

Article

Investigations on the Microstructure of an Aluminium Nitride Layer and Its Interface with the Aluminium Substrate (Part I)

Anja Buchwalder ^{1,*}, Jan Böcker ¹ , Eugen Hegelmann ¹ and Volker Klemm ²

¹ Institute of Materials Engineering, Technische Universität Bergakademie Freiberg, 09599 Freiberg, Germany; jan.boecker@iwt.tu-freiberg.de (J.B.); eugen.hegelmann.ext@zeiss.com (E.H.)

² Institute of Materials Science, Technische Universität Bergakademie Freiberg, 09599 Freiberg, Germany; volker_klemm@gmx.de

* Correspondence: anja.buchwalder@iwt.tu-freiberg.de; Tel.: +49-3731-39-3543

Abstract: In principle, the plasma nitriding of Al based substrates is a well-known process, though it remains extremely challenging from both the technological point of view and the aspect of stress loading conditions. In order to improve the latter, a duplex treatment consisting of plasma nitriding and subsequent surface remelting using electron beam technology was employed. The focus of this paper (part I) was on the characterisation of the initial microstructure after plasma nitriding. This should create the basis for a better understanding of the processes taking place or changes in the subsequent duplex treatment. This was done with the help of high-resolution imaging and analysis tools in the scanning and transmission electron microscope as well as XPS analyses. Special attention was paid to the nitriding mechanism at the interface as a function of the local microstructural constituents of the hypereutectic Al alloy substrate (Al solid solution, primary silicon, and intermetallic phases). While the main part of the nitride layer formed consisted of AlN and small fractions of pure Al in the diffusion paths, other nitrides and oxides could also be detected in the area of the interface.

Keywords: plasma nitriding; Al alloy; electron beam; remelting; interface



Citation: 