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ENHANCING THE CORROSION RESISTANCE OF Al-Zn-Mg-Cu ALUMINUM ALLOYS THROUGH MODIFICATION WITH TITANIUM CARBIDE POWDER

Annotation. Improving the characteristics of industrial alloys, particularly their corrosion resistance, is a relevant task for both metallurgists and materials science specialists. The implementation of new technologies and the selection of materials for specific operating conditions stimulate the development of technological methods for altering the characteristics of base alloys. The investigation and application of new effective modifiers and modification technologies represent an important research direction. Under certain operating conditions, aluminum alloys, particularly the Al-Zn-Mg-Cu system, are subjected to significant corrosive influences, which negatively affect their mechanical properties and longevity. Therefore, the challenge lies in the necessity to develop new approaches and technologies. Specifically, this study proposes a method for modifying the alloys using titanium carbide powder and investigates the effect of this modification on the corrosion resistance of the studied alloy. The aim of the work is to establish the relationship between the structure, physical-mechanical properties, and corrosion resistance. To achieve this goal, modification of alloys V93 and V95 with titanium carbide powder was carried out, and the microstructures and corrosion resistance before and after modification were studied. Corrosion tests, including laboratory methods, encompassed the determination of general, intergranular, and corrosion cracking, which allowed for the assessment of the effectiveness of the proposed modification method. The results obtained confirmed the effectiveness of modifying the studied alloys with titanium carbide of 15 µm particle size. Observations of corrosion processes indicated a reduction in overall corrosion, with the area of corrosion sites decreasing from 70% to 50% after modification. There was also a significant reduction in intergranular corrosion in alloy V95, indicating an improvement in its corrosion resistance. In both modified alloys, intergranular corrosion was not observed, and corrosion cracking of the base metal was absent during the 60-day test period. The test results indicate an increase in corrosion resistance after modification.
Keywords: aluminum alloys, corrosion resistance, alloy modification, titanium carbide, physical and mechanical properties, corrosion tests

Statement of the Problem. The development and implementation of novel manufacturing methods are critical for the advancement and optimization of production processes, as their application enhances technological efficiency and reduces raw material and energy consumption. Innovations such as forming technologies for components using additive methods,

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the creation of composite materials with specific properties, automation and robotization of production, as well as the latest thermal treatment technologies, contribute to enhancing the characteristics of machines and equipment distinguished by high productivity, reliability, durability, and competitiveness. Among these innovative technologies, significant attention is given to alloy modification techniques, which involve the introduction of minute particles of other materials into the melt of the base metal, such as aluminum. This process aims to alter the physical and mechanical properties of the alloys, including their strength, plasticity, corrosion resistance, and manufacturability, by changing the crystalline structure of the alloy with micro- and nanoscale particles.

In various fields of mechanical engineering, wrought aluminum alloys of the Al-Zn-Mg-Cu system are utilized for the fabrication of critical structural components, specifically alloys V93 and V95. These alloys exhibit high mechanical properties and significant corrosion resistance [3, 4], which substantiates their relevance and appropriateness for application under critical operating conditions. However, under specific operational conditions, components made from these alloys may be subjected to simultaneous influences from several types of corrosion, negatively impacting the durability and reliability of the structures [5, 9]. This research focuses on studying the effect of modification on the properties of wrought aluminum alloys V93 and V95 of the Al-Zn-Mg-Cu system, particularly regarding their corrosion resistance and the assessment of their suitability for use under critical operating conditions.

Analysis of Recent Research and Publications. The analysis of results from numerous contemporary studies indicates an active exploration of various approaches to modifying aluminum and other alloys, aimed at achieving a targeted change in the characteristics of the base material. To summarize the approaches, modifiers can be classified according to their influence into the following groups [2, 5, 16]. *First-order modifiers* influence the structure by altering the energy characteristics, namely the activation energy and surface tension during the nucleation of a new phase. *Second-order modifiers* affect the structure by acting as solid phase nuclei. *Third-order modifiers*, known as inoculators “coolers”, lower the metal temperature and increase the crystallization rate, thereby slowing down the development of element liquation and reducing the overheating of the melt during crystallization.

Modification is considered one of the most effective methods for improving the quality of cast products. It contributes to the elimination of columnar and fan-like structures, grain and dendrite refinement, the achievement of a homogeneous microstructure, as well as the enhancement of the mechanical and corrosion properties of alloys [3, 4, 5, 7].

