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Research article

Научная статья



Effect of lithium on the anodic behavior of AlTi0.1 aluminum conducting alloy in NaCl electrolyte environment

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Abstract: Aluminum ranks as the fourth most conductive metal, trailing behind silver, copper, and gold in electrical conductivity. Annealed aluminum demonstrates an approximate 62 % conductivity of the International IACS compared to annealed standard copper, which registers 100 % IACS at $t = 20^\circ\text{C}$. Because of its low specific gravity, aluminum exhibits twice the conductivity per unit mass compared to copper, showcasing its potential economic advantage as a material for conducting electricity. For equal conductivity (in terms of length), an aluminum conductor exhibits a cross-sectional area 60 % larger than that of copper, while weighing only 48 % of copper's mass. However, the widespread use of aluminum as a conductor in electrical engineering is often challenging and sometimes unfeasible due to its inherent low mechanical strength. Enhancing this crucial property is achievable through the addition of dopants. However, this approach tends to elevate mechanical strength at the cost of noticeable reductions in electrical conductivity. This study investigates the impact of lithium addition on the anodic behavior of an A5 aluminum conductor alloy, specifically modified with 0.1 wt.% Ti (AlTi0.1 alloy), within a NaCl electrolyte environment. The experiments were conducted utilizing the potentiostatic method in potentiodynamic mode at a potential sweep rate of 2 mV/s. Results indicate that the introduction of lithium to the AlTi0.1 alloy leads to a shift in the potentials of free corrosion, pitting, and repassivation towards positive values. Additionally, the corrosion rate decreases by 10–20 % with the incorporation of 0.01–0.50 wt.% Li. Moreover, varying concentrations of chloride ions in the NaCl electrolyte prompt fluctuations in the corrosion rate of the alloys and a shift in electrochemical potentials towards the negative range.

Key words: AlTi0.1 aluminum alloy, lithium, potentiostatic method, stationary potential, corrosion potential, corrosion rate, NaCl electrolyte.

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Влияние лития на анодное поведение алюминиевого проводникового сплава AlTi0.1 в среде электролита NaCl

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Аннотация: Среди всех известных металлов алюминий по электропроводности занимает 4-е место после серебра, меди и золота. Электропроводность отожженного алюминия составляет приблизительно 62 % IACS от электропроводности отожженной

стандартной меди, которая при $t = 20\text{ }^{\circ}\text{C}$ принимается за 100 % IACS. Однако благодаря малому удельному весу алюминий обладает проводимостью на единицу массы в 2 раза большей, чем медь, что дает нам представление об экономической выгоды применения его в качестве материала для проводников. При равной проводимости (одна и та же длина) алюминиевый проводник имеет площадь поперечного сечения на 60 % больше, чем медный, а его масса составляет только 48 % от массы меди. В большинстве случаев в электротехнике использование алюминия в качестве проводника затруднено, а часто и просто невозможно из-за его низкой механической прочности. Повышение этого значимого показателя возможно за счет введения легирующих добавок. В таком случае механическая прочность возрастает, вызывая, однако, заметное снижение электропроводности. В работе исследовано влияние добавки лития на анодное поведение алюминиевого проводникового сплава марки А5, модифицированного 0,1 мас.% Ti (сплава AlTi0.1), в среде электролита NaCl. Эксперименты проведены потенциостатическим методом в потенциодинамическом режиме при скорости развертки потенциала 2 мВ/с. Показано, что добавка лития в сплав AlTi0.1 способствует смещению потенциалов свободной коррозии, питтингообразования и репассивации в положительную область значений, а скорость коррозии при введении 0,01–0,50 мас.% Li снижается на 10–20 %. В зависимости от концентрации хлорид-иона в электролите NaCl отмечен рост скорости коррозии сплавов и смещение электрохимических потенциалов в область отрицательных значений.

Ключевые слова: алюминиевый сплав AlTi0.1, литий, потенциостатический метод, стационарный потенциал, потенциал коррозии, скорость коррозии, электролит NaCl.

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Introduction

In many instances within electrical engineering, utilizing aluminum as a conductor poses challenges and, at times, becomes unfeasible due to its inherent low mechanical strength. Furthermore, conductive aluminum, when subjected to cold deformation to enhance its strength, tends to lose this enhanced property at temperatures around 100 °C. While it's possible to enhance its mechanical strength by introducing dopants to create alloys [1–3], this improvement often leads to a notable decrease in electrical conductivity [4–7].

