of composite antifriction coatings represents. Tribocrystallochemistry (a phrase derived from the two words - friction and crystal chemistry) of composite antifriction coatings is a frontier field of knowledge that studies the possibility of developing composites taking into account the crystalline structure of substances included in each subsystem of the tribological system, predicting their tribological properties, explaining the processes of friction and wear of mating surfaces. Undoubtedly, the formulated definition of ‘tribocrystallochemistry of composite antifriction coatings’ will be refined over time, but this requires lengthy additional fundamental theoretical and practical research.

Figure 1 presents a conceptual diagram of the relations between tribocrystallochemistry and sciences and bases from the point of view of developing and studying composite antifriction coatings, as well as explaining the processes occurring in the friction zone [7, 17].

Apparently, the basis for the development of a new direction ‘Tribocrystallochemistry of composite antifriction coatings’ is development of the following theoretical and applied research areas:

- chemical nanoconstruction of tribosystem surfaces;
- modeling of tribological properties of a tribosystem;
- application, development of equipment and methods for conducting a complex of scientific and experimental studies to confirm the phenomenon of tribocrystallochemistry of composite antifriction coatings as a field of scientific knowledge and to expand its use in mechanical engineering;
- technological risks.

**Figure 1.** A conceptual diagram of the relationships of tribocrystallochemistry of composite antifriction coatings.

Chemical nanoconstruction of the tribosystem surfaces can be understood as a process of synthesis of theoretical research and technological methods for creating / constructing / selecting, etc. surfaces involved in friction with previously known properties [7].

Crystal-chemical engineering is understood as a complex of theoretical studies based on structural modeling methods [7].

Studies proved that the relative motion of individual atoms or their aggregates from one position to another occurs during martensitic transformations, dislocations and vacancies of the crystal lattice (defects), etc. [20].
Figure 2 shows a diagram of the relationships of chemical nanoconstruction of surfaces involved in friction.

![Diagram of relationships of chemical nanoconstruction of surfaces involved in friction](image)

**Figure 2.** Diagram of the relationships of chemical nanoconstruction of surfaces involved in friction.

Each surface, whether it is a coating and/or reverse friction pair (possibly a steel surface), must be considered from the point of view of phase composition, their possible structural states, physical and mechanical properties (tribotechnical), as well as phase-disordered state [7].

Figure 3 shows idealized images of surfaces (with possible phase composition and modifiers distributed over the surface and/or in volume) obtained on the basis of studies on the development of composite nickel-phosphorus coatings obtained by chemical deposition [6].

![Idealized images of surfaces](image)

**Figure 3.** Idealized images of surfaces (with a possible phase composition distributed over the surface and/or in volume) involved in friction, using the example of a composite nickel-phosphorus coating obtained by chemical deposition: a) precipitated nickel-phosphorus coating (without heat treatment); b) precipitated nickel-phosphorus coating modified with BN and PTFE (without heat treatment); c) heat-treated nickel-phosphorus coating; d) heat-treated nickel-phosphorus coating modified with BN and PTFE; e) heat-treated nickel-phosphorus coating subjected to tribomechanical action; f) heat-treated nickel-phosphorus coating modified with BN and PTFE, subjected to tribomechanical action; g) friction pair - nickel-phosphorus coating - metal surface (in the absence of tribomechanical effects); h) friction pair - nickel-phosphorus coating, modified with BN and PTFE - metal surface (in the absence of tribomechanical effects); i) friction pair - nickel-phosphorus coating - metal surface (during tribomechanical impact on each other); j) friction pair - nickel-phosphorus coating, modified with BN and PTFE - metal surface (during tribomechanical impact on each other).
Figure 4 shows several options of phase structures derived from phosphorus-containing compounds in the Ni-P system. Description of the characteristics of occupied lattice complexes includes a symbol of the crystallographic position and its positional symmetry [6].

\[
\begin{align*}
\text{I} & \text{4} \ (8) \ / \ 24\text{Ni}: 3*8(\text{g}) \ 1 \\
& \quad 8\text{P}: 8(\text{g}) \ 1
\end{align*}
\]

\[
\text{B2} \ (8) \ / \ 24\text{Ni}: 6*4(\text{c}) \ 1 \\
& \quad 8\text{P}: 2*4(\text{c}) \ 1
\]

\[\text{Ni}_3\text{P}\]

\[\text{Ni}_{12}\text{P}_5\]

\[\text{P}6_3\text{mc} \ (3) \ / \ 20\text{Ni}: 2(\text{a})3\text{m}+6(\text{c})\text{m}+12(\text{d})\text{l} \\
& \quad 16\text{P}: (2(\text{a})+2(\text{b}))3\text{m}+2*6(\text{c})\text{m}
\]

\[\text{Cmc}2_1(8) \ / \ 40\text{Ni}: 2*4(\text{a})\text{m}+4*8(\text{b})\text{l} \\
& \quad 32\text{P}: 4*4(\text{a})\text{m}+2*8(\text{b})\text{l}
\]

\[\text{Ni}_5\text{P}_4\]

\[\text{Ni}_3\text{P}\; \text{b) Ni}_{12}\text{P}_5; \text{c) Ni}_5\text{P}_4.\]

To explain the processes of rearrangement of crystalline structures and phase transformations, it is necessary to strive to create energy models of surfaces involved in friction, based on the application of energy concepts of crystal chemistry, band theory, etc. [21].

