

Article

Diffusion Nitride Surface Layers on Aluminum Substrates Produced by Hybrid Method Using Gas Nitriding

Michał Tacikowski¹, Jacek Słoma^{2,*}, Rafał Jakiela³, Szymon Marciniak¹, Ryszard Diduszko^{4,5} and Tadeusz Wierzchoń¹

¹ Faculty of Materials Science and Engineering, Warsaw University of Technology, ul. Wołoska 141, 02-507 Warsaw, Poland; michal.tacikowski@pw.edu.pl (M.T.); szymon.marciniak@pw.edu.pl (S.M.); tadeusz.wierzchon@pw.edu.pl (T.W.)

² Department of Production Engineering, Institute of Mechanical Engineering, Warsaw University of Life Sciences, ul. Nowoursynowska 166, 02-787 Warsaw, Poland

³ Polish Academy of Science, Institute of Physics, Al. Lotników 32/46, 02-668 Warsaw, Poland; jakiela@ifpan.edu.pl

⁴ National Centre for Nuclear Research, ul. Andrzeja Sołtana 7/3, 05-400 Otwock-Swierk, Poland; ryszard.diduszko@ncbj.gov.pl

⁵ Łukasiewicz Research Network-Institute of Microelectronics and Photonics, al. Lotników 32/46, 02-668 Warsaw, Poland; ryszard.diduszko@imif.lukasiewicz.gov.pl

* Correspondence: jacek_sloma@sggw.edu.pl; Tel.: +48-22-593-45-85

Abstract: While gas nitriding of steel is currently used in industry, nitriding of aluminum alloys remains an open challenge. The main obstacle is aluminum's high susceptibility to passivation. The oxide film provides an effective barrier to nitrogen diffusion. Attempts to overcome this problem have mainly focused on glow discharge nitriding using cathode sputtering of an oxide layer. The produced AlN layers exhibit no diffusion zone and show limited performance properties. In this work, the effect of hybrid treatment aimed at producing diffusion layers of nitrides other than AlN on aluminum alloys was investigated on the model system of iron nitride–aluminum substrate. Hybrid treatment combines an electrochemical process involving the removal of the aluminum oxide layer from the substrate, its subsequent iron plating, and a further gas nitriding in high-purity ammonia. The obtained results prove that the hybrid treatment allows the production, at 530 °C/10 h, of diffusion layers of Fe₃N iron nitrides on aluminum substrates with a nitrogen diffusion zone range in aluminum of ca. 12 μm. In alloys containing magnesium, its unfavorable effect on the nitrogen diffusion and the functional properties of the layers was observed. An interesting direction for further research is hybrid treatment of precipitation-hardened alloys without magnesium.

Keywords: aluminum alloys; gas nitriding; hybrid method; diffusion; diffusive layers; wear resistance



Citation: Tacikowski, M.; Słoma, J.; Jakiela, R.; Marciniak, S.; Diduszko, R.; Wierzchoń, T. Diffusion Nitride Surface Layers on Aluminum Substrates Produced by Hybrid Method Using Gas Nitriding. *Metals* **2024**, *14*, 524. <https://doi.org/10.3390/met14050524>

Academic Editors: Guosong Wu, Jiapeng Sun and Hao Wu

Received: 30 March 2024

Revised: 26 April 2024

Accepted: 27 April 2024

Published: 29 April 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

While gas nitriding technology of various steel grades is widely used in industry for surface treatment of machine parts and tools, as it increases their functional properties and durability, its use for products made of aluminum and its alloys remains an open challenge. Although aluminum nitride (AlN) formed during the nitriding process has a number of interesting properties such as hardness of approximately 1530 HV, melting point of 2572 K, modulus of elasticity of 400 GPa, and thermal conductivity of 320 Wm⁻¹K⁻¹ [1], the production of AlN surface layers on aluminum alloys in practice encounters a number of obstacles that have not yet been definitively overcome. Meanwhile, the development of an effective, accessible and possibly universal method of nitriding aluminum alloys to improve the functional properties of their surfaces would open up new, broad perspectives for the use of these alloys in previously unavailable applications. They could be used for tribologically exposed elements which operate in conditions requiring high surface hardness and wear resistance.

The need for appropriate solutions for surface engineering methods of aluminum alloys is even more topical due to the constantly growing demand for light alloys in modern technology, dictated by practical, technical, economic, and ecological reasons. Ecological considerations are a particular motivation, as the stake is to reduce fuel and energy consumption and therefore CO₂ emissions to the atmosphere by reducing the weight of vehicles and moving parts of machines and devices.

1.1. Aluminum Nitriding—State of the Art

The main obstacle affecting the possibility of producing aluminum nitride layers is the natural high tendency of aluminum for passivation, resulting in the presence of a thin layer of aluminum oxide, Al₂O₃, which constitutes an effective barrier to diffusion processes, and in particular the diffusion of nitrogen into the substrate. Thermochemical treatments which are effective when removing oxide passive film from steel (e.g., reduction of the oxide with hydrogen, thermal decomposition, or mechanical removal) will not work for aluminum. The thermodynamic stability, and thus tenacity, of the oxide, as well as the high formation kinetics of Al₂O₃, cause the oxide film to be restored as soon as the metal is exposed to atmospheric oxygen [1]. From Arai's work in the mid-1980s [2], it became clear that nitriding of aluminum alloys is in fact possible if it is carried out under glow discharge conditions. Since that discovery, further investigations have been carried out [3–9] focused on the development of technological solutions based on cathode sputtering performed during the nitriding process and conducted under glow discharge conditions enabling the removal of the passive oxide coating and the control of the aluminum substrate's possible re-oxidation processes.

Moreover, there are other difficulties in nitriding aluminum alloys. These include the practical lack of nitrogen solubility in aluminum [9], which reduces the possibility of the formation of diffusion, gradient precipitation hardened solution zones in the substrate supporting the surface AlN zone, as well as the relatively low melting point of aluminum alloys, significantly limiting the maximum processing temperature and, as a result, the nitriding kinetics [9]. Early research carried out in the field of plasma-assisted nitriding of aluminum alloys [3] confirmed that nitriding under glow discharge conditions, in particular the phenomenon of cathodic sputtering, creates favorable conditions for the growth of surface layers of aluminum nitride of the AlN type with thickness up to a few μm. It was shown that even in medium vacuum conditions (10⁻²–1 Pa), a typical industrial facility for plasma nitriding steel can be successfully used to carry out the processes [5]. At the same time, the beneficial effect of the AlN layer on tribological resistance was confirmed [3]. However, attention was drawn to potential problems related to adhesion, susceptibility to cracking, and spalling of the AlN layers under increased load. This was due to the lack of a gradient of properties in the substrate and the large difference of hardness between the nitride layer and the relatively soft substrate. It was also pointed out that in practice it is necessary to limit the thickness of the produced AlN layers to ca. 3 μm [3] since thicker layers were more susceptible to cracking because of the state of high stresses generated during the cooling process due to the high difference in the thermal expansion of aluminum and AlN (23 × 10⁻⁶ K⁻¹ and 5 × 10⁻⁶ K⁻¹ respectively) [3]. It should be emphasized that the problem of the difference in the thermal expansion coefficients of the nitride layer and the substrate becomes critical in terms of the risk of the AlN layer adhesion loss when it is necessary to carry out the precipitation hardening heat treatment of the previously nitrided aluminum, e.g., group of dural grades.

Apart from conventional glow discharge nitriding, other methods of obtaining aluminum nitride layers were investigated [1], including ion implantation [10,11], intensified plasma techniques [12–15], and laser nitriding processes [16,17]. Investigations concerning the application of active screen plasma nitriding [18–20] were recently reported. Other recent reports that cover the studies of new concepts covering plasma nitriding of friction stir welded joints, the atmospheric-pressure non-thermal plasma technique, and AlN/Al₂O₃ coating produced by the microarc oxidation method [21–23] were also recently reported.

Also noteworthy is the work on the use of fluidized bed nitriding, in which the effectiveness of the method was demonstrated in both ammonia and nitrogen environments [24]. Also worth mentioning are some interesting model studies [25] showing the possibility of creating layers based on aluminum nitride with a thickness of approximately 400 μm under the reduced pressure of a nitrogen atmosphere and in the presence of magnesium powder. Other studies showing the effectiveness of similar solutions were recently reported [26]. The beneficial effect of magnesium as an alloying element in an aluminum substrate on the kinetics of nitriding under glow discharge conditions was also earlier described [5,9]. However, an unfavorable phenomenon accompanying glow discharge nitriding related to the formation of a high near-surface concentration of magnesium in the form of zones of magnesium, MgO, which negatively impacts the effects of nitriding machine parts in industrial practice, was also reported [27].

The analysis of the state of art of aluminum nitriding, summarized above, leads to the conclusion that although using cathodic sputtering under glow discharge conditions makes it possible to overcome the problem of aluminum passivation and produce aluminum nitride layers on aluminum alloys, no direct application prospects are achieved, despite a significant improvement in functional properties, such as surface hardness and tribological wear resistance. This is due to the fact that in glow nitriding processes, it is not possible to create layers of a diffusion and gradient nature which would make a significant difference in the properties. This must lead to problems with the adhesion of AlN layers, especially under increased concentrated contact loads, in particular in wear conditions, resulting in the so-called ice-on-mud effect. Similarly, when it is necessary to apply a hardening heat treatment to previously nitrided precipitation-hardened aluminum alloys, e.g., dural groups, due to the more than fourfold difference in the thermal expansion, cracking and spalling of the AlN layers may occur during the heating or cooling operations. One should also remember that due to the high level of stress, the maximum thickness of the AlN layers must be limited to an empirically determined value of 3 μm [3], above which cracks in the layers are generated.

Another serious difficulty is the formation of a near-surface zone of magnesium oxide of the MgO type during nitriding, which is susceptible to cracking [27]. As a result, research on the development of methods for producing nitrided layers on aluminum alloys has been recently focused on other alternative surface engineering solutions. The new investigated solutions are aimed at strengthening the load-bearing capacity of the substrate in hybrid processes based on the use of electron beam (EB) [28,29] and laser processes [30,31] as well as thermal spray [32] combining the alloying of near-surface zones of the alloy with their subsequent nitriding.

1.2. Hybrid Treatment Concept

The present work proposes the concept of producing diffusion layers of nitrides of metals other than aluminum nitride on aluminum alloys, using a hybrid treatment combining sequential modification of the substrate surface consisting of the elimination of the passive layer of aluminum oxide in an electrochemical process, its protection by using a deposition of a coating of a nitride-forming metal, and the subsequent nitriding of the thus prepared substrate in the gas process. The effectiveness of similar hybrid solutions combining nitriding in glow discharge variant with previous precoating of the substrate with a metal coating was demonstrated in our works in the area surface engineering of steels [33], magnesium alloys [34], and aluminum alloys [1,35]. The hybrid treatment is an alternative for the production of nitrides on aluminum alloys based on the PVD technologies. The investigation of CrN, TiN [1], and AlN [36] as well as composite [37,38] coatings produced on aluminum substrates by different PVD methods was reported. The advantage of the proposed solution over the alternative of depositing adhesive nitride coatings using PVD methods [1], resulting in the absence of a gradient in the substrate, would be, under appropriate conditions, the formation of gradient diffusion nitride layers on aluminum alloys diffusion bonded with the substrate. The concept was based on the

premise that, on the one hand, as observed on magnesium alloys [35], a diffusive zone of intermetallic phases connecting the substrate with the coating may be formed, and on the other hand, that nitrogen will diffuse into the aluminum-based substrate through the nitride-forming metal coating. It was assumed that despite the very limited solubility of nitrogen in aluminum (2×10^{-4} at.% [20]), diffusion may occur, especially by grain boundaries, and this may lead to precipitation processes, which should be beneficial in terms of potential precipitation hardening in the diffusion zone. In fact, the AlN aluminum nitride fine precipitates, due to their high hardness, high elastic modulus, and low coefficient of thermal expansion, may act as effective reinforcement particles as, e.g., demonstrated in [39]. It was also assumed that the presence of alloying elements in alloyed substrates may have a beneficial effect on the solubility of nitrogen in aluminum. In the present study, a simple coating/substrate model system was selected, in which aluminum substrate was plated with an iron coating to be nitrided later in a gas process in a high-purity ammonia environment using a prototype gas installation with an adequately high tightness class. The use of certified high-purity ammonia and appropriate construction and tightness of the reactor and gas distribution installations was aimed at creating conditions that would limit the access of oxygen to the nitrided composite iron/aluminum substrate and, as a consequence, reduce the risk of aluminum re-oxidation during nitriding.

