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Original Empirical Research

Microarc Molybdenum Steel Saturation Using Ammonium Molybdate

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Abstract

Introduction. One of the most significant challenges in modern materials science is increasing the reliability and durability of tools and machine parts. To address this issue, it is essential to develop high-hardness coatings with enhanced properties. Typically, high-energy techniques are employed for this purpose, but they require complex and costly equipment, limiting their widespread use. Therefore, problem of creating such coatings remains a significant challenge. An effective and affordable approach to creating these coatings on steel products is microarc surface alloying from a coating pre-applied to the surface of the hardened products. The aim of the work was to assess the potential of diffusion molybdenum saturation for creating such coatings. Ammonium molybdate was used as the diffusant agent.

Materials and Methods. To achieve the aim of this study, we used thermodynamic analysis of chemical reactions that can occur within the temperature range of the microarc heating process. For each reaction, we calculated the change in standard Gibbs energy, which allowed us to determine the feasibility and range of occurrence. An experimental study of the microarc molybdenum saturation process was conducted using ammonium molybdate on steel 20 samples using a laboratory setup. The surface current density was set at 0.53 A/cm², and the duration of the process was 6 minutes.

Results. The Gibbs free energy changes for chemical reactions that can occur during the thermal decomposition of ammonium molybdate have been calculated. An experimental study has shown the formation of a molybdenum coating, and the concentration of molybdenum in the diffusion layer has been determined. On the surface of the samples, carbides Mo_2C and Fe_3Mo_3C have been found. The dependence of the coating depth on the content of diffusant in the coating and its thickness has been determined.

Discussion and Conclusion. Thermodynamic analysis has shown that atomic molybdenum can be formed through direct reduction or with the intermediate formation of molybdenum dioxide. The research has confirmed the formation of a diffusion coating on steel after microarc saturation with molybdenum, and the depth of this coating depends on the amount of diffusant in the coating and its thickness. These findings will be used to develop technological processes for microarc molybdenum plating of steel products.

Keywords: microarc surface alloying, diffusion molybdenum saturation, formation of a high-hardness coating

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Оригинальное эмпирическое исследование

Микродуговое молибденирование стали с использованием молибдата аммония

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Аннотация
Введение. Одной из актуальных проблем современного материаловедения является повышение надежности и долговечности инструмента и деталей машин. Для ее решения целесообразно создание высокотвердых покрытий с повышенными эксплуатационными характеристиками. Как правило, для этого используется высокоэнергетическое воздействие на материал. Однако оно требует использования сложного и дорогостоящего оборудования и не получило широкого распространения. Поэтому в настоящее время проблема создания таких покрытий остается актуальной. Эффективным и недорогим методом создания таких покрытий на стальных изделиях является микродуговое поверхностное легирование из обмазки, предварительно наносимой на поверхность упрочняемых изделий. Целью работы являлась оценка возможности создания таких покрытий с помощью диффузионного молибденирования с использованием молибдата аммония в качестве источника диффузанта.
Материалы и методы. Для достижения цели исследования использовали термодинамический анализ химических реакций, протекание которых возможно в температурном диапазоне процесса микродугового нагрева. Для каждой реакции рассчитывали изменение стандартной энергии Гиббса, что позволило определить возможность и диапазон их протекания. Экспериментальное исследование процесса микродугового молибденирования с использованием молибдата аммония выполнено с использованием лабораторной установки на образцах из стали 20; поверхностная плотность тока составляла 0,53 А/см^2; продолжительность процесса — 6 минут.
Результаты исследования. Рассчитаны зависимости изменения свободной энергии Гиббса для химических реакций, протекание которых возможно при термическом разложении молибдата аммония. Экспериментально установлено формирование молибденированного покрытия и определена концентрация молибдена в диффузионном слое. На поверхности образцов обнаружены карбиды Mo_2C и Fe_3Mo_3C. Определена зависимость глубины покрытия от содержания диффузанта в обмазке и ее толщины.
Обсуждение и заключение. Анализ полученных уравнений показал возможность образования атомарного молибдена прямым восстановлением или через промежуточное образование диоксида. Результаты экспериментальных исследований подтвердили образование диффузионного покрытия на стали после микродугового насыщения молибденом. Глубина такого покрытия зависит от содержания диффузанта в обмазке и ее толщины. Полученные результаты могут быть использованы при разработке технологических процессов микродугового молибденирования стальных изделий.