The impact of various alloying elements on both the electrical conductivity and strength of aluminum reveals that the most substantial enhancement in hardness occurs upon the inclusion of poorly soluble alloying elements like Fe, Zr, Mn, Cr, Ti, Ca, and Mg. These elements significantly differ in atomic diameters from aluminum. Given that electrical conductivity stands as a paramount parameter for a conductor material, the selection of alloying elements should carefully consider their influence on altering this property [8–11].

Presently, several theories regarding modification exist, yet a consensus remains elusive in addressing this issue concerning aluminum alloys. This complexity arises primarily due to the intricacies of the modification process, which is reliant on melting and casting conditions. Additionally, the presence of uncontrolled impurities and elements may impact the refinement of the original alloy grain. The additive introduced as a modifier, as exemplified by titanium in our case, should fulfill specific prerequisites:

- exhibit adequate stability in the melt without altering the chemical composition;

- possess a higher melting point than that of aluminum;

- demonstrate structural and dimensional compatibility between the crystal lattices of the modifier and aluminum [12; 13].

The primary function of modifiers lies in reducing surface tension on crystal faces, facilitating an accelerated nucleation rate of crystallization centers. This decelerates crystal growth, consequently augmenting the number of crystallization centers and refining the overall structure. However, there exists no definitive classification distinguishing modifiers into the first and second kinds or dopants, given the absence of substances solely soluble in liquid states and entirely insoluble in solid states [14; 15].

Aspects concerning the corrosion and electrochemical behavior of aluminum alloys are detailed in [16–21].

This study aimed to investigate the impact of lithium addition on the corrosion and electrochemical behavior of A5 aluminum, which was modified with 0.1 wt.% Ti (AlTi0.1 alloy).

Research methods for assessing corrosion and electrochemical characteristics of alloys

Alloy samples were prepared using aluminum grade A5 (State Standard GOST 110669-01), titanium grade TG-90 (State Standard GOST 19807-91), and lithium grade LE-1 (State Standard GOST 8774-75). These alloys were produced in SShOL type furnaces, casting rods with a diameter of 8 mm and a length of 140 mm

into graphite molds for electrochemical studies. The end of the electrode served as the working surface, while the non-working part of the samples was insulated with a resin mixture (comprising 50 % rosin and 50 % paraffin). Before immersion in the working solution, the end part of each sample underwent cleaning with sandpaper, polishing, degreasing, thorough washing with alcohol, and then immersion in a NaCl electrolyte solution. The temperature of the solution within the cell was maintained consistently at 20 °C using an MLSh-8 thermostat.

The electrochemical testing of the samples was conducted employing the potentiostatic method in potentiodynamic mode, utilizing a PI-50-1.1 pulse potentiostat with a potential sweep rate set at 2 mV/s within a NaCl electrolyte environment. The reference electrode employed was silver chloride, while the auxiliary electrode used was platinum. The investigation of the electrochemical behavior of ternary alloys followed the methodology outlined in [22–26].

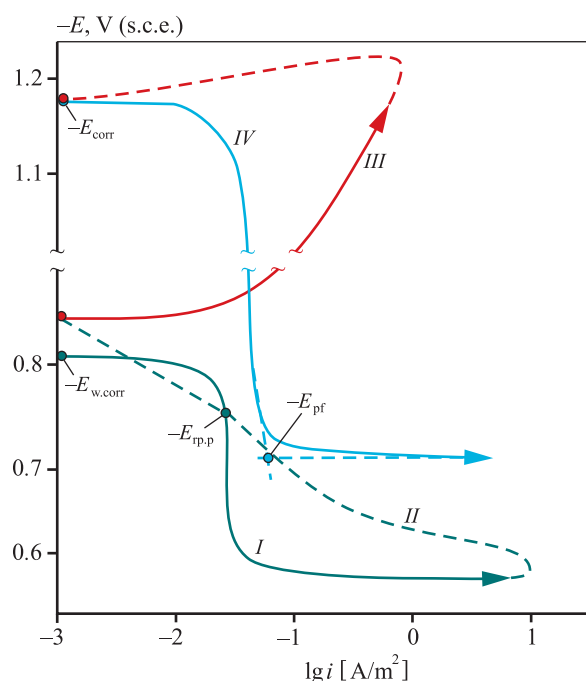


Fig. 1. Full polarization curve (at a potential sweep rate of 2 mV/s) of AlTi0.1 aluminum conducting alloy in a 3.0 % NaCl electrolyte environment