The aim of the work was to investigate the effects of producing diffusive nitride layers on aluminum substrates using the surface treatment of aluminum substrates in a hybrid process combining initial modification of the substrate surface in an electrochemical process, including removal of the passive aluminum oxide coating and deposition of a nitride-forming metal coating with subsequent gas nitriding in a high-purity ammonia environment.

2. Materials and Methods

2.1. Substrate Materials

The subject of the work was the production of diffusion nitride layers on aluminum and its alloys based on a new hybrid treatment combining gas nitriding with prior modification of the surface of the aluminum substrate in an electrochemical process involving the removal of the passive aluminum oxide coating and then protecting it against re-passivation by applying a metallic coating, in particular from the group of nitride-forming metals (Figure 1).

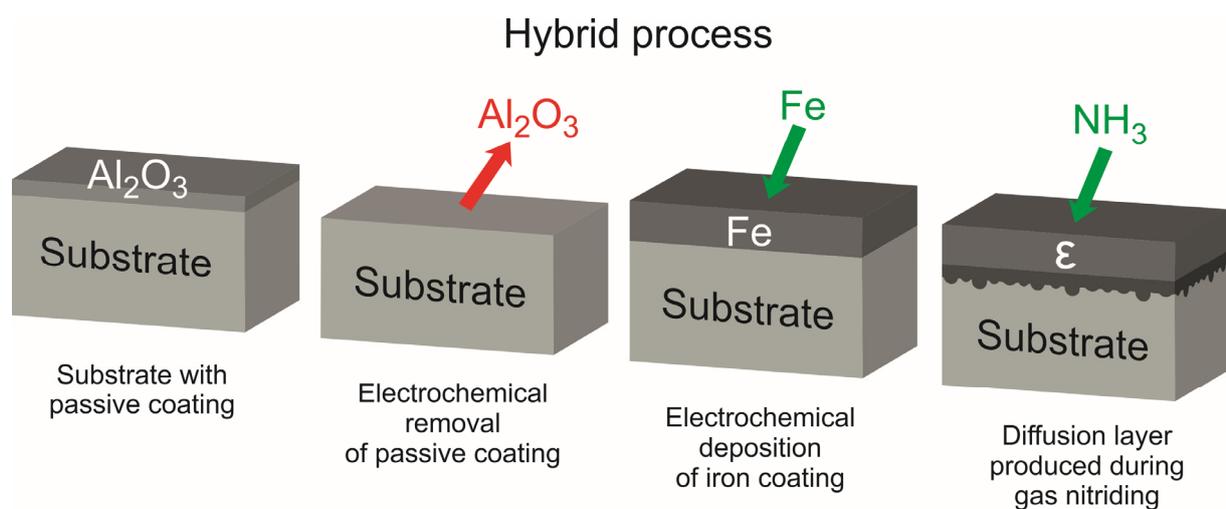


Figure 1. The schematic presentation of the hybrid process used to produce diffusion iron nitride layers on aluminum substrates.

The tests were carried out on commercial alloys from the copper–magnesium and zinc–copper–magnesium dural groups and on reference materials, i.e., technical aluminum and aluminum–magnesium alloy. The chemical composition of materials is given in Table 1.

Table 1. Chemical compositions of the investigated substrate materials according to the standards ⁽¹⁾ PN-EN 573-3+A1: 2022-11, adapted from [40], ⁽²⁾ UNI SPERIMENTALE 3057 (1950), adapted from [41].

Material	Substrate Denotation	Chemical Composition [wt.%]								
		Cu	Mg	Mn	Zn	Cr	Si	Ni	Fe	Al
EN AW-1050A ⁽¹⁾	Al	max 0.05	max 0.05	max 0.05	max 0.07	-	max 0.25	-	max 0.4	rest
AlCu4Mg1 ⁽¹⁾	S1	4.3 ± 0.5	0.75 ± 0.35	0.7 ± 0.3	-	-	-	-	-	rest
AlCu2Mg2NiSi ⁽¹⁾	S2	2.2 ± 0.3	1.6 ± 0.2	-	-	-	0.85 ± 0.35	1.05 ± 0.25	1.05 ± 0.25	rest
AlZn6Mg2Cu2 ⁽¹⁾	S3	1.7 ± 0.3	2.3 ± 0.5	0.4 ± 0.2	6 ± 1	0.175 ± 0.075	-	-	-	rest
G-AlMg7 ⁽²⁾	S4	-	7 ± 0.6	0.35 ± 0.15	-	-	-	-	-	rest

The selection of the alloys was dictated in particular by the different contents of magnesium, which, according to the literature data [9], facilitates the formation of aluminum nitride layers during nitriding processes under glow discharge conditions. The alloys were selected from among commercial materials, bearing in mind that achieving the intended, positive results of the experiment would create the prospect of implementing the developed technology in industrial conditions. The materials examined in this study subjected to hybrid treatment were used in a cold worked state, i.e., rolled in accordance with the producer's technology, referred to in this study as the as-delivered state (ADS). In one of the tested variants of the substrate, the layer system for the AlCu2Mg2NiSi alloy (S2) (Table 2) was the system with a substrate heat-treated in the precipitation hardening process (with oversaturation at 530 °C/1 h and aging at 200 °C/1 h).

Table 2. Investigated variants of the coating–substrate system.

Coating—Substrate System	Denotation	Coating Type	Coating Thickness [μm]	Substrate	Substrate State
-	Al	-	-	EN AW-1050A	ADS ⁽¹⁾
Cu-Al	Cu-Al	Cu	~1	EN AW-1050A	ADS
Cr-Al	Cr-Al	Cr	~1	EN AW-1050A	ADS
Ni _{ch} -Al	NiP-Al	chemical Ni	~1	EN AW-1050A	ADS
Ni-Al	Ni-Al	Ni	~1	EN AW-1050A	ADS
Fe-Al	Fe_1-Al	Fe	~1	EN AW-1050A	ADS
γ'-Al	γ'-Al	Fe ₄ N (γ')	~1	EN AW-1050A	ADS
ε-Al	ε-Al	Fe ₃ N (ε)	~1	EN AW-1050A	ADS
Fe-Al	Fe_5-Al	Fe	~5	EN AW-1050A	ADS
Fe-S1	Fe-S1	Fe	~5	AlCu4Mg1	ADS
Fe-S2	Fe-S2	Fe	~5	AlCu2Mg2NiSi	ADS
Fe-S2	Fe-S2_HT	Fe	~5	AlCu2Mg2NiSi	HT ⁽²⁾
Fe-S3	Fe-S3	Fe	~5	AlZn6Mg2Cu2	ADS
Fe-S4	Fe-S4	Fe	~5	G-AlMg7	ADS

⁽¹⁾ ADS—the as-delivered state, ⁽²⁾ HT—heat treated/precipitation hardened.

2.2. Coatings

Cylindrical and rectangular plate samples with dimensions of $\text{Ø}12 \times 3$ mm and $3 \times 10 \times 20$ mm, respectively, were prepared from the materials described above (Table 1). These samples constituted the substrates. The substrates were mechanically processed by grinding with 1000-grade sandpaper in order to obtain a uniform surface with relatively low roughness. Metallic coatings were electrochemically plated on the as prepared substrates. Variants of the coating–substrate systems are given in Table 2. In two cases, iron coatings on aluminum were preliminarily nitrided in order to obtain a coating variant with well-defined iron nitride, i.e., of the ϵ or γ' type (Table 1, variant γ' -Al ϵ -Al).

In the initial, preliminary stage of the study, the diffusion of nitrogen in technically pure aluminum (Al) was investigated in a few variants of the coating–substrate model system, in which thin (approx. 1 μm) coatings of metals such as chromium, copper, nickel (deposited by chemical and electrochemical methods), and iron were applied in order to choose the optimal coating–substrate variant for further investigation. The metallic coatings were produced using the electrochemical method, in accordance with the standard procedure available in the subject literature [42], preceded by the removal of the passive aluminum oxide layer as an effective protection against re-passivation. Due to the fact that the results of the preliminary examination showed a beneficial effect of iron on the diffusion of nitrogen into the aluminum substrate, the iron coating–alloy substrate system was selected for further research on the nitride diffusion layers on the aluminum substrates produced in hybrid processes (Table 2). Aluminum alloys with different magnesium content varying from ca. 0.75 to 7 wt.% of magnesium, listed in Table 1, were used as the base material. Iron is a metal that is easily nitrided in gas nitriding processes, in which layers of iron nitrides can be produced with precisely controlled chemical and phase composition and, as a result, with the intended performance properties. The thickness of iron coatings applied on alloy substrates did not exceed 5 μm . In order to determine the influence of the phase composition of the nitride layers on the diffusion of nitrogen into aluminum, variants of aluminum substrates coated with γ' and ϵ -type iron nitride were prepared (Table 2). On AlCu2Mg2NiSi alloy (S2) substrates, exploratory tests were carried out on the influence of the substrate condition after heat treatment in the precipitation hardening process.

2.3. Thermo-Chemical Treatment

In the second stage of the hybrid processing, the substrates with metal coatings were gas nitrided at a temperature of 530 $^{\circ}\text{C}$ for 10 h. This temperature was selected as the maximum acceptable, taking into account the relatively low melting point of the AlCu4Mg1 alloy (S1) [9]. Nitriding was carried out in an atmosphere of 5N ammonia, which ensures that gas contamination with trace of oxygen is at the level of a maximum of 2 ppm. The processes were carried out in a device equipped with a quartz retort, a gas supply installation, and equipment with an appropriately high tightness class. The aim of these precautions was to limit as much as possible the contamination of the nitriding atmosphere with oxygen and, as a result, to limit the risk of oxygen access to the aluminum substrate and thus to avoid its re-oxidation. It should be noted that in the case of the nitriding of substrates covered with a nitride-forming metal coating, including iron, the process transforms the coating into a nitride layer through which the nitrogen actually migrates to the proper aluminum substrate. To eliminate the risk of spalling of the coatings from the substrate during sample heating and cooling, the rate of these operations was controlled by extending their time to 1 h for heating and 5 h for cooling.

2.4. Methods

The investigation of the nitriding effect on the examined materials was based on the near-surface zone chemical composition analysis using Secondary-Ion Mass Spectroscopy (SIMS), which allows us to determine the distributions of nitrogen and other elements. The tests were performed in a Cameca IMS6F spectrometer (Cameca, Gennevilliers, France). SIMS measurement was conducted using a cesium (Cs^+) primary beam, and secondary

ions as MeCs⁺ clusters were analyzed. The method of measuring nitrogen as NCs⁺ and oxygen as OCs⁺ clusters has been described elsewhere [43].

Nitrided aluminum substrates precoated with metal surface layers were subjected to the examination of microstructure, surface morphology, chemical composition, phase composition, and selected properties such as hardness, adhesion, and wear resistance.