Ключевые слова: микродуговое поверхностное легирование, диффузионное насыщение молибденом, формирование высокотвердого покрытия

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Introduction. The formation of high-hardness coatings on steel products is one of the most important tasks of materials science [1]. Therefore, methods for obtaining coatings due to a highly concentrated energy flow to the material have been proposed, including laser treatment [2], plasma heating [3], electro-chemical thermal treatment [4], heating in an electrolyte [5], microarc oxidation [6], ion plasma treatment [7], electric spark alloying [8], and combinations of these techniques [9]. However, these methods are not widely used due to high energy consumption and the need to use complex and expensive equipment. Therefore, the problem of creating reinforcing coatings on steel products remains relevant.

An effective method of surface hardening is microarc alloying. In this process, the products are placed in a metal container filled with carbon powder, and an electric current is passed through the container. Microarc discharges occur between the product and the powder medium, which results in diffusion saturation of the steel surface with carbon and an alloying element [10]. This method accelerates diffusion processes and significantly reduces the duration of saturation compared to other methods. It also does not require complex and energy-intense equipment [11]. Microarc alloying can be used to create carbide coatings. The source of alloying elements is a coating applied to the treated surface [12]. Diffusion coatings can also be created by saturating the surface with molybdenum. For this purpose, inexpensive and widely available compounds can be used. For example, an inexpensive and complex microelement fertilizer — ammonium molybdate $(NH_4)_2MoO_4$ can be used. However, the possibility of using it in the composition of a coating can only be determined through thermodynamic analysis.

The aim of the study was to investigate the potential and conditions for using ammonium molybdate for surface molybdenum plating of steel.

Materials and Methods. To achieve the aim of the study, we used a thermodynamic analysis method. According to this method, the change in free energy of a chemical reaction was represented as the sum of enthalpies of formation of substances obtained as a result of reaction, minus the sum of the enthalpy of formation of the initial substances [13]. The possibility of a reaction was determined in the temperature range at which the Gibbs energy change had a negative value. This took into account the dependence of heat capacity on temperature [14]:

$$C_P = a_1 + b_1 \cdot T + d_1 \cdot T^{-2}. \quad (1)$$

Gibbs energy ΔG_T^0 was calculated as:

$$\frac{\Delta G_T^0}{T} = \frac{\Delta H_{298}^0}{T} - \Delta S_{298}^0 - \left(M_0 \Delta a + M_1 \Delta b + M_{-2} \Delta d \right), \quad (1)$$

where Δa, Δb, Δd — algebraic sums of coefficients a_1, b_1 and d_1 in formula (1); M_0, M_1 and M_2 — integral functions [13].

Table 1 presents the initial data [15] for calculations.

Table 1

Initial data for thermodynamic calculations

Substance	$-\Delta H^0_{298}$, kJ/mol	S^0_{298}, J/molK	C_{p298}, J/molK	$C_p = a_1 + b_1T + d_1T^{-2}$, J/mol		
				a	$b \cdot 10^3$	$d \cdot 10^{-5}$
C	0.000	5.744	8.540	17.170	4.270	–8.790
CO	110.600	197.680	29.130	28.430	4.100	–0.460
CO_2	393.777	213.820	37.140	44.170	9.040	–8.540
H_2	0.000	130.520	28.830	27.300	3.270	0.500
H_2O	241.990	188.850	33.599	30.020	10.720	0.330
CH_4	74.850	186.190	35.710	14.320	74.660	–17.430
Mo	0.000	28.600	24.100	21.670	6.950	–
MoO_2	589.100	46.280	55.980	67.800	12.600	–13.000
MoO_3	745.200	77.740	75.020	56.900	56.500	–
NH_3	45.940	192.660	35.630	29.800	25.480	–1.670
N_2	0.000	199.900	29.100	27.880	4.270	–
NO_2	33.500	240.200	37.500	42.160	9.550	–6.990

To experimentally verify the calculation results, microarc alloying of cylindrical steel samples with a diameter of 12 mm and a length of 35 mm was performed. An electrically conductive gel with the addition of ammonium molybdate powder was used to make the coating.

Microarc alloying was performed according to method [10], surface electric current density was 0.53 A/cm^2, heating duration was 6 minutes. After processing, the samples were sanded and polished according to the standard procedure, followed by etching with Rzheshotarsky reagent. A Neophot-21 microscope, an ARL X'TRA-435 diffractometer in Cu-Kα radiation, and a ZEISS CrossBeam 340 electron microscope with an Oxford Instruments X-max 80 microanalyzer were used for metallographic studies.