E_{pf} – potential of pitting formation; $E_{rp,p}$ – repassivation potential; E_{corr} – corrosion potential

Рис. 1. Полная поляризационная кривая (при скорости развертки потенциала 2 мВ/с) алюминиевого проводникового сплава AlTi0.1 в среде электролита – 3,0 %-ного NaCl

E_{pf} – потенциал питтингообразования; $E_{rp,p}$ – потенциал репассивации, E_{corr} – потенциал коррозии

For instance, Fig. 1 illustrates the comprehensive polarization diagram concerning the initial AlTi0 aluminum alloy in a 3 % NaCl electrolyte. The samples underwent potentiodynamic polarization, initially moving positively from the established immersion potential until a sharp increase in current denoting pitting (Fig. 1, curve *I*). Subsequently, the samples were polarized in the opposite direction (Fig. 1, curve *II*), and the repassivation potential ($E_{rp,p}$) was determined either from the intersection of curves *I* and *II* or from the inflection point in curve *II*. Following this, the process moved towards the cathode region, reaching a potential value of –1.2 V to eliminate oxide films from the electrode surface (Fig. 1, curve *III*) by alkalization near the electrode surface. Finally, the samples were once again polarized in the positive direction (Fig. 1, curve *IV*), enabling determination of the primary electrochemical parameters pertaining to the alloy's corrosion process from the anodic curves.

The corrosion current (i_{corr}), regarded as the primary electrochemical characteristic of the corrosion process, was computed utilizing the cathodic curve. This calculation considered the Tafel slope ($b_k = 0.12$ V) and the understanding that in neutral environments, the pitting corrosion process of aluminum and its alloys is governed by the cathodic reaction involving oxygen ionization. The corrosion rate, on the other hand, is expressed as a function of the corrosion current according to the formula:

$$K = i_{corr} \kappa,$$

where $\kappa = 0.335$ g/(A·h), representing the electrochemical equivalent of aluminum.

Results and discussion

The findings from the investigations of corrosion and electrochemical behavior of the AlTi0.1 aluminum alloy, incorporating varying amounts of lithium in a NaCl electrolyte environment, indicate a noticeable shift in the free corrosion potential ($E_{w,corr}$) towards positive values (Fig. 2). Notably, a higher concentration of the modifying component (lithium) correlates with a more positive $E_{w,corr}$ value. Furthermore, transitioning from 0.03 % NaCl to 3.0 % NaCl, results in a more negative $E_{w,corr}$, irrespective of the quantity of the modifying additive (Li) in the AlTi0.1 alloy.

Table summarizes the corrosion and electrochemical behavior of the examined AlTi0.1 alloy across NaCl electrolyte with various concentrations. The table illustrates that an increase in lithium content within the initial AlTi0.1 sample leads to the displacement of