Metallographic examinations were carried out using a Reichert metallographic microscope, type MeF-2 (Vienna, Austria). Observations were performed in reflected polarized light at magnifications ranging from 50 to 1000 times. The surface morphology of the samples was observed in a scanning electron microscope (SEM) using Hitachi devices type S-3500N (Tokyo, Japan) and Axia Chemi SEM Thermo Fisher Scientific (Waltham, MA, USA) apparatuses. Surface scans and point measurements of elemental content were also performed using energy dispersive spectroscopy microanalysis (EDS). The phase composition of the gas nitrided aluminum substrates was determined using X-ray diffraction (XRD). Measurements were carried out on a Rigaku SmartLab 3 kW diffractometer (Tokyo, Japan). For the apparatus, the radiation source was a Cu K α cathode and a wavelength of 1.5418 Å, with operating parameters of U = 40 kV and I = 30 mA. The Bragg–Brentano measuring geometry was used with a measuring step of $\Delta 2\theta$ 0.02°.

Selected mechanical properties of the produced layers were also tested, including surface hardness and wear resistance. Martens universal hardness was measured using the Depth Sensing Indentation (DSI) method using a Mikrohardnes tester from CSEM (Switzerland). A Vickers indenter and loads from 10 to 30 N were used. Frictional wear resistance tests were carried out using the disc-on-block method under sliding friction conditions, using an Amsler type A-135 device. The counter-body was a $\varnothing 40 \times 10$ disc made of heat-treated C45 steel with a hardness of ca. 35 HRC. The tests were carried out under a load of 10 N. The tests lasted 1 h. Linear wear was used as the measure of wear.

3. Results and Discussion

3.1. SIMS Analyses

3.1.1. Metal–Aluminum Substrate Systems

In the first stage of the work, preliminary research was carried out to verify the effectiveness of the proposed method of producing nitride layers on aluminum alloys in a hybrid process, in particular confirming the thesis that nitrogen can diffuse into the aluminum-based substrate through an appropriate outside metallic coating and form a diffusion zone. For this purpose, technically pure aluminum substrates were electroplated with coatings of selected metals. The test used coatings as thin as possible, with a nominal thickness of approximately 1 μm . The coatings were produced by typical electrochemical methods used in practice, with prior treatment aimed to effectively eliminate the passive layer on the substrate. The as-prepared substrates were subjected to the gas nitriding process at a temperature of 530 °C and a time of 10 h in a partially dissociated 5N ammonia environment (with dissociation approx. 30%). The effects of nitriding were assessed based on the analysis of nitrogen distributions in the substrate determined by the SIMS method. The test results are shown in Figure 2.

The SIMS analyses of the nitrogen distribution measurements clearly confirm that in the case of the aluminum substrate subjected to gas nitriding in as-delivered state, the nitrogen is extremely effectively blocked by an only ca. 2 nm [44] thick natural Al₂O₃ passive film. However, once the oxide layer is electrochemically removed in the first stage of the hybrid process (Figure 1) and replaced by the metal coating in the second stage, the situation changes. The results show that under the adopted test conditions, nitrogen diffuses into the substrates through metallic coatings on aluminum; however, the maximum nitrogen level and its range vary greatly. Moreover, nitrogen diffuses to a depth of approximately 5 μm even in technically pure aluminum uncovered with a metallic coating. A similar diffusion range, with approximately an order of magnitude higher nitrogen concentration in the substrate, is observed in the case of copper and nickel coatings applied using the electroless chemical method (NiP-Al). Electroplating aluminum

with nickel or iron has a beneficial effect on the diffusion of nitrogen in aluminum with the effect of nickel being the stronger. This is most likely related to the catalytic effect of nickel and iron on the dissociation of ammonia. The nitrogen concentration in the substrate at a depth of approximately 10 μm is approximately two and three orders of magnitude higher in the case of iron and nickel coatings than in uncoated aluminum. The concentration of nitrogen that diffuses through electroplated nickel coating is similar, as in the case of iron coatings, and reaches the level of $10^{23} \text{ at}\cdot\text{cm}^{-3}$. However, in the case of aluminum precoated with chrome, a different effect is observed, as it does not favor the diffusion of nitrogen into the substrate but only increases its maximum concentration. As one can assume, this is related to the formation of a diffusion zone of an intermetallic compound of the Cr-Al type [45], most likely constituting a barrier to nitrogen migration. It should be noted that the different effects of chemical and electroplated nickel coatings are most likely due to their different phase composition; chemical nickel coatings, unlike electroplated nickel coatings, contain, depending on the deposition conditions, from 4 to 12% phosphorus, which comes from phosphorus compounds used in the standard bath for electroless deposition. The chemical nickel coating, after deposition amorphous, crystallizes during heating, creating a eutectic mixture of Ni_3P -type phosphide and nickel with phosphide being the dominant phase. Substrates previously chemically nickel-plated have been successfully used by us in hybrid technologies for producing boride layers on steel based on the diffusion of boron from gas carriers (BCl_3) through the coatings to the substrate [46]; hence, in this work it was assumed that a similar solution in the case of nitriding will be effective. As one can see, nitrogen behaves differently than boron, the reasons for which are unclear at the current stage of research. As it can be assumed, nitrogen migrates in the substrate, most likely along the grain boundaries [3], creating locally fine, nanometric nitride precipitates in the diffusion zone. It cannot be ruled out that under the iron nitride layer, where the nitrogen concentration reaches the highest values, a more or less continuous thin zone or local areas of the more thermodynamically stable aluminum nitride may be formed. Experimental confirmation of this hypothesis will require further in-depth TEM research, going beyond the scope and goals of this work.

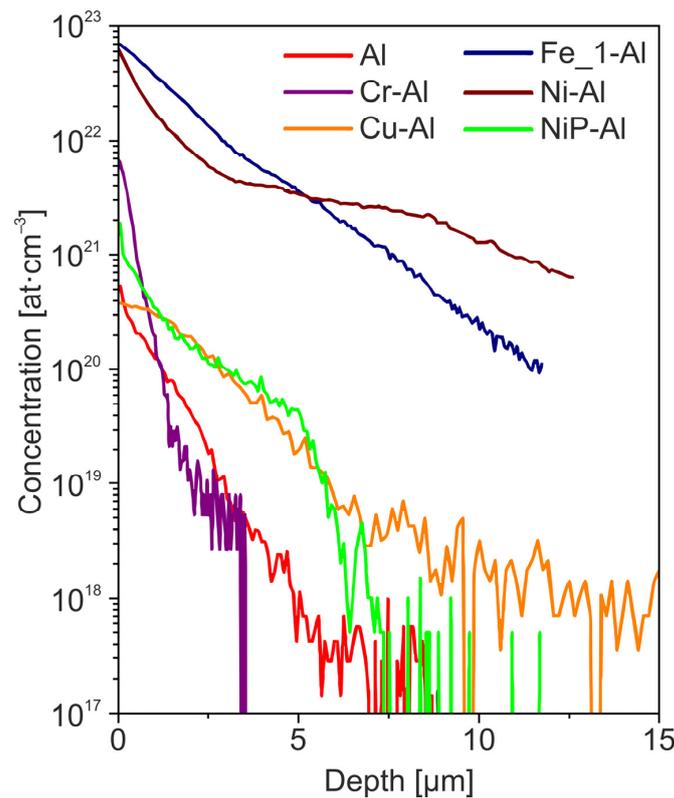


Figure 2. Nitrogen distributions in the substrate of gas-nitrided (530 °C/10 h) technically pure aluminum samples previously covered with coatings of selected metals (SIMS).

3.1.2. Iron Nitride–Aluminum Substrate System

The analysis of the nitrogen distributions presented in Figure 2 indicates that the variants of aluminum substrates with a nickel and iron coating meet the assumptions of the proposed hybrid processing concept and enable obtaining a nitrogen diffusion zone in the substrate. The assumption of the proposed concept was also to create diffusion layers in a hybrid process, the outer zone of which will be a layer of metal nitride produced from the coating metal predeposited on the aluminum substrate. Although both metals, as well as nickel, form nitrides, the model system of iron coating–aluminum substrate was chosen for the further research due to the ease of production and control of the iron nitriding in gas process, resulting in the desired nitrogen content and phase composition of the nitride layers. During nitriding, such a system relatively quickly transforms into an iron nitride layer–aluminum substrate system. Depending on the conditions of the nitriding process, in particular the value of the nitrogen potential, the process will result in a different phase composition of the layer (ϵ , γ'), which may have a significant impact on the transport of nitrogen to the aluminum substrate. In order to select optimal nitriding conditions for the diffusion of nitrogen through the nitride layer into the aluminum substrate, two model systems nitrided at 530 °C were subjected to an analysis of nitrogen diffusion in the substrate, in which an ϵ -type iron nitride layer was produced on an aluminum substrate in one variant (ϵ -Al), and in the other variant a (γ' -Al) γ' -type nitride layer (Table 2). The results of this experiment are shown in Figure 3. The analysis of nitrogen distribution in the substrate clearly shows that due to the clearly higher nitriding kinetics, the processes should be carried out in conditions that lead to the formation of ϵ -type iron nitride layers on the aluminum substrate. This nitride, due to its relatively high solubility and, as a result, high nitrogen supply, paired with and may favor the transport of nitrogen to the substrate.

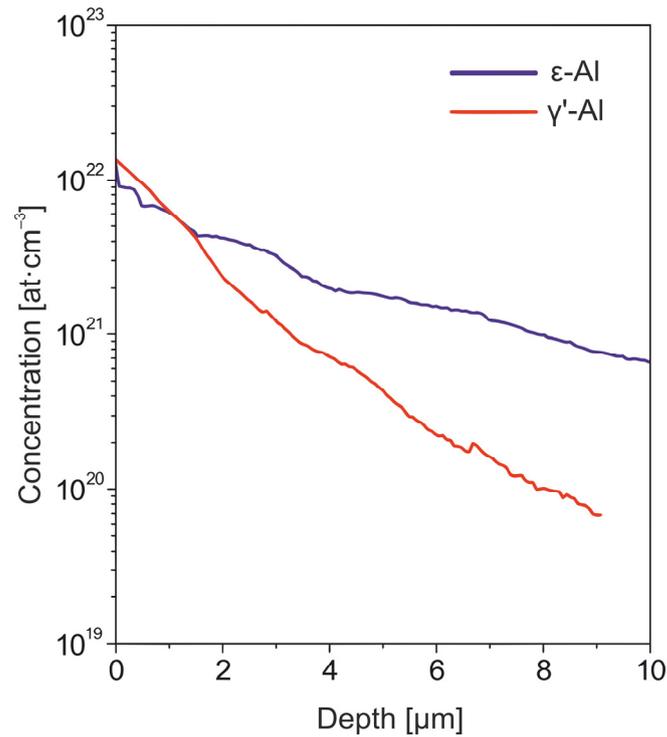


Figure 3. Nitrogen distributions in the aluminum substrate in gas-nitrided (530 °C/10 h) technically pure aluminum samples previously covered with ϵ and γ' iron nitride coatings (SIMS).

The nitrogen distributions obtained by the SIMS method for substrates of three commercial aluminum alloys, technically pure aluminum and a model aluminum–magnesium alloy, hybrid processed in the gas nitriding process at 530 °C for 10 h, and previously covered with electroplated iron coatings, are shown in Figure 4.