The conventional industrial method for modifying aluminum alloys using sodium salts has limited effectiveness due to the low melting point of these modifiers, leading to their rapid dissolution in the molten metal. This restricts the ability of sodium salts to provide the necessary grain refinement and to form stable crystallization centers, which, in turn, prevents the achievement of desired mechanical and technological characteristics of the alloys. Consequently, contemporary research favors the use of dispersive refractory materials, which demonstrate better results in modifying aluminum alloys [6-8].

Aluminum alloys from the Al-Zn-Mg-Cu system are widely used in stressed structures across various industries, including construction, automotive manufacturing, as well as in the production of aviation and aerospace technology. This is due to their favorable combination of physical and mechanical properties, workability, and corrosion resistance [1, 3]. Industrial aluminum alloys from this system are characterized by strengths in the range of 400-450 MPa while maintaining high ductility [2, 4, 6, 17]. The primary methods for further improving the mechanical properties of aluminum alloys include solid solution strengthening, dispersion strengthening, thermomechanical treatment, and modification [2, 6, 7].

Currently, a promising direction is the application of dispersive refractory modifiers, namely: carbides, nitrides, borides, as well as pure metals. The influence of modifiers in the form of dispersive additives lies in creating additional artificial crystallization centers in the melt. For this, such additives must be proportionate to the sizes of critical nuclei of the matrix phase and capable of providing their enough quantity for forming a fine-dispersed structure in the casting. Specifically, the modification with refractory powdered titanium carbide is widely used for producing structural elements with high physical-mechanical properties. The results presented in works [2, 5] indicate that the optimal modifier for aluminum alloys is powdered titanium carbide with particle sizes of 10–15 μm [2, 11, 12].

Powdered titanium carbide has a high melting point, making it suitable for use in processes that require significant temperatures, such as aluminum alloy casting. This allows for the avoidance of its melting during processing. The addition of this material contributes to the creation of new crystallization centers in the melt, ensuring uniformity and a fine-dispersed structure, thus improving the mechanical properties of the alloys. The effect of titanium carbide on aluminum alloys positively impacts their strength, ductility, and corrosion resistance, making them more suitable for use in structures with high mechanical performance requirements. Additionally, titanium carbide easily integrates into the structure of alloys, enhancing their workability and improving processing techniques. Thus, the use of modifiers, particularly powdered titanium carbide, demonstrates significant potential in the creation of new alloys with enhanced strength and workability, opening new opportunities for optimizing the properties of aluminum alloys in various industrial applications.

Purpose of the Study. The purpose of this study is to investigate the changes in the structure, physical and mechanical properties, and corrosion resistance of wrought aluminum alloys V93 and V95 of the Al-Zn-Mg-Cu system after their modification with titanium carbide powder. To achieve this goal, the following tasks are outlined:

1) modify aluminum alloys V93 and V95 of the Al-Zn-Mg-Cu system using titanium carbide powder with a particle size of 15 μm,

2) examine the microstructure of these alloys in their initial state and after corrosion testing, as well as before and after modification,

3) conduct corrosion tests to investigate the following types of corrosion: general corrosion, exfoliation corrosion, intergranular corrosion, and stress corrosion cracking.

Statement of the main research material. This study investigates the corrosion properties of V93 and V95 alloys both before and after modification. To improve the quality and processability of Al-Zn-Mg-Cu aluminum alloys, their melts were modified using fine titanium carbide-based powders. Titanium carbide powder was chosen based on the compatibility

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of the crystal lattices of aluminum and TiC (both having face-centered cubic lattices) and the difference in atomic radii between aluminum and TiC.

Corrosion testing is a fundamental practical method for corrosion control and can be categorized into three primary groups: laboratory, field, and operational tests [18, 19]. *Laboratory* tests are conducted under conditions that can be precisely defined and controlled, although they often differ from the actual conditions experienced in practice. Laboratory testing is employed to study the mechanisms of corrosion, for comparative assessment of corrosion resistance of metals and alloys, as a control tool during the development of new corrosion-resistant alloys, for adjusting the composition and processing technology of alloys, and for many other purposes. *Field* and *operational* tests are necessary for selecting the most suitable materials capable of functioning in environments with varying degrees of corrosivity and for determining their service life.