In accordance with the Hess law [22], it is possible to calculate the thermal effects of a wide variety of chemical processes, which depend only on the type and state of the starting materials and reaction products.

Table 1 shows the formulas for determining energy of the crystal lattice, which can be calculated by the generalized theory, the Born – Land equation, the Born – Mayer equation, Kapustinsky equation, etc. [23].

Figure 4. Options for occupied positions in possible phase structures: 
a) Ni$_3$P; b) Ni$_{12}$P$_5$; c) Ni$_5$P$_4$. 
Table 1. Methods for calculating lattice energy

| Methods                        | Formula                                                                 |
|--------------------------------|-------------------------------------------------------------------------|
| Generalized                    | \[ U = -(NAe^2/R) + \phi(R) \]                                         |
| The Bourne-Lande equation      | \[ U_0 = -A/R_0(1-1/n) \]                                              |
| The Bourne-Mayer Equation      | \[ U_0 = -A/R_0(1-\rho/R_0) \]                                         |
| Kapustinsky equation           | \[ U_K = -287(mz A z X)/(r A+r X)[1-0.345/(r A+r X)] \]                 |

Technological design enables you to:
- substantiate the composite coating composition;
- determine the interaction of components in the coating;
- to develop and optimize a prototype technology for producing composite coatings;
- choose a pair of friction, taking into account the necessary predictive tribotechnical properties;
- choose / develop / modify equipment for coating, etc. [6,7,17].

Using simulation, it is possible to conduct an analysis, to conduct a visual experiment and to study a complex system of composite antifriction coating both during design and during its operation in the friction zone. This leads to a decrease in time for the general design of the friction-unit, a reduction in the cost of scientific and practical research, and a reduction in technological risks.

The modeling of tribotechnical properties of the tribosystem is based on the methodology for predicting substances with specified properties [6,7,17]. Calculation of tribotechnical characteristics can be implemented based on the data of crystal-chemical design (modeling of structural parameters and characteristics of the phase-disordered state of the surfaces of the tribosystem) [17].

Experimental studies enable to determine:
- macroscopic properties of substances included in the coating, depending on their atomic, supratomic structure, molecular and supramolecular structure, with dimensions from units to a thousand angstroms;
- tribological properties of the tribosystem at the macro and nanoscale, including under extreme operating conditions, such as high pressure, vacuum, low and high temperatures, etc.;
- a change in the microstructure in the form of point defects, dislocations, interfaces, microcracks, pores, etc.;
- substantiate the mechanisms of structural and conformational transformations, phase transitions, self-organization in tribocrystalline chemical nanoscale systems of composite coatings, etc. [6,7,17-25].

Technological risks in the development of composite antifriction coatings are associated, first of all, with the selection and creation of surfaces that are unable to work on friction and wear, with the failure to achieve the planned theoretical tribological properties of the coatings, unsatisfactory experimental studies, etc. The decision support information system will contribute to more productive development of composite antifriction coatings for friction units. It will be possible to work with this system, including through cloud technologies, with the possibility of processing data on-line. It is assumed that the information system for the development of composite antifriction coatings will consist of a database system based on:
- a complex of scientific knowledge in relation to a new scientific field of tribocrystallochemistry of composite antifriction coatings;
- results of theoretical and experimental studies;
- industrial testing of composite antifriction coatings;
- introduction of scientific foundations of tribocrystallochemistry in pedagogical, scientific, research, commercial, non-commercial and creative activities, etc.

3. Summary

1. Based on the analysis of the work of specialists involved in friction, wear and research conducted by the author, based on scientific achievements in the field of physical chemistry of solids,
mechanochemistry, crystallography and crystal chemistry, and others, the author introduces a new term – ‘tribocrystallochemistry of composite antifriction coatings’.

2. A conceptual scheme of the relationships of tribocrystallochemistry of composite antifriction coatings based on interdisciplinary scientific theoretical and technical-technological fields of knowledge and applied aspects of creating composites is developed.

3. Based on the stated concept, with a certain degree of certainty, it can be assumed that further expansion of the range of scientific knowledge and research in the field of tribocrystallochemistry will allow the development and implementation of new composites with predictable properties or previously considered unattainable.

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