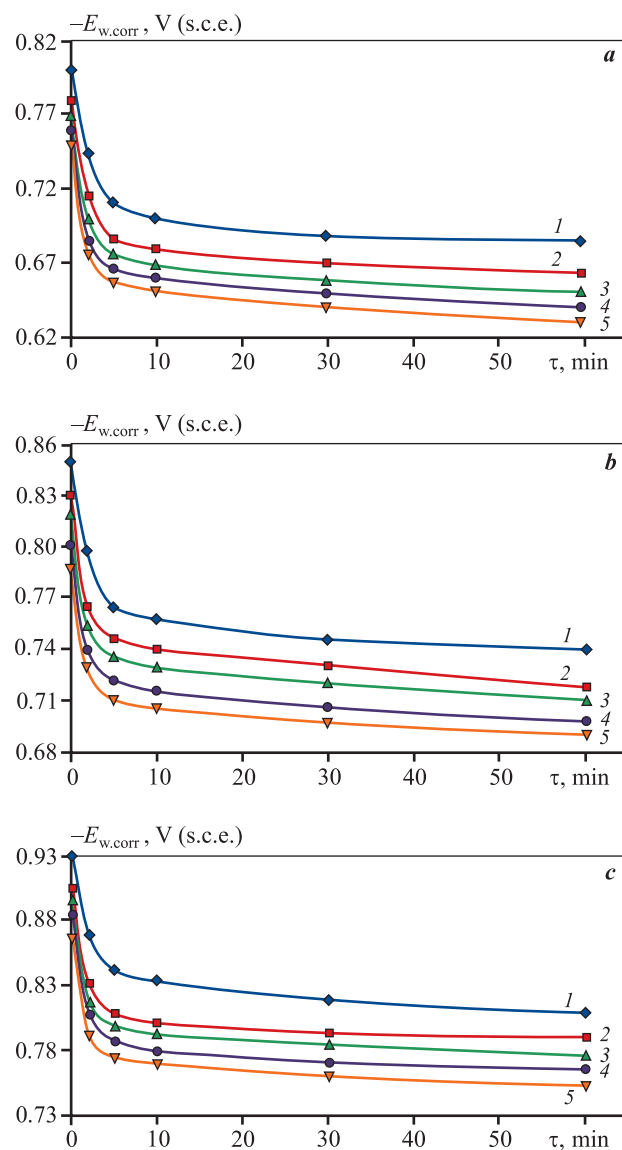


Fig. 2. Potential of free corrosion plotted against time for the initial AlTi0.1 aluminum conducting alloy (1) and lithium-modified alloys (2–5) in NaCl electrolyte environment, wt.%: 0.03 (a), 0.3 (b) and 3.0 (c) Li, wt.%: 0 (1), 0.01 (2), 0.05 (3), 0.10 (4), 0.50 (5)

Рис. 2. Временная зависимость потенциала свободной коррозии исходного алюминиевого проводникового сплава AlTi0.1 (1) и модифицированных литием образцов (2–5) в среде электролита NaCl, мас.%.: 0,03 (a), 0,3 (b) и 3,0 (c) Содержание Li, мас.%.: 0 (1), 0,01 (2), 0,05 (3), 0,10 (4) и 0,50 (5)

corrosion, pitting, and repassivation potentials toward the positive range. This shift is attributed to the establishment of a stable oxide film on the electrode surface within the NaCl environment.

Alloys containing 0.01–0.5 % lithium exhibit a corrosion rate 10–20 % lower than that of the original AlTi0.1 sample.

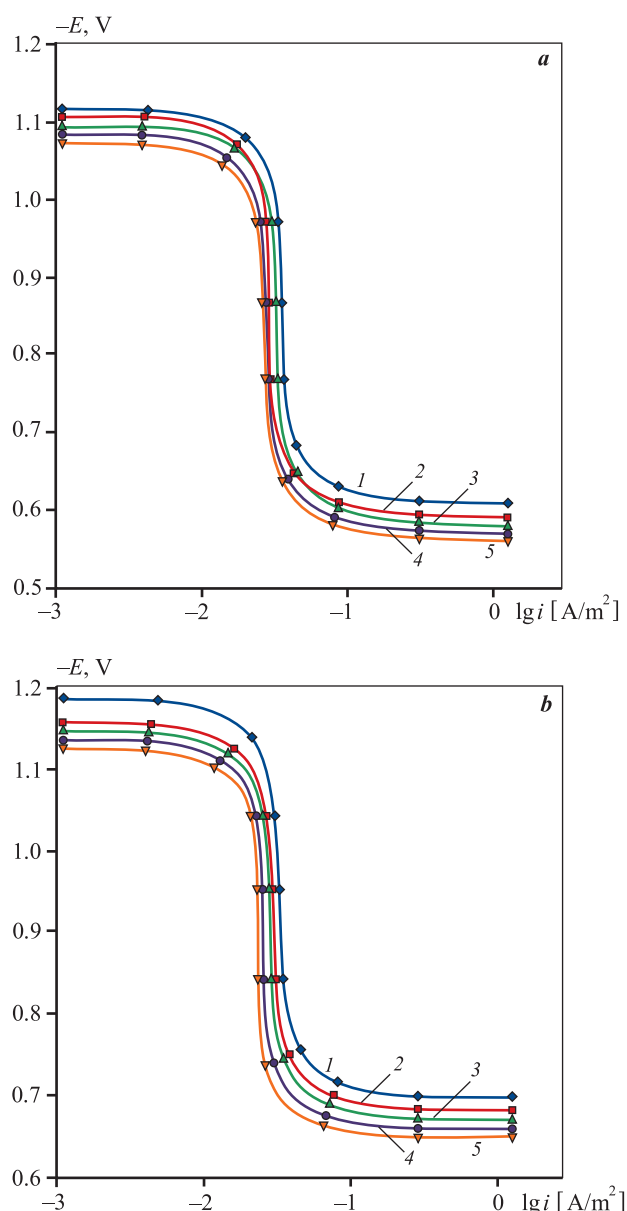


Fig. 3. Anode branches of potentiodynamic curves (potential sweep rate 2 mV/s) of the initial AlTi0.1 aluminum conducting alloy (1) and lithium-modified variants (2–5) in NaCl electrolyte environment 0.03 % (a) and 3.0 % (b) Li, wt.%: 0 (1), 0.01 (2), 0.05 (3), 0.10 (4) and 0.50 (5)