Table 1 presents the characteristics of carbides [20], specifically those with cubic crystal lattices (titanium carbide TiC and others based on refractory metals). Carbon atoms occupy interstitial positions between the metal atoms, forming interstitial phases. Many carbides with cubic structures exhibit wide regions of homogeneity. This explains why the removal of some carbon atoms from the carbide lattice does not lead to the destruction of the compound or significant changes in its properties.

Table 1

Properties of Carbides

Carbide	βMoC	γWC	TiC
Melting Temperature, T (°C)	2522	2780	3067
Hardness, HRA	74	80	93

In TiC, the carbon content can vary from 20% to 50% (atomic) without significant alteration of the type and properties of the crystal lattice. However, there exists the possibility of substituting the missing carbon atoms in the carbide with other atoms (such as oxygen, nitrogen, etc.). To determine the corrosion resistance of aluminum alloys modified with titanium carbide powder, tests were conducted to assess general, intergranular, and exfoliation corrosion, as well as corrosion cracking. The study utilized microstructural analysis methods and corrosion testing methods for general, intergranular, exfoliation corrosion, and corrosion cracking.

Intergranular corrosion was evaluated according to standard methodology [15]. The tests were conducted in the following solution: 30 g of NaCl + 10 cm³ of HCl. The solution temperature was maintained at +22±1°C, and the duration of the test was 24 hours. Flat samples measuring 20 × 10 × 3 mm were cut from the castings. The assessment was performed metallographically using an optical microscope NEOPHOT–2. The characteristics of the corrosion and the maximum depth of intergranular corrosion were recorded [5, 6]. *Exfoliation corrosion* is a type of corrosion that primarily develops parallel to the deformation vector generated during the rolling or pressing of the semi-finished product and is accompanied by the formation of cracks in that direction, detachment of individual metal particles, or complete destruction of the samples or components [7, 8]. This type of corrosion mainly occurs along the boundaries of elongated grains. *Corrosion cracking* is a type of metal degradation caused by the simultaneous action of a corrosive environment and nominally static tensile stress, resulting in the formation of cracks [5, 11, 12]. During the corrosion cracking test, the samples were cyclically immersed in a 3% NaCl solution: 10 minutes in the solution, followed by 50 minutes in air. The duration of the tests was 45 days.

To obtain comparative data on the corrosion resistance of the alloys, tests for general corrosion were conducted according to the standard methods used in industrial enterprises [13, 14]. To simulate harsh operating conditions, a method was chosen that involved testing under conditions of 100% relative humidity, as well as a method involving periodic exposure to a 3% sodium chloride (NaCl) solution at room temperature. The assessment of the corrosion resistance of aluminum alloys was based on changes in the appearance of the samples and variations in mass.

Findings. Analysis of the test results showed that all investigated aluminum alloys, after modification, regardless of surface condition, exhibit sufficiently high corrosion resistance when tested under conditions of 100% relative humidity; corrosion damage is virtually absent. After three cycles of testing, unmodified samples exhibited surface darkening characterized by isolated spots and points. After ten cycles of testing in the humidity chamber, the surfaces of aluminum alloys V93 and V95 prior to modification with titanium carbide powder showed darkening in the form of spots covering up to 70% of the surface area, while post-modification, this coverage was reduced to 50%.

The results of the general corrosion tests indicate that modification with titanium carbide powder leads to enhanced corrosion resistance of the alloys due to a reduction in the corrosion rate: for alloy V93 by 10.8% to 16.7%, and for alloy V95 by 5.6% to 6.3%. The improvement in corrosion resistance can be attributed to the refinement of the structure of the aluminum alloys. During modification, the length of numerous interfacial boundaries increases. Intermetallics and impurity atoms that were located at the interfacial boundaries in the alloy prior to modification become distributed over a significantly larger area after modification. Consequently, they exert less negative influence on the corrosion resistance of the aluminum alloys. Figure 1 presents the microstructures of the investigated alloy before and after modification with titanium carbide powder. An important role is also played by the stressed state of the modified structure. The introduction of dispersed titanium carbide powder makes the microvolumes of wrought alloys more energetically stressed, which enhances their corrosion resistance.