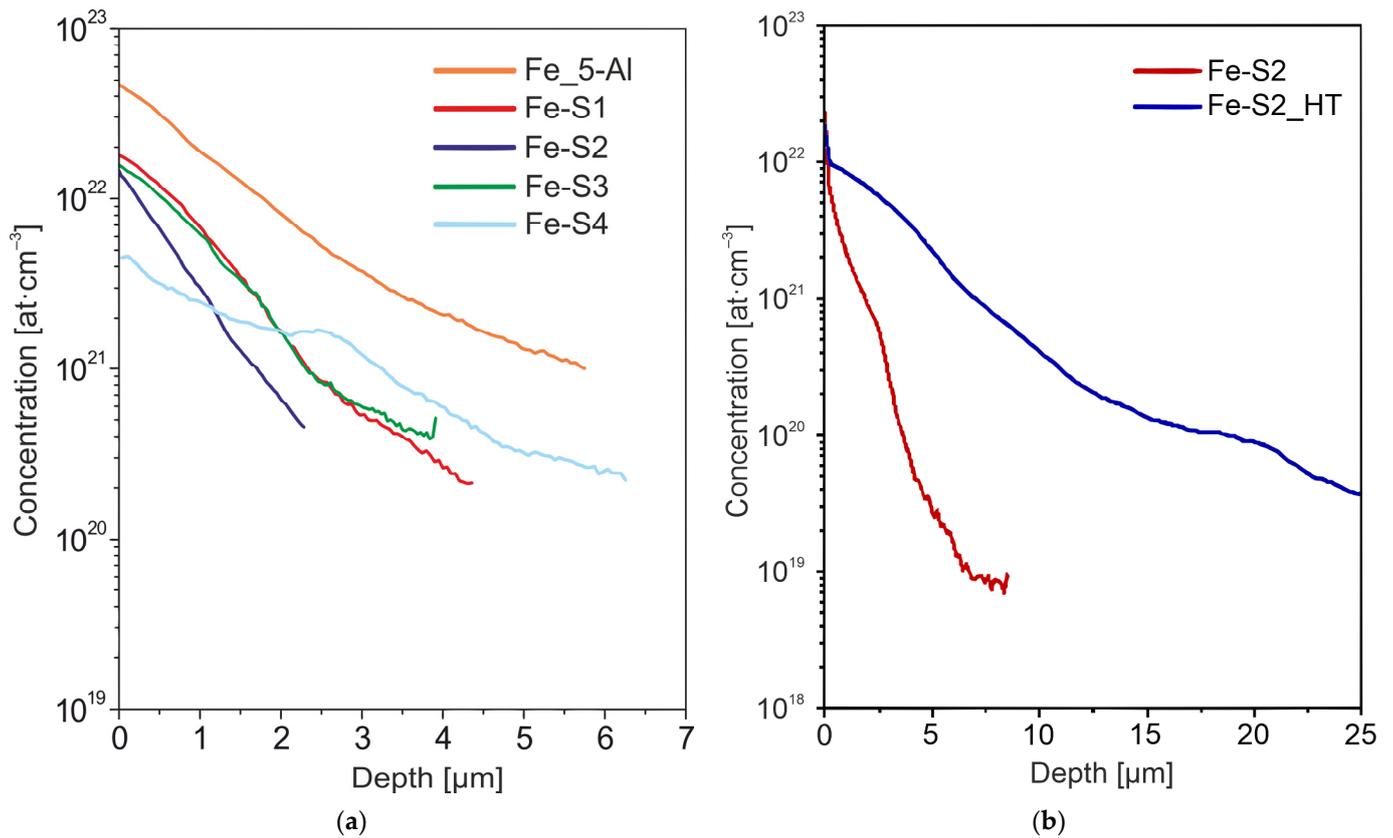


Figure 4. SIMS nitrogen distributions in the substrate: (a) aluminum alloys and aluminum of technical purity, covered with an iron coating and gas nitrided (530 °C/10 h); (b) AlCu₂Mg₂NiSi alloy as-delivered state (ADS) and after preliminary heat treatment–precipitation hardening (HT), covered with a coating iron and gas nitrided (530 °C/10 h).

As can be seen (Figure 4a), the highest nitrogen concentrations are achieved in the aluminum (Al) substrate. The presence of magnesium in all durals, contrary to its beneficial effect on the kinetics of aluminum nitride formation, AlN, in glow nitriding processes [9] described in the literature, limits the concentration and range of nitrogen diffusion in the substrate compared to aluminum. Only for the G-AlMg7 alloy with highest magnesium content (Fe-S4 variant), the diffusion range seems to be comparable to aluminum, but the nitrogen concentration reaches levels that are an order of magnitude lower. In turn, research on the influence of the substrate condition on the nitriding efficiency conducted on the AlCu₂Mg₂NiSi (S2) alloy, the results of which are shown in Figure 4b, shows that the preliminary precipitation hardening heat treatment of the substrate has a significant impact on the diffusion of nitrogen in the aluminum substrate. Analysis of the distribution of other elements present in the aluminum substrate of nitrided aluminum alloys allows for the detection of increased oxygen concentration (Figure 5a).

In the zone of the substrate adjacent to the outer layer of the iron nitride, next to aluminum, a much higher concentration of magnesium than the nominal content in the alloy is also observed, and its level clearly correlates with the magnesium content in the aluminum alloy. The segregation of magnesium in the near-surface zone of aluminum substrates is most likely the result of selective back diffusion of magnesium from the core to the surface, where it reacts with oxygen which may be supplied in trace amounts in the nitriding atmosphere. According to the mechanism described by Kimura et al. [45], magnesium will also reduce aluminum oxide Al₂O₃ which may locally occur as persisting residues of the passive layer fragments. As a result of the back diffusion of magnesium and its oxidation reaction, magnesium oxide, MgO, is formed, the presence of which in the near-surface zone of aluminum substrates may be the reason for the reduced kinetics of the

magnesium diffusion observed in alloyed substrates containing magnesium (Figure 4). The magnesium content in the alloy most likely increases the share of oxide in the near-surface zone, intensifying the influence of magnesium on the kinetics of nitrogen diffusion in the substrate, which is reflected in the behavior of the G-ALMg7 alloy (Figure 4a). It should also be noted that the reduction of Al_2O_3 oxide with magnesium leads to the formation of pure aluminum “in statu nascendi”, which undoubtedly favors the reaction with atomic nitrogen diffusing to the substrate and the creation of the AlN nitride effect [45]. However, it cannot be ruled out that nitrogen in the diffusion zone combines not only with aluminum but also locally with magnesium, forming magnesium nitride, Mg_3N_2 [47]. The recent advanced transmission electron microscopy investigations provide the evidence of the Mg_3N_2 -type magnesium nitride formation in the layers produced in plasma nitrided aluminum–silicon alloy substrate [48].

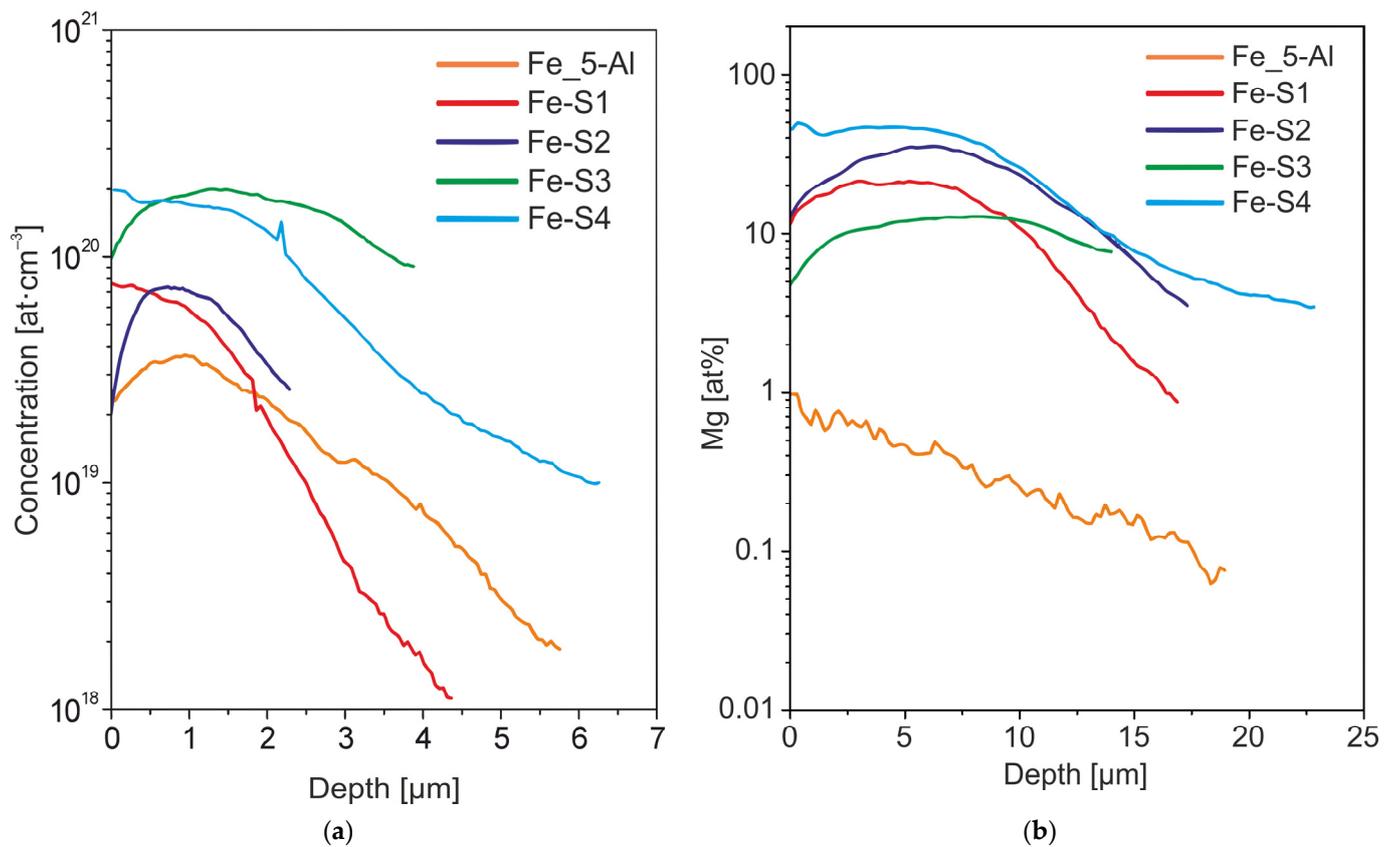


Figure 5. Distributions of oxygen (a) and magnesium (b) in the substrate in gas-nitrided (530 °C/10 h) aluminum alloy and technical grade aluminum samples previously covered with an iron coating.

3.2. Microstructure and Surface Morphology of Layers

The surface morphology of the examined aluminum substrates with an ϵ -type iron nitride layer produced in a hybrid process is shown in Figure 6, while Figure 7 shows the microstructures of the cross-sections of these substrates. It can be concluded that the surface morphology of the layers is diverse. In the initial as-deposited state, the iron coating surface composed of fine crystallites exhibits uniform appearance (Figure 6a). The iron nitride layers have a more or less heterogeneous structure and differ in appearance depending of the substrate variant. Thus, e.g., in the of S3 substrate (Figure 6e), the relatively coarse nitride particles form the layer, while for the S4 substrate (Figure 6f), the surface is relatively smooth. The layers' surface morphology is characterized by a large surface development, which results from the fact that there are bulges of various sizes and shapes formed on the surface of the layer. The bulges are most accentuated for S1 substrate (Figure 6c). The cracking and detachment of the bulges from the layer reveals fragments of the substrate of