Рис. 3. Анодные ветви потенциодинамических кривых (скорость развертки потенциала 2 мВ/с) исходного алюминиевого проводникового сплава AlTi0.1 (1) и модифицированных образцов (2–5) в среде электролита NaCl, мас.%.: 0,03 (a) и 3,0 (b) Содержание Li, мас.%.: 0 (1), 0,01 (2), 0,05 (3), 0,10 (4) и 0,50 (5)

Consequently, the introduction of lithium into the aluminum conducting alloy AlTi0.1 assists in diminishing the rate of anodic corrosion, as indicated by the shift of the anodic branches in the potentiodynamic curves towards the positive region (Fig. 3). Notably,

Corrosion and electrochemical characteristics of AlTi0.1 aluminum conducting alloy with varying lithium modifications in NaCl electrolyte environment

Коррозионно-электрохимические характеристики алюминиевого проводникового сплава AlTi0.1, модифицированного литием, в среде электролита NaCl

NaCl, wt.%	Li, wt.%	Electrochemical potentials, V (s.c.e.)				Corrosion parameters	
		$-E_{w,corr}$	$-E_{corr}$	$-E_{pf,p}$	$-E_{tp,p}$	i_{corr} , A/m ²	$K \cdot 10^3$, g/(m ² ·h)
0.03	0.0	0.685	1.120	0.610	0.660	0.048	16.0
	0.01	0.663	1.100	0.591	0.640	0.045	15.0
	0.05	0.650	1.090	0.582	0.630	0.043	14.4
	0.1	0.640	1.080	0.570	0.620	0.041	13.7
	0.5	0.630	1.071	0.560	0.610	0.039	13.0
0.30	0.0	0.740	1.150	0.650	0.690	0.068	22.7
	0.01	0.718	1.132	0.630	0.669	0.065	21.7
	0.05	0.710	1.125	0.619	0.660	0.062	21.1
	0.1	0.698	1.112	0.610	0.650	0.061	20.4
	0.5	0.690	1.100	0.600	0.641	0.059	19.7
3.00	0.0	0.809	1.180	0.700	0.750	0.086	28.8
	0.01	0.790	1.165	0.682	0.733	0.083	27.8
	0.05	0.776	1.154	0.670	0.725	0.081	27.1
	0.1	0.765	1.143	0.661	0.716	0.079	26.4
	0.5	0.752	1.130	0.650	0.705	0.077	25.7

the anodic curves associated with the modified alloys are situated to the left of the curve representing the original AlTi0.1 sample, implying a somewhat lower anodic corrosion rate across all examined environments (see Fig. 3).

Figure 4 demonstrates the corrosion rates of the AlTi0.1 alloy relative to lithium content and NaCl electrolyte concentration. It was observed that the addition of lithium to the AlTi0.1 alloy consistently decreases its corrosion rate across all NaCl electrolyte environments under consideration.

Figure 5 illustrates the corrosion current density of the AlTi0.1 aluminum conducting alloy in relation to varying lithium content across different concentrations of NaCl electrolyte. It's evident that as the concentration of the modifier increases, corrosion decreases. Within the range of 0.05–0.50 wt.% lithium concentration in the AlTi0.1 alloy, optimal conditions emerge, exhibiting minimal corrosion rates for these alloys. With an elevation in chloride ion content, there is a noticeable

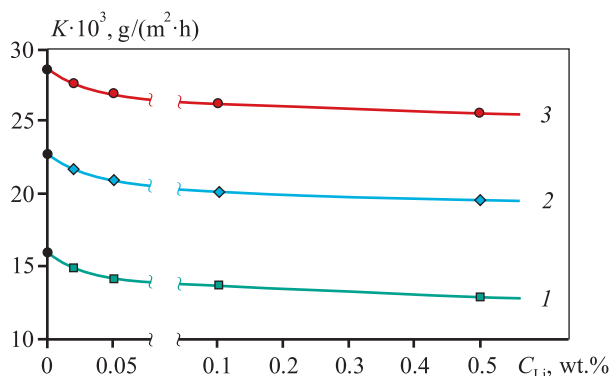


Fig. 4. Corrosion rate variations of the AlTi0.1 aluminum conducting alloy plotted against lithium content in NaCl electrolyte environment, wt.%: 0.03 (1), 0.3 (2) and 3.0 (3)