Aluminum alloys of the Al-Zn-Mg-Cu system are characterized by intergranular corrosion [2, 9, 10]. The sensitivity to intergranular corrosion arises due to the structural inhomogeneity of grain boundaries, the precipitation of secondary phases, the depletion or enrichment of adjacent regions of the α-solid solution with alloying elements, and the formation of sub-microscopic and microscopic voids due to the flow and coagulation of vacancies. In the modified alloys under investigation, a tendency toward intergranular corrosion has not been

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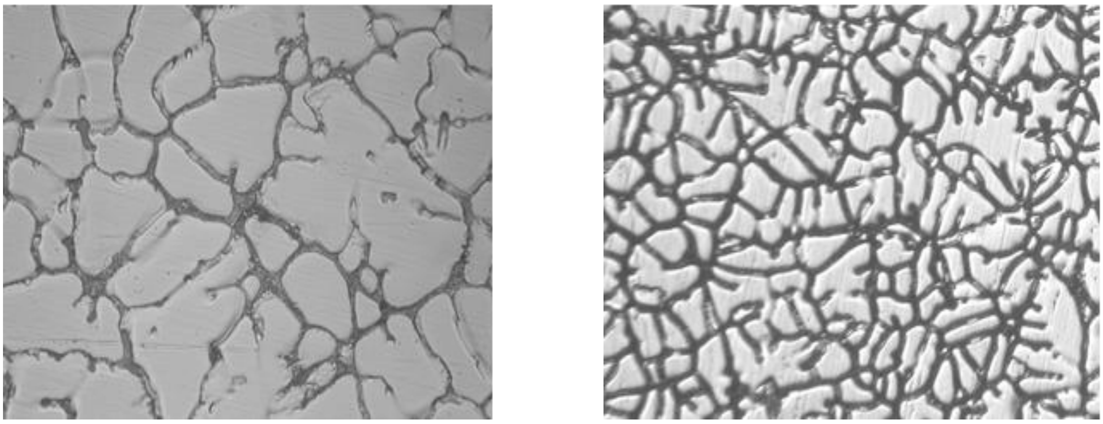
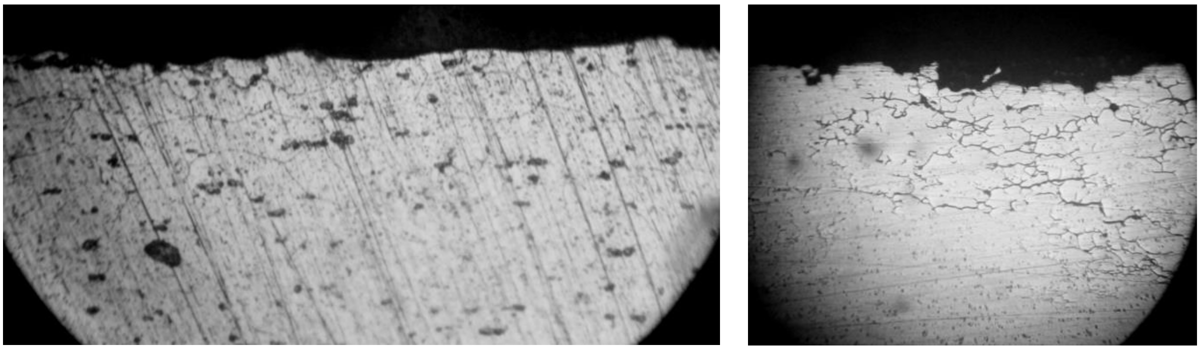
observed. In alloy V95, a β-phase has been identified in the form of a network along the grain boundaries (Figure 2, a), with intergranular corrosion originating from pitting on the β-phase (Figure 2, b).

In the wrought alloy, the modification with titanium carbide leads to a reduction in the precipitation of the β-phase and its uniform distribution throughout the volume of the workpiece, resulting in the absence of susceptibility to intergranular corrosion. Since the alloys of the Al-Zn-Mg-Cu system are categorized as deformable and are utilized in welded structures, significant indicators include exfoliation corrosion and corrosion cracking. The results of the tests for exfoliation corrosion of alloys V93 and V95, both before and after modification, are presented in Table 2.



a b

Figure 1 — Microstructures of the wrought alloy V95 (×200):
a — before modification; b — after modification



a b

Figure 2 — Tests for intergranular corrosion of alloy V95: a — β-phase in the form of a network along the grain boundaries (×500); b — intergranular corrosion originating from pitting on the β-phase (×100)

Table 2

Results of Exfoliation Corrosion Tests for Alloys V93 and V95

Alloy	Exfoliation Corrosion	Rating
V93	Blisters with a diameter of 2–3 mm across the entire surface	5
V95	Blisters with a diameter of 2–3 mm covering 10% of the area	4
V95 + TiC	No blisters present	2

Corrosion cracking was evaluated on the base metal and the weld joint produced by gas tungsten arc welding. The test results are presented in Table 3.