different size (Figure 6b,d,f). It is worth noting that in the case of the layers on the G- AlMg7 (S4) alloy, with the highest magnesium content, significant spalling covering approximately 50% of the surface of the layer was observed. Analysis of the cross-sections of the tested samples (Figure 7) shows that as-deposited iron coating (Figure 7a) exhibits relatively low development, uniform thickness, and good adherence to the substrate. The cross-section metallographic observation shows low adhesion of the iron nitride layers manifested by the occurrence of areas of layer spalling which are extensive in the case of the G- AlMg7 (S4) alloy (Figure 7f) and localized in the case of aluminum substrate (Figure 7b). In iron-precipitated substrates subjected to gas nitriding, the iron nitride layers as produced appear to be more or less corrugated (Figure 7b–e). The corrugations are the most accentuated in the case of the low-magnesium dural (S2) substrate (Figure 7c). Such a phenomenon can be interpreted in terms of the accommodation of the large difference in thermal expansion of the coating and the substrate, where the aluminum base substrate expands more than the coating material. This leads to plastic deformation (stretching) of the iron coating heated to the nitriding temperature and then to the as-produced iron nitride layer corrugation during cooling after the process due to greater shrinkage of the substrate. As can be seen on the investigated sample cross-section shown in Figure 7, in the case of alloyed substrates (Figure 7c–f), dark zones of uneven thickness are formed under the iron nitride layer. X-ray phase analysis (Figure 8), apart from the presence of F_3N -type iron nitride in the outer layer within the detection limits, does not indicate the presence of AlN aluminum nitride layers in the substrate. For the dural type substrates (S2–S3) (Figure 7c–e), the thickness of these zones under the iron nitride layer increases with the magnesium content in the alloy, which is believed to be related to the increased level of concentration and diffusion range of magnesium, as well as oxygen in the near-surface zone of the individual alloy substrates revealed by the SIMS analysis (Figure 5). Thus, the thickest dark zones, locally up to even ca. $15\ \mu\text{m}$ large, occur in the zinc (S3) dural (Figure 7e). The X-ray microanalysis (EDS) in the dark zone area (Figure 9) confirms the simultaneous presence of oxygen, magnesium, and aluminum. This is also confirmed by tests of the chemical composition of the substrate where the outer layer of nitrides was exfoliated (Figure 10). Referring these observations to the above-cited works by Kimura et al. [49], it can be concluded that in the structure of the dark zones in alloy substrates next to aluminum, there is most likely magnesium oxide of the MgO type or a mixed oxide of the Al_2MgO_4 type. Observation of the morphology of the fragment of the substrate under the iron nitride layer, exposed as a result of flack out of the nitride zone fragment (Figure 10), reveals that the oxide zone is covered with a network of cracks, which indicates its poor mechanical properties. It is worth noting the heterogeneous appearance of the surface of the oxide zone at the spatter site, including the presence of lighter areas, morphologically different from the dark areas covered with the mesh, as well as the presence of small light precipitates, most probably nitrides. However, the mechanism of nitrogen transport through the oxide zone into aluminum substrates requires further advanced research beyond the scope of this work, although it seems reasonable to suggest that the discontinuities in the oxide zone may constitute pathways for nitrogen access to the alloyed aluminum substrate [33]. As can be expected, due to the selective core diffusion of magnesium (an alloying element of all tested durals) and its local reaction with oxygen, the formation of magnesium oxide zones under the nitride layer in the aluminum substrate is a phenomenon that negatively affects the potential application aspects of the produced layers. It should be noted that the phenomenon of magnesium giant segregation in the near-surface zone was earlier reported by other authors [50]. It was also observed as manifested by the formation of large oxide areas on nitrided components in the case of aluminum alloy machine parts subjected to nitriding processes under glow discharge conditions in an industrial device [35]. Some promising attempts to solve this problem in view of an industrial implementation of the technology were reported. Thus, some selected properties of diffusion iron nitride layers produced on a commercial AlCu2Mg2NiS aluminum alloy from the dural group for aviation applications were examined and the results are described in the next chapter.

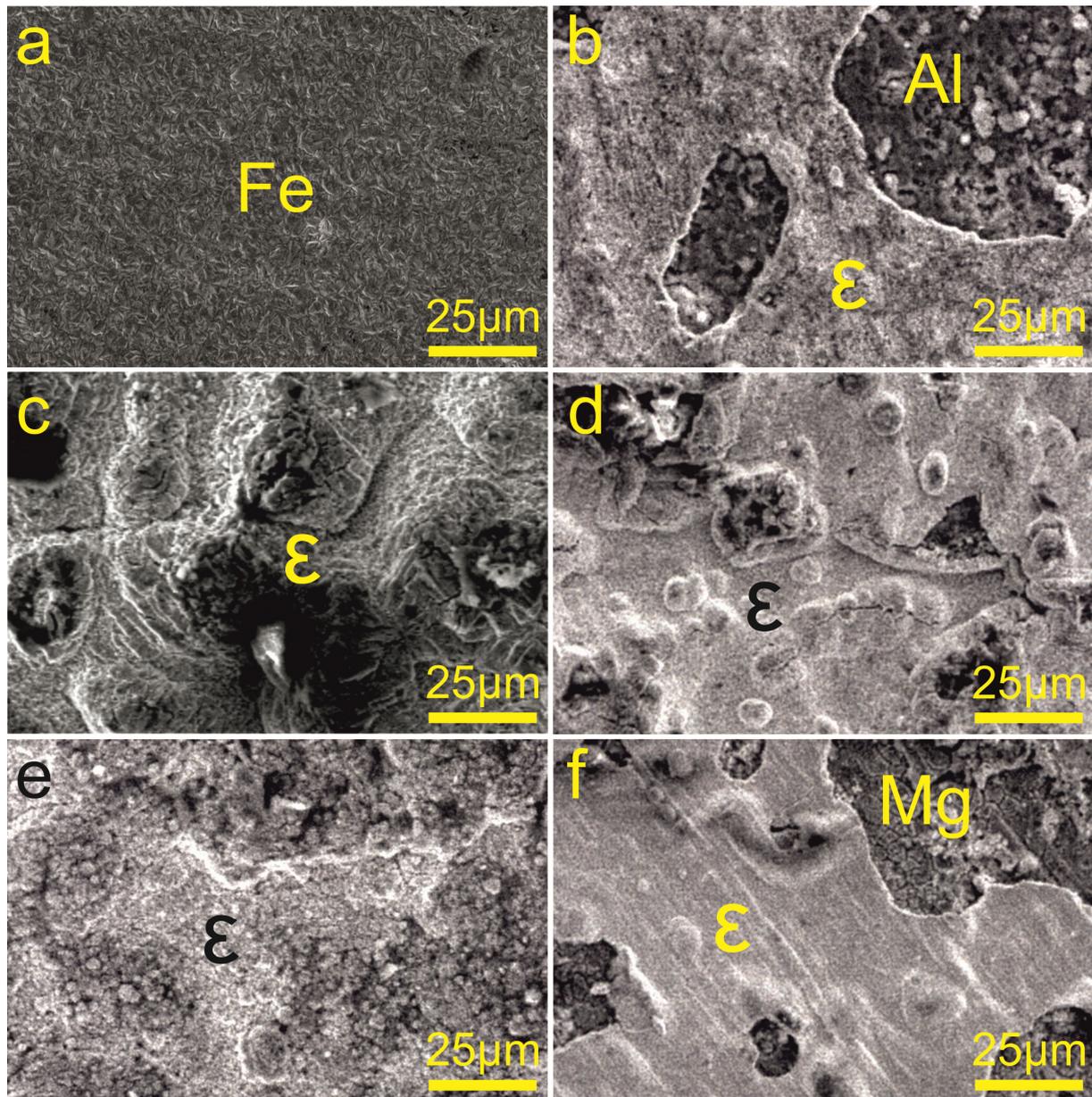


Figure 6. Surface morphology (SEM) of aluminum substrates covered with an iron coating (a) in the initial as-deposited state and (b–f) after gas nitriding in the hybrid method on (b) technical aluminum EN AW-1050A (A1); (c) AlCu4Mg1 alloy (S1); (d) AlCu2Mg2NiSi alloy (S2); (e) AlZn6Mg2Cu2 alloy (S3); (f) G-AlMg7 alloy (S4).

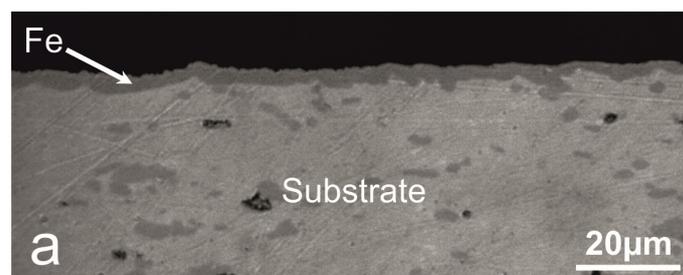


Figure 7. Cont.

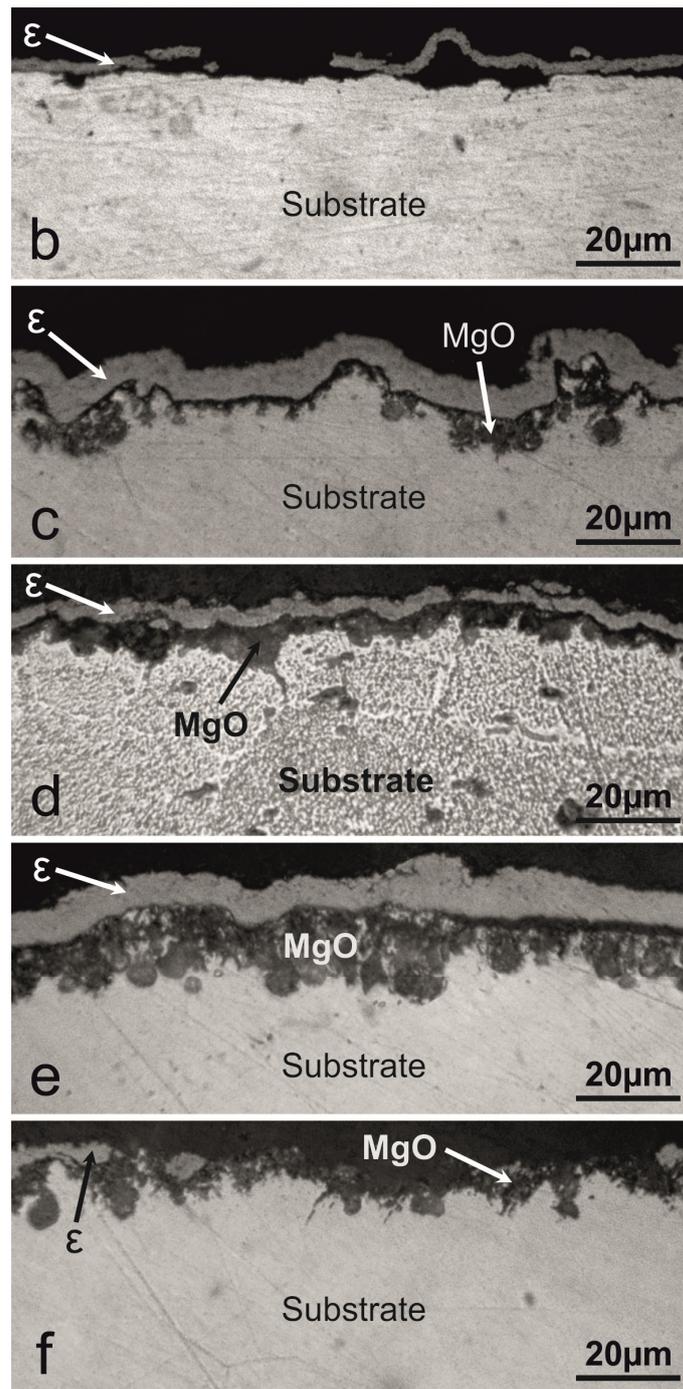


Figure 7. Cross section metallography of aluminum substrates covered with an iron coating (a) in the initial as-deposited state and (b–f) after gas nitriding in the hybrid process on (b) technical aluminum EN AW-1050A (A1); (c) AlCu4Mg1 alloy (S1); (d) AlCu2Mg2NiSi alloy (S2); (e) AlZn6Mg2Cu2 alloy (S3); (f) G-AlMg7 alloy (S4).