Research Results. When ammonium molybdate was heated, a reaction occurred:

$$(NH_4)_2MoO_4 = MoO_3 + H_2O + 2NH_3$$

During thermal decomposition of coal powder, gaseous substances were released [16], which could be reducing agents of atomic molybdenum according to schemes $MoO_3 \rightarrow Mo$ or $MoO_3 \rightarrow MoO_2 \rightarrow Mo$.

Chemical reactions and calculation results according to the above-described method are presented in Table 2. For each reaction, dependence ΔG_T^0 was calculated, the possibility (Yes/No) and the temperature range of the reaction during microarc heating were determined.

Table 2

Calculation results and the possibility of chemical reactions in the process of microarc heating

No.	Reaction	Dependence ΔG_T^0	Possibility of reaction
1	$MoO_3+3C=Mo+3CO$	383.100 – 0.490·T	Yes, > 509°C
2	$2MoO_3+3C=2Mo+3CO_2$	130.600 – 0.230·T	Yes, > 295°C
3	$MoO_3+C=MoO_2+CO$	33.500 – 0.147·T	Yes, the entire range
4	$2MoO_3+C=2MoO_2+CO_2$	–41.550 – 0.061·T	Yes, the entire range
5	$MoO_3+3CO=Mo+3CO_2$	–103.550 + 0.008·T	No
6	$MoO_3+CO=MoO_2+CO_2$	–134.760 + 0.026·T	No
7	$MoO_3+3H_2=Mo+3H_2O$	–24,830.000 – 61.180·T	Yes, the entire range
8	$4MoO_3+3CH_4=4Mo+3CO_2+6H_2O$	463,800.000 – 903.200·T	Yes, > 240°C
9	$4MoO_3+CH_4=4MoO_2+CO_2+2H_2O$	–221,800.000 – 238.200 T	Yes, the entire range
10	$3MoO_3+CH_4=3MoO_2+CO+2H_2O$	–86,300.000 – 263.800 T	Yes, the entire range
11	$7MoO_3+2NH_3=7MoO_2+2NO_2+3H_2O$	–258,000.000 + 554.200·T	Yes, < 190°C
12	$3MoO_3+2NH_3 \rightarrow 3MoO_2+N_2+3H_2O$	–446,900 + 143.800·T	Yes, the entire range
13	$MoO_2 + C = Mo + CO_2$	181.070 – 0.169 T	Yes, > 799°C
14	$MoO_2 + 2C = Mo + 2CO$	350.500 – 0.353 T	Yes, > 720°C
15	$MoO_2 + 2CO = Mo + 2CO_2$	76.050 – 0.094 T	Yes, > 536°C
16	$MoO_2 + 2H_2 = Mo + 2H_2O$	77,612.000 – 56.472 T	Yes, > 1,100°C

Thus, thermodynamic analysis confirmed the possibility of using ammonium molybdate as part of the coating during molybdenum plating. Reactions 1, 2, 7, 8 provided direct reduction, reactions 3, 4, 9, 10, 11, 12 — reduction with an intermediate stage of dioxide formation and further reactions 13, 14, 15, 16.

To experimentally verify the results obtained, microarc surface alloying of the samples was performed using a coating containing ammonium molybdate. The analysis of the samples confirmed the formation of a layer of α-solid molybdenum solution on their surface, followed by a zone with high carbon content and then the initial structure (Fig. 1).

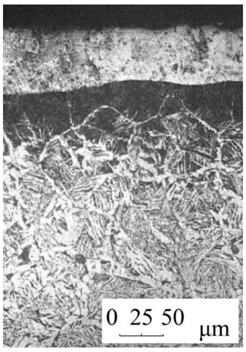

Fig. 1. Microstructure of the surface of steel 20 after saturation with molybdenum

Molybdenum content in steel by layer depth is shown in Figure 2.

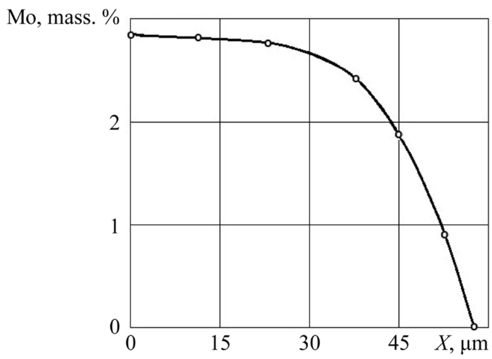

Fig. 2. Mo distribution by diffusion layer depth.
The content of the diffusant powder in the coating — 50%, its thickness — 1.0 mm

The formation of Mo_2C and Fe_3Mo_3C carbides on the surface of the samples was established by X-ray phase analysis (Fig. 3).