Table 3

Corrosion Cracking of Base Metal and Weld Joints of Alloys B93 and B95

Alloy	Corrosion Cracking			
	Base Metal		Weld Joints	
	Stress	Testing Duration Until Cracking, days	Stress, MPa	Testing Duration Until Cracking, days
V93	0,9σ_B	more than 55	200	45
V95	0,9σ_B	more than 55	200	55
V95 + TiC	0,9σ_B	more than 55	200	more than 55

Conclusions. The modification of wrought aluminum alloys of the Al-Zn-Mg-Cu system was conducted using titanium carbide powder with a particle size of 15 µm. Tests of the alloys for general corrosion revealed that after ten cycles, corrosion spots occupying 70% of the surface were observed on the unmodified samples, whereas only 50% was noted on the modified samples. This indicates a reduction in the corrosion rate in the modified samples. A decrease in the manifestation of intergranular corrosion was observed in the alloy samples of B95 after modification: from a score of four in the unmodified samples to a score of two in the modified ones. Intergranular corrosion was not detected in the modified alloys B93 and B95. Corrosion cracking of the base metal of the Al-Zn-Mg-Cu system alloys was not observed over a period of 60 days of testing. In the welded joint of the modified B95 alloy, an increase in the time to cracking was noted. No corrosion cracking was detected after 60 days of testing. The results of industrial tests confirmed a significant increase in the corrosion resistance of wrought modified aluminum alloys.

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Підвищення корозійної стійкості алюмінієвих сплавів Al-Zn-Mg-Cu шляхом модифікування порошковим карбідом титану

Покращення характеристик промислових сплавів, зокрема їх корозійної стійкості, є актуальним завданням як для металургів, так і для фахівців із матеріалознавства. Впровадження нових технологій та вибір матеріалів для специфічних умов експлуатації стимулюють розробку технологічних методів зміни *характеристик вихідних сплавів. Дослідження та впровадження нових ефективних модифікаторів і технологій модифікування є важливим напрямком досліджень. За певних умов експлуатації алюмінієві сплави, зокрема системи Al-Zn-Mg-Cu, піддаються значним корозійним впливам, що негативно позначається на їх механічних характеристиках і довговічності. Отже, проблема полягає в необхідності розробки нових підходів та технологій. Зокрема, в роботі пропонується метод модифікування означених сплавів порошковим карбідом титану, а також досліджується вплив такого модифікування на корозійну стійкість досліджуваного сплаву. Метою роботи є встановлення зв'язку між структурою, фізико-механічними властивостями та корозійною стійкістю. Для досягнення мети проведено модифікування порошковим карбідом титану сплавів В93 та В95, а також досліджені мікроструктури й корозійна стійкість до і після модифікування. Корозійні випробування, зокрема лабораторні, охоплювали визначення загальної, розшарувальної, міжкристалітної корозії та корозійного розтріскування, що дозволило оцінити ефективність запропонованого методу модифікування. Одержані результати підтвердили ефективність модифікування досліджуваних сплавів порошковим карбідом титану фракції 15 мкм. Спостереження за корозійними процесами вказали на зменшення загальної корозії, а саме площа корозійних осередків зменшилася з 70% до 50% після модифікування. Також було досягнуто значного зниження розшарувальної корозії в сплаві В95, що свідчить про покращення його корозійної стійкості. В обох модифікованих сплавах не спостерігалася міжкристалітна корозія, а корозійне розтріскування основного металу було відсутнє протягом 60 днів випробувань. Результати випробувань свідчать про підвищення корозійної стійкості після модифікування.*

Ключові слова: алюмінієві сплави, корозійна стійкість, модифікування сплавів, порошковий карбід, фізико-механічні властивості, корозійні випробування

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