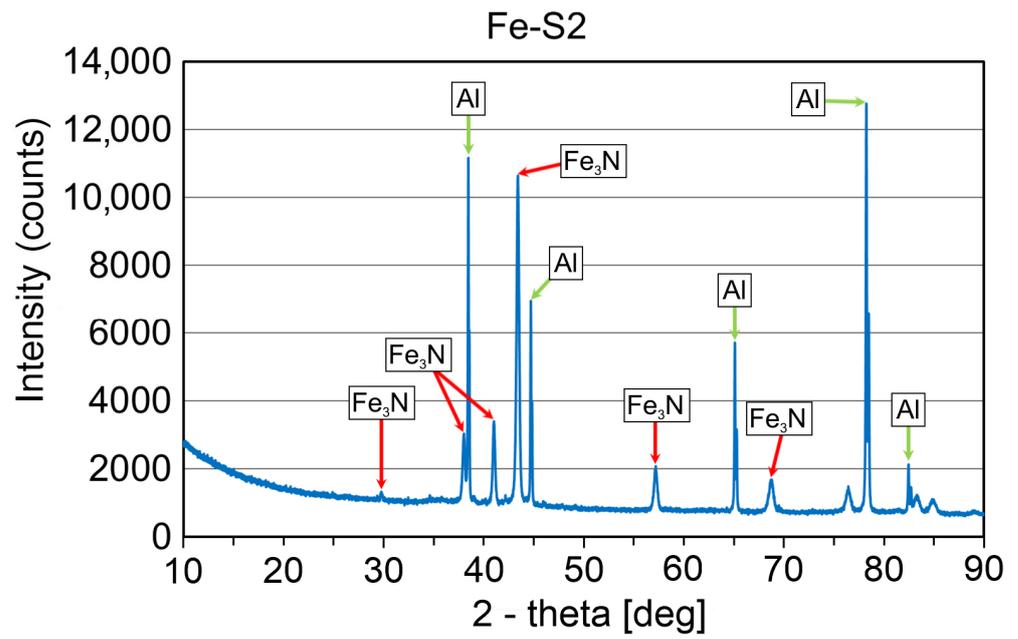


Figure 8. The X-ray diffraction analysis for gas-nitrided (530 °C/10 h) AlCu2Mg2NiSi alloy previously covered with an iron coating.

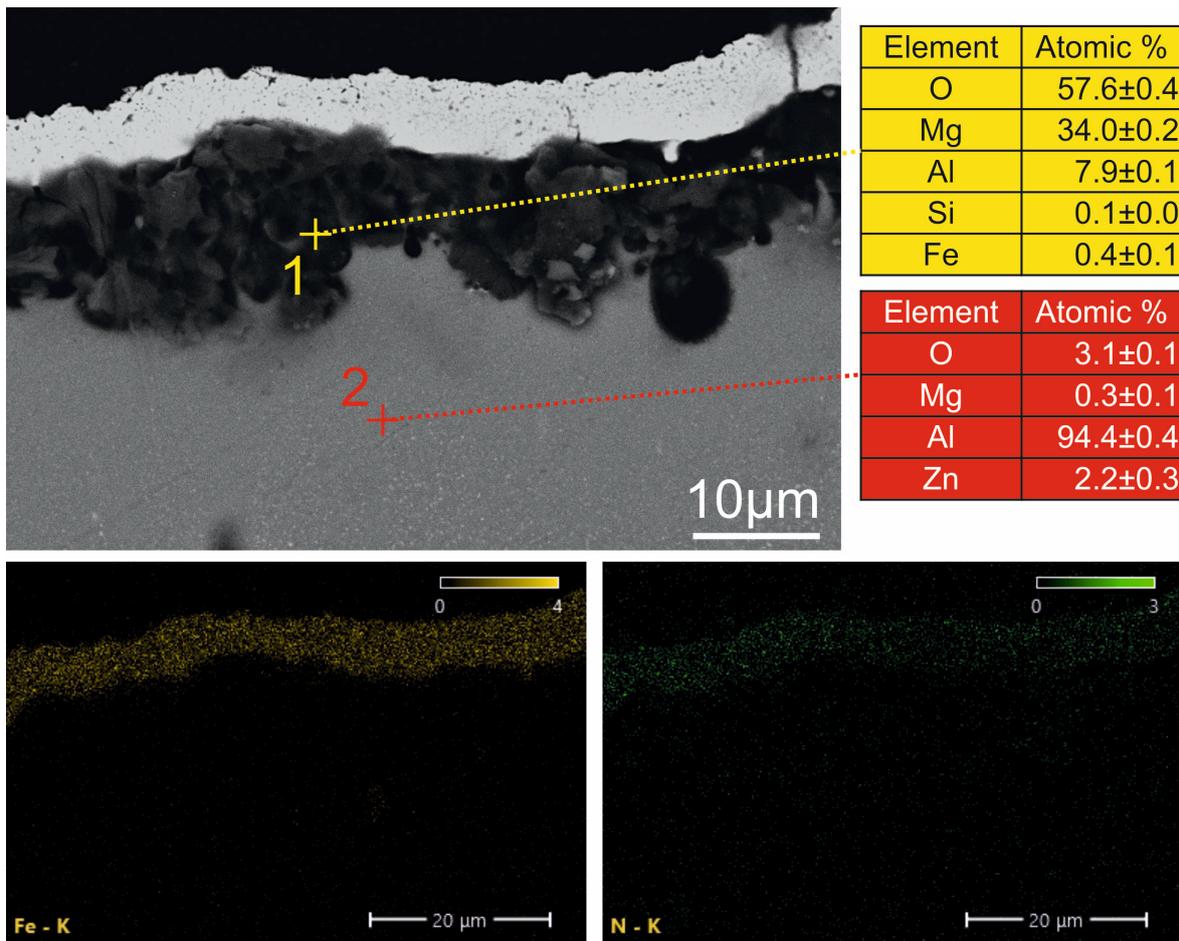


Figure 9. Cont.

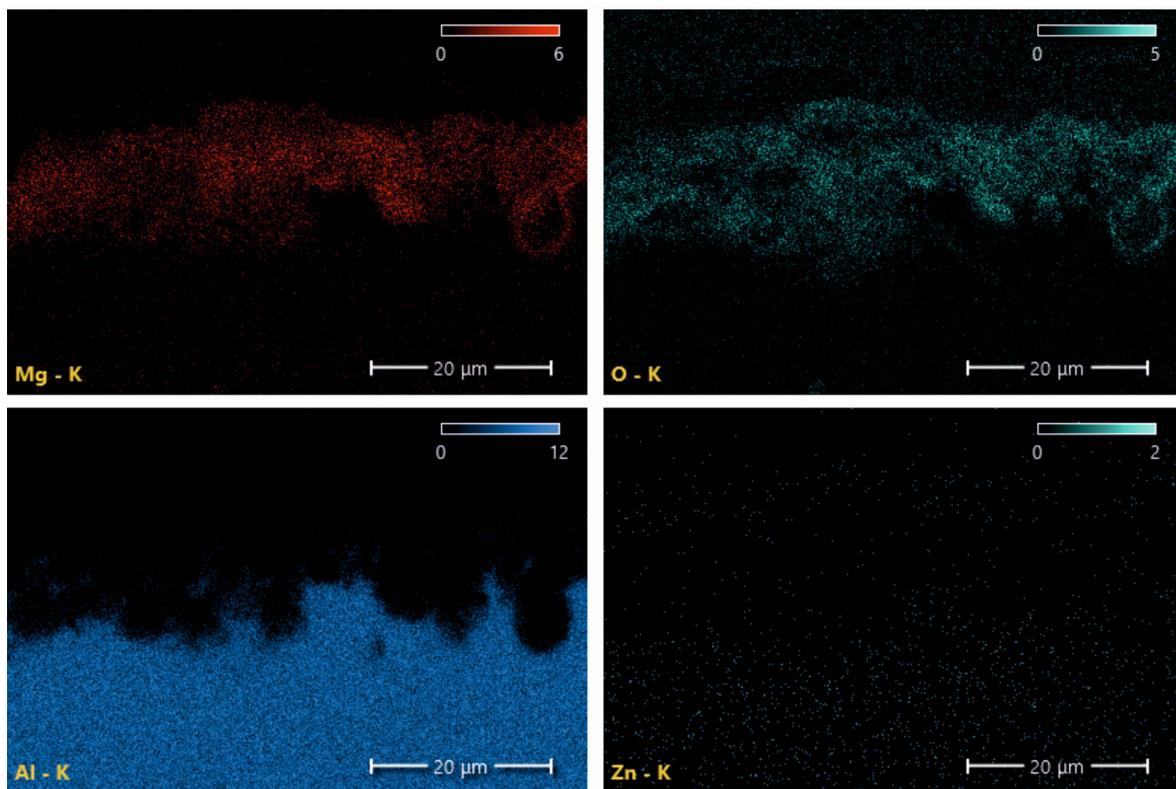


Figure 9. Chemical composition and element distribution in the dark zone in the aluminum substrate adjacent to the outer iron nitride layer for gas-nitrided (530 °C/10 h) AlZn6Mg2Cu2 alloy previously covered with an iron coating (EDS point and surface X-ray microanalysis).

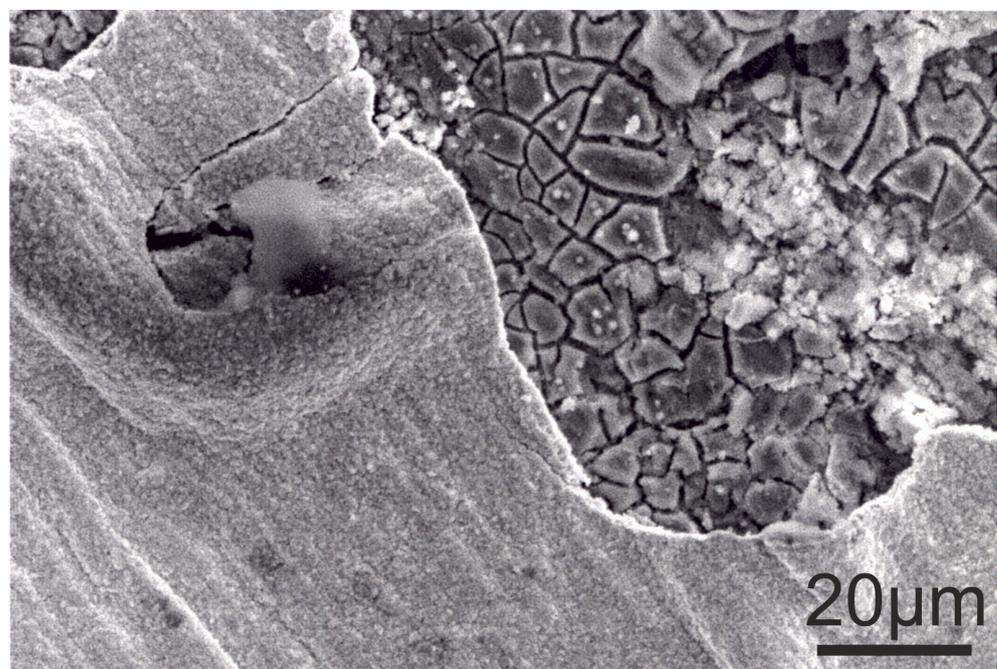


Figure 10. View (SEM) of the substrate in the area where the outer layer of iron nitride produced in hybrid process on the G-AlMg7 alloy has been exfoliated.