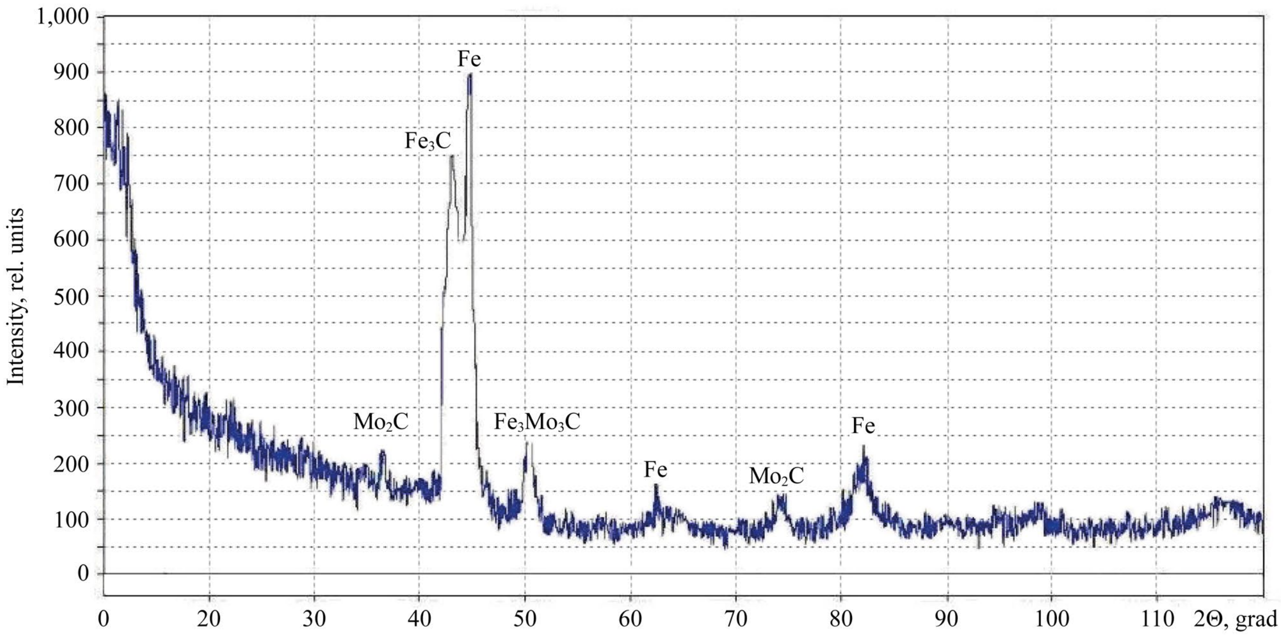

Fig. 3. X-ray diffractogram of the surface

Figure 4 shows the dependence of the coating thickness on the amount of diffusant powder in the coating.

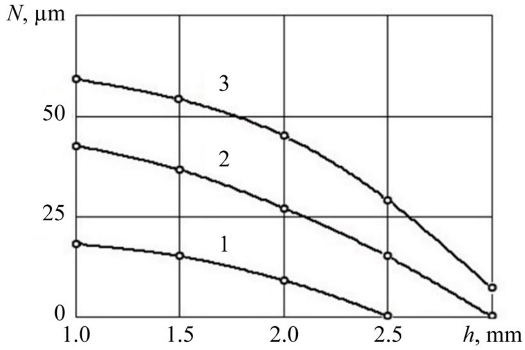

Fig. 4. Dependence of depth H of the diffusion layer on thickness h of the coating layer and the content of the diffusant powder: dependencies 1, 2, 3 correspond to 10; 30; 50 (vol. %)

To achieve the highest coverage, the diffusant content in the coating should be 50 vol. %, and the thickness of the coating layer on the treated surface should be 1 mm.

Discussion and Conclusion. The calculation results shows that a coating consisting of ammonium molybdate powder and a binder can be used for the process of microarc molybdenum plating of steel. As a result of microarc saturation, a molybdenum coating is formed, consisting of an α-solid solution of molybdenum with inclusions of carbides, then a carbonized zone is located, passing into the initial structure. The thickness of the coating is determined by the content of the diffusant in the coating and its thickness. The largest coating thickness (50–55 μm) was obtained at a diffusant content of 50 vol. % and coating thickness of 1 mm. The results of the study are planned to be used in the development of technological processes for microarc molybdenum plating of steel products.

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Claimed Contributorship:

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YuM Dombrovsky: experimental studies, determination of technological parameters of the surface alloying process, analysis of the results obtained.

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