Рис. 4. Зависимость скорости коррозии алюминиевого проводникового сплава AlTi0.1 от содержания в нем лития и концентрации электролита NaCl, мас. %: 0,03 (1), 0,3 (2) и 3,0 (3)

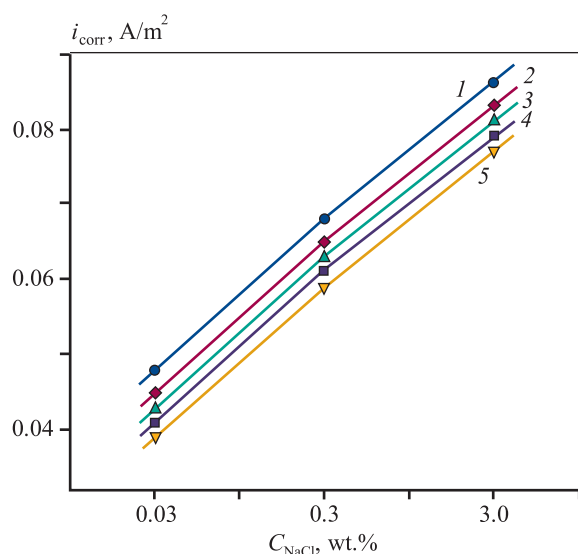


Fig. 5. Corrosion current density comparison between the initial AlTi0.1 aluminum conducting alloy (1) and lithium-modified alloys (2–5) in relation to the concentration of NaCl electrolyte

Li, wt.‰: 0 (1), 0.01 (2), 0.05 (3), 0.10 (4), 0.50 (5)

Рис. 5. Зависимость плотности тока коррозии исходного алюминиевого проводникового сплава AlTi0.1 (1) и модифицированных образцов с литием (2–5) от концентрации электролита NaCl

Содержание Li, мас.‰: 0 (1), 0,01 (2), 0,05 (3), 0,10 (4) и 0,50 (5)

increase in the corrosion rate for both the original aluminum alloy and the lithium-modified variant.

Conclusions

Aluminum alloys are highly chemically reactive materials that readily react with oxygen, resulting in the immediate formation of thin oxide films on their surface. Under natural conditions, these films typically reach a thickness of 0.01–0.02 μm and can be increased to 5 or 50 μm through chemical or anodic oxidation [27; 28].

The corrosion resistance of aluminum and its alloys in various aggressive environments significantly depends on the resistance of the oxide film. Additionally, it relies on the chemical composition of the alloy and the surface's heat treatment. It's worth noting that the presence of impurities such as iron, nickel, tin, lead, and other elements forming various phases adversely impacts this resistance [28]. Moreover, the corrosion resistance of such materials is influenced not only by their chemical composition but also by the crystallization nature of excessive phases that determine their structure and form of deposition. Modification (refinement) of binary and ternary eutectics in the alloy structure can

substantially alter both mechanical properties and corrosion resistance.

Enhancing the characteristics of aluminum alloys is closely tied to the advancement of new materials and the implementation of sophisticated technological processes in melting and casting. These advancements ensure improved technical and economic indicators in production and the use of resulting products. The quality of these products is also contingent on the chemical composition and structure of the cast metal [27; 28].

The beneficial impact of lithium addition on the anodic properties of the AlTi0.1 aluminum conducting alloy cannot solely be attributed to the enhancement of electrochemical parameters during the anodic process or the densification of the protective phase layer of oxides by poorly soluble oxidation products. The corrosion resistance of aluminum is also affected by structural changes resulting from modification with titanium and lithium, specifically the size of crystal phases within the alloy structure. Metals characterized by low interatomic bonds, thus low melting points, strength, and hardness, can serve as modifiers for alloy structures. This category includes alkali metals.

Consequently, the positive influence of lithium addition on the anodic characteristics and corrosion rates of the AlTi0.1 aluminum conducting alloy in NaCl electrolyte has been confirmed. These observed patterns can be leveraged in developing new aluminum-based conductor alloys tailored for electrical engineering and cable technology requirements.

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