3.3. Properties of Layers

The results of the property tests, including surface hardness, layer adhesion, and frictional wear resistance, are shown in Figures 11–13. The results of surface hardness measurements (Figure 11) show that the nitriding process of the AlCu2Mg2NiSi alloy previously covered with an iron coating results in a decrease in hardness from 187HV0.1 to 70HV0.1 for the core and from 207HV0.1 to 66HV0.1 for the surface as a result of the alloy softening during nitriding. It should be noticed that the formation of the diffusive iron nitride layer with a hard outside zone of the ϵ -type iron nitride does not result in surface hardening. The reason for this decline is the presence of a much less hard and brittle oxide layer under the hard layer of iron nitrides, which undoubtedly reduces the load-bearing capacity of the substrate under the layer and, as a result, may lead to the so-called ice-on-mud effect, which involves the collapse of a layer under a relatively low load. The scratch test (Figure 12) reveals spalling of the layer in the vicinity of the scratch, indicating poor adhesion of the nitride layer to the magnesium oxide zone in the substrate. The roll-on-block wear test under 10 N load shows an approximately 70% decrease in final wear value (Figure 13). In summary of the property examination, it should be concluded that diffusion layers of iron nitrides on an alloy from the AlCu2Mg2NiSi dural group show the potential to improve tribological properties also under high surface loads, provided that the problem of low load bearing capacity caused by the formation of zones in the aluminum substrate is eliminated. The only effective solution seems to be the selection of a precipitation hardening alloy that does not contain magnesium, e.g., EN AM-92205 (EN AM-Al Ti10 (B)), a type from the Al-Ti group. An interesting direction in the development of the hybrid method would also be to design, by analogy to steel, special aluminum alloys dedicated to nitriding with micro-additions of nitride-forming alloy elements, intended to produce fine nitrides in the diffusion zone, and thus to obtain a hardness gradient, between the hard outer nitride layer and a relatively low-hardness substrate.

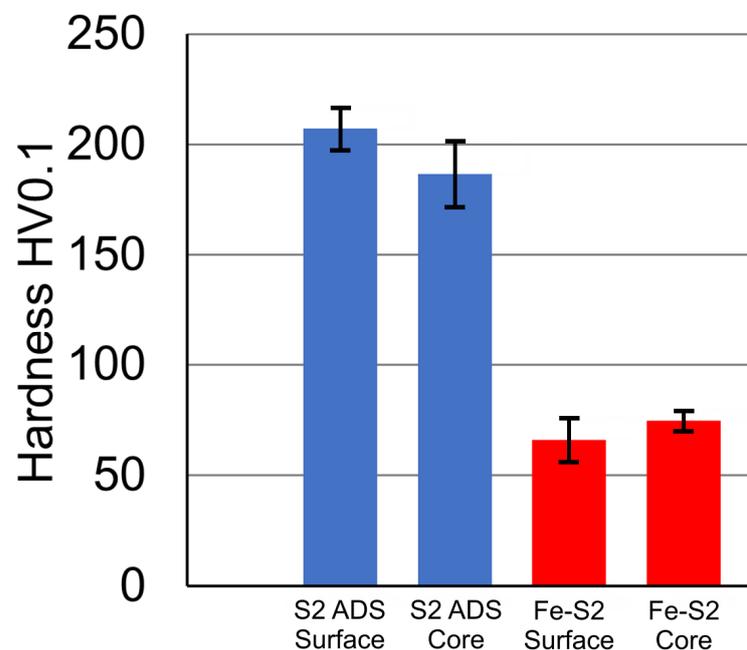


Figure 11. Hardness HV0.1 of the surface and core of the AlCu2Mg2NiSi alloy covered with an iron coating for as-delivered (ADS) and gas-nitrided (530 °C/10 h) variants.

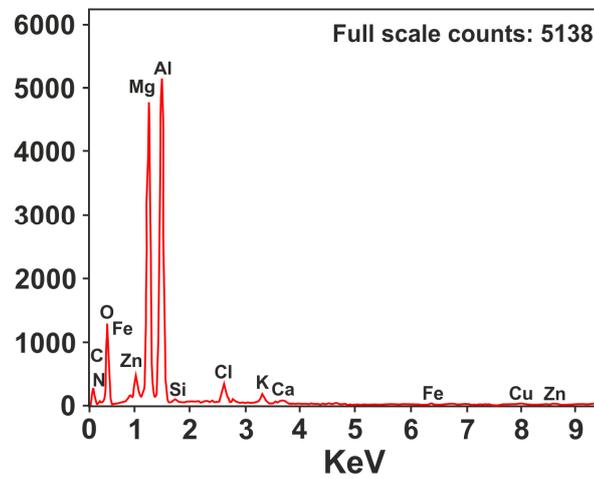
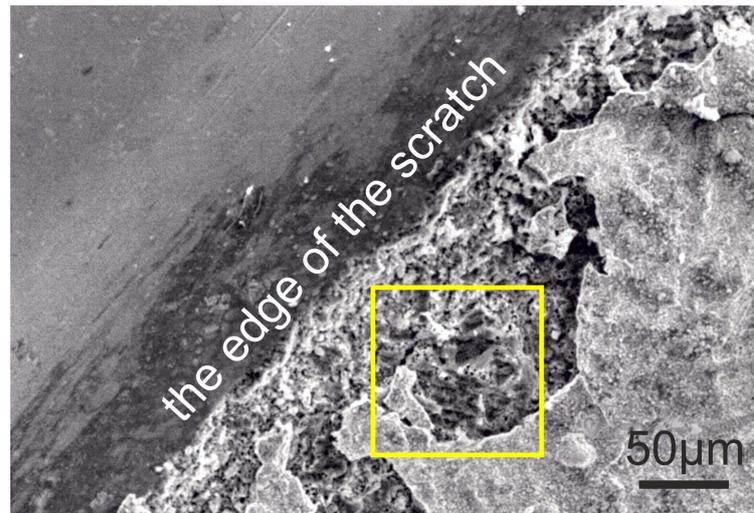


Figure 12. View of the scratch edge vicinity: scratch test of gas-nitrided (530 °C/10 h) AlCu2Mg2NiS aluminum alloy previously covered with an iron coating and EDS surface analysis of the subsurface zone exposed after spalling off the outer iron nitride coating.

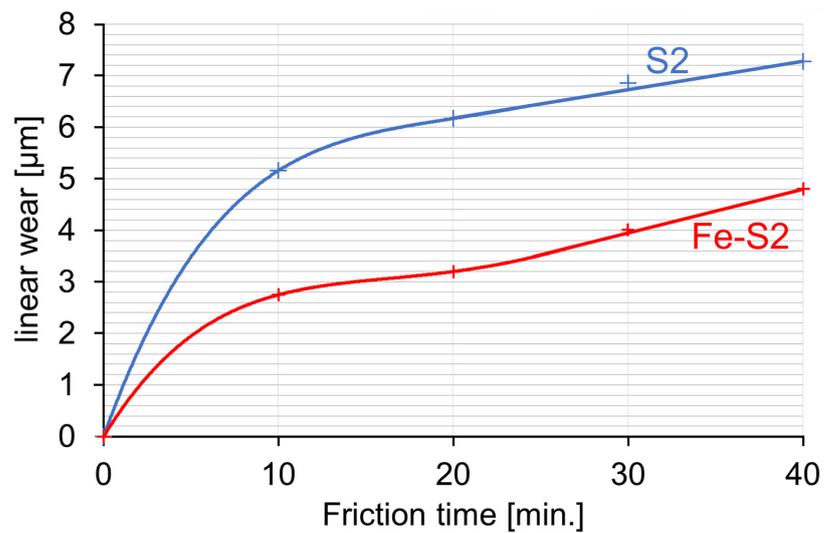


Figure 13. AlCu2Mg2NiS alloy linear wear in the roll-on-disc test under 10 N load alloy in as-delivered state ADS (S2) and after hybrid treatment (Fe-S2).

4. Conclusions

1. The results of the work prove that a surface treatment of aluminum substrates, consisting of subsequent electrochemical processes aimed to remove the passive aluminum oxide layer and then protect the substrate against its re-oxidation by plating with a coating of one of such metals as chromium, copper, nickel and iron, combined with gas nitriding, is an effective hybrid method enabling the diffusion of nitrogen through the protective coating into the aluminum substrate, resulting in the formation of a diffusion layer. The most favorable nitriding effects are obtained at 530 °C/10 h in the case of electroplated iron and nickel coatings, for which the nitrogen range in the substrate reaches approximately 12 µm and its concentration in the diffusion zone is at the level of 1023 at·cm⁻³. An important measure ensuring the efficiency of nitriding, by reducing the risk of the re-passivation of aluminum, is the use of high-purity ammonia in the processes, which guarantees limiting gas contamination with traces of oxygen at a maximum of 2 ppm.
2. Treatment of aluminum substrates in a hybrid process combining in sequence the removal of the passive aluminum oxide layer, iron coating deposition, and gas nitriding carried out at a temperature of 530 °C for 10 h, enabling the diffusion of nitrogen into the substrate, and the nitriding of the iron coating, is an effective method of producing diffusion nitride layers on aluminum substrates with a surface the Fe₃N-type iron nitride zone and a nitrogen diffusion zone in the substrate.
3. In the case of the hybrid processing of iron-precoated dural-type aluminum alloy substrates, the formation of a magnesium oxide zone, most likely of the MgO type, is observed in the substrate near-surface zone. The thickness of this zone, which can reach several µm, depends on the magnesium content in the alloy. The formation of the magnesium oxide zone is the result of the selective diffusion of magnesium towards the surface, where it reduces the aluminum oxide residues of the passive coating and reacts with oxygen, present as trace contamination of the ammonia atmosphere. Although the magnesium oxide zone decreases the hardness and adhesion of the diffusive layers of iron nitride with a nitrogen diffusion zone in the substrate produced on the AlCu2Mg2NiS dural, improved wear resistance by approximately 70% is observed, as demonstrated in the roll-on-block test, under loads up to 10 N.
4. The suggested direction for further research for obtaining the perspectives for industrial application of the proposed hybrid treatment of aluminum alloys using gas nitriding requires, first of all, eliminating the problem of the near-surface segregation of magnesium. It may be achieved by selecting an appropriate aluminum alloy that does not contain magnesium, e.g., from the Al-Ti group, which would be best for precipitation hardening in order to increase the load-bearing capacity of the substrate and thus reduce the risk of the so-called ice-on-mud effect characteristic for hard layer–soft substrate systems.

Author Contributions: Conceptualization, M.T., J.S. and T.W.; methodology, M.T., J.S., R.J., S.M. and R.D.; validation, M.T.; formal analysis, M.T., J.S., R.J., S.M. and R.D.; investigation, M.T., R.J., S.M. and R.D.; resources, M.T.; data curation, M.T., R.J., S.M. and R.D.; writing—original draft preparation, M.T.; writing—review and editing, J.S. and T.W.; visualization, J.S.; supervision, T.W.; funding acquisition, M.T. All authors have read and agreed to the published version of the manuscript.

Funding: This study was supported by the Faculty of Materials Science and Engineering of the Warsaw University of Technology.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Dong, H. (Ed.) *Surface Engineering of Light Alloys*; Woodhead Publishing Limited: Oxford, UK; Cambridge, UK; New Delhi, India, 2010; pp. 323–397.
2. Arai, T.; Fujita, H.; Tachikawa, H. Ion Nitriding of Aluminum and Aluminum Alloys. In Proceedings of the First International Conference Ion Nitriding, Cleveland, OH, USA, 15–17 September 1986; pp. 37–41.
3. Chen, H.-Y.; Stock, H.-R.; Mayr, P. Plasma-Assisted Nitriding of Aluminum. *Surf. Coat. Technol.* **1994**, *64*, 139–147. [[CrossRef](#)]
4. Renevier, N.; Czerwiec, T.; Billard, A.; von Stebut, J.; Michel, H. A Way to Decrease the Aluminum Nitriding Temperature: The Low Pressure Arc-Assisted Nitriding Process. *Surf. Coat. Technol.* **1999**, *116–119*, 380–385. [[CrossRef](#)]
5. Reinhold, R.; Naumann, J.; Spies, H.-J. Plasma nitriding of aluminum alloys. In Proceedings of the Seminar Heat Treatment and Surface Engineering of Light Alloys, Budapest, Hungary, 15–17 September 1999; pp. 341–349.
6. Telbizova, T.; Parascandola, S.; Kreissig, U.; Gunzel, R.; Moller, W. Mechanism of Diffusional Transport during Ion Nitriding of Aluminum. *Appl. Phys. Lett.* **2001**, *76*, 1404–1406. [[CrossRef](#)]
7. Visuttipitukul, P.; Aizawa, T.; Kuwahara, H. Advanced Plasma Nitriding for Aluminum and Aluminum Alloys. *Mater. Trans.* **2003**, *44*, 2695–2700. [[CrossRef](#)]
8. Visuttipitukul, P.; Aizawa, T. Wear of Plasma-Nitrided Aluminum Alloys. *Wear* **2005**, *59*, 482–489. [[CrossRef](#)]
9. Spies, H.-J.; Dalke, A. Nitriding of Aluminium and its Alloys. In *ASM Handbook Volume 4E: Heat Treating of Nonferrous Alloys*; Totten, G.E., Ed.; ASM International: Almere, The Netherlands, 2016; pp. 302–306. ISBN 978-1-62708-112-2.
10. Kanno, I.; Nomoto, K.; Nishijima, P.; Nishiura, T.; Okada, T.; Katagiri, K.; Mori, H.; Iwamoto, K. Tribological Properties of Aluminum Modified with Nitrogen Ion Implantation and Plasma Treatment. *Nucl. Instrum. Methods Phys. Res. B* **1991**, *59–60*, 920–924. [[CrossRef](#)]
11. Blawert, C.; Mordike, B. Plasma Immersion Ion Implantation of Pure Aluminum at Elevated Temperatures. *Nucl. Instrum. Methods Phys. Res. B* **1997**, *127–128*, 873–878. [[CrossRef](#)]
12. Meletis, E.; Yan, S. Formation of Aluminium Nitride by Intensified Plasma Ion Nitriding. *J. Vac. Sci. Technol. A* **1991**, *9*, 2279–2284. [[CrossRef](#)]
13. Hino, H.; Fujita, I.; Nishikawa, M. Nitriding of Zirconium and Aluminium by Using ECR Nitrogen Plasmas. *Plasma Sources Sci. Technol.* **1991**, *5*, 424–428. [[CrossRef](#)]
14. Jarms, C.; Stock, H.-R.; Mayr, P. Nitrieren von Aluminium im Hochfrequenz-Plasma. *HTM J. Heat Treat. Mater.* **1996**, *51*, 113–118. (In German) [[CrossRef](#)]
15. Ebisawa, T.; Saikudo, R. Formation of Aluminum Nitride on Aluminum Surfaces by ECR Nitrogen Plasmas. *Surf. Coat. Technol.* **1996**, *86–87*, 622–627. [[CrossRef](#)]
16. Carpena, E.; Schaaf, C. Laser Nitriding of Iron and Aluminum. *Appl. Surf. Sci.* **2002**, *186*, 100–104. [[CrossRef](#)]
17. Barnikel, J.; Bergmann, H.W.; Reichstein, S. Aufbau und Eigenschaften von lasernitrierten Randschichten auf Aluminiumwerkstoffen. *HTM J. Heat Treat. Mater.* **1998**, *53*, 337–342. (In German) [[CrossRef](#)]
18. Taherkhani, K.; Soltanieh, M. Composite coatings created by new method of active screen plasma nitriding on aluminium alloy 6061. *J. Alloys Compd.* **2018**, *741*, 1247–1257. [[CrossRef](#)]
19. Taherkhani, K.; Soltanieh, M. Investigation of nanomechanical and adhesion behavior for AlN coating and AlN/Fe₂₋₃N composite coatings created by Active Screen Plasma Nitriding on Al 1050. *J. Alloys Compd.* **2019**, *783*, 113–127. [[CrossRef](#)]
20. Taherkhani, K.; Soltanieh, M. Spectroscopy study of composite coating created by a new method of active screen plasma nitriding on pure aluminium. *Surf. Coat. Technol.* **2020**, *393*, 125820. [[CrossRef](#)]
21. Phulera, N.; Kaushik, S.; Kshetri, R.; Kanojia, N.; Rawat, K.; Uniyal, V. Effects of plasma nitriding on mechanical, tribological and corrosion properties of friction stir welded joints of Al 2024. *Mater. Today Proc.* **2021**, *46*, 6726–6732. [[CrossRef](#)]
22. Ma, Z.; Sun, H.; Zheng, H.; Zhao, Y.; Sui, S.; Zhang, C.; Ni, G. Aluminum surface nitriding by an atmospheric-pressure non-thermal plasma technique. *Jpn. J. Appl. Phys.* **2022**, *61*, 026001. [[CrossRef](#)]
23. Lee, J.-L.; Kuo, K.-N.; Chiu, K.K.-S.; Kao, J.-Y.; Lin, B.-H. Feasibility Study of AlN/Al₂O₃ Coating on Aluminum Alloy Using Microarc Oxidation Method. *IEEE Trans. Plasma Sci.* **2016**, *44*, 3148–3152. [[CrossRef](#)]
24. Okumiya, M.; Tsunekawa, Y.; Murayama, T. Surface modification of aluminium using ion nitriding and fluidized bed. *Surf. Coat. Technol.* **2001**, *142–144*, 235–240. [[CrossRef](#)]
25. Kent, D.; Drennan, J.; Schaffer, G.B. A morphological study of nitride formed on Al at low temperature in the presence of Mg. *Acta Mater.* **2011**, *59*, 2469–2480. [[CrossRef](#)]
26. Soni, R.; Sarin, V.K.; Rao, P.; Srinivasan, E.; Basu, S.N. Growth of AlN coating on Al-6061 alloy surface. *Surf. Coat. Technol.* **2024**, *476*, 130254. [[CrossRef](#)]
27. Quast, M.; Stock, H.-R.; Mayr, P. Plasma assisted nitriding of aluminum-alloy parts. *Met. Sci. Heat Treat.* **2004**, *46*, 299–304. [[CrossRef](#)]
28. Dalke, A.; Buchwalder, A.; Spies, H.-J.; Biermann, H.; Zenker, R. EB Surface Alloying and Plasma Nitriding of Different Al Alloys. *Mater. Sci. Forum* **2011**, *690*, 91–94. [[CrossRef](#)]
29. Klemm, M.; Haase, I.; Rose, A.; Zenker, R.; Franke, R.; von Hehl, A.; Franke, A. Liquid Phase Surface Engineering of Aluminium and Aluminium Alloys Using Novel Electron Beam Deflection Techniques and Its Influence on Microstructure-Property Relationships. *Int. Heat Treat. Surf. Eng.* **2012**, *6*, 171–177. [[CrossRef](#)]
30. Gjønnes, L.; Olsen, A. Laser-Modified Aluminium Surfaces with Iron. *J. Mater. Sci.* **1994**, *29*, 728–735. [[CrossRef](#)]

31. Almeida, A.; Anjos, M.; Vilar, R.; Li, R.; Ferreira, M.G.S.; Steen, W.M.; Watkins, K.G. Laser Alloying of Aluminium Alloys with Chromium. *Surf. Coat. Technol.* **1995**, *70*, 221–229. [[CrossRef](#)]
32. Dalke, A.; Buchwalder, A.; Zenker, R.; Spies, H.-J. Effect of Nitride Layer Thickness on Reciprocating Sliding Wear Behavior of AlN Layers on Spray-Formed Al Alloys. *Tribol. Lett.* **2019**, *67*, 6. [[CrossRef](#)]
33. Tacikowski, M.; Ulbin-Pokorska, I.; Wierzchoń, T. Microstructure of the composite oxynitrided chromium layers produced on steel by a duplex method. *Surf. Coat. Technol.* **2006**, *201*, 2776–2781. [[CrossRef](#)]
34. Tacikowski, M.; Kamiński, J.; Rudnicki, J.; Borowski, T.; Trzaska, M.; Wierzchoń, T. The effect of the diffusive, composite chromium nitride layers produced by a hybrid surface treatment on the corrosion behaviour of AZ91D magnesium alloy. *Vacuum* **2011**, *85*, 938–942. [[CrossRef](#)]
35. Maseekh, M.H.; Ataiwi, A.H.; Dawood, J.J. Reducing erosion rate of aluminum—Copper alloy by surface processes. *AIP Conf. Proc.* **2023**, *2834*, 070002. [[CrossRef](#)]
36. Figueroa, U.; Salas, O.; Oseguera, J. Production of AlN films: Ion nitriding versus PVD coating. *Thin Solid Films* **2004**, *469–470*, 295–303. [[CrossRef](#)]
37. Staszuk, M. Investigations of CrN/TiO₂ coatings obtained in a hybrid PVD/ALD method on Al-Si-Cu alloy substrate. *Bull. Pol. Acad. Sci. Tech. Sci.* **2023**, *71*, e144622. [[CrossRef](#)]
38. Nakamura, M.; Kubota, S.; Suzuki, H.; Haraguchi, T. Wear and Friction Characteristics of AlN/Diamond-Like Carbon Hybrid Coatings on Aluminum Alloy. *J. Mater. Eng. Perform.* **2015**, *24*, 3789–3797. [[CrossRef](#)]
39. Gao, T.; Li, Z.; Hu, K.; Bian, Y.; Liu, X. Assessment of AlN/Mg–8Al Composites Reinforced with In Situ and/or Ex Situ AlN Particles. *Materials* **2021**, *14*, 52. [[CrossRef](#)]
40. PN-EN 573-3+A1: 2022-11; Aluminium and Aluminium Alloys—Chemical Composition and Form of Wrought Products—Part 3: Chemical Composition and Form of Products. PKN: Warsaw, Poland, 2022.
41. UNI SPERIMENTALE 3057; Primary magnesium-aluminium alloy for casting. (Mg 7%). UNI: Rome, Italy, 1950.
42. Bagdach, S. *Poradnik Galwanotechnika*, 3rd ed.; Wydawnictwa Naukowo-Techniczne WNT: Warsaw, Poland, 2002. (In Polish)
43. Jakiela, R. The Role of Atmospheric Elements in the Wide Band-Gap Semiconductors. *Acta Phys. Pol. A* **2019**, *136*, 916–939. [[CrossRef](#)]
44. Gorobez, J.; Maack, B.; Nilius, N. Growth of Self-Passivating Oxide Layers on Aluminum—Pressure and Temperature Dependence. *Phys. Status Solidi B* **2021**, *258*, 2000559. [[CrossRef](#)]
45. Zhang, F.; Ding, Y.; Yan, S.; He, J.; Yin, F. Microstructure evolution and mechanical performance of Cr-N/Al-Cr multilayer coatings produced by plasma nitriding Cr-coated Al alloy. *Vacuum* **2020**, *180*, 109540. [[CrossRef](#)]
46. Tacikowski, M.; Łukaszewicz, G.; Kulka, M.; Diduszko, R.; Wierzchoń, T. The Effect of Chemical Composition on the Microstructure and Properties of Multicomponent Nickel-Based Boride Layers Produced on C45 Steel by the Hybrid Method. *Coatings* **2024**, *14*, 197. [[CrossRef](#)]
47. Aizawa, T.; Kuwahara, H.; Luangvaranunt, T. Surface Modification of Magnesium Base Alloys by Gas/Plasma Nitridation. *Mater. Sci. Forum* **2000**, *350–351*, 247–252. [[CrossRef](#)]
48. Buchwalder, A.; Böcker, J.; Hegelmann, E.; Klemm, V. Investigations on the Microstructure of an Aluminium Nitride Layer and Its Interface with the Aluminium Substrate (Part I). *Coatings* **2022**, *12*, 618. [[CrossRef](#)]
49. Kimura, A.; Shibata, M.; Kondoh, K.; Takeda, Y.; Katayama, M.; Kanie, T.; Takada, H. Reduction mechanism of surface oxide in aluminum alloy powders containing magnesium studied by x-ray photoelectron spectroscopy using synchrotron radiation. *Appl. Phys. Lett.* **1997**, *70*, 3615–3617. [[CrossRef](#)]
50. Bolduc, M.; Popovici, D.; Terreault, B. Giant segregation effect and surface mechanical modification of aluminum alloys by oxygen plasma source ion implantation. *Nucl. Instrum. Methods Phys. Res. B* **2001**, *175–177*, 458–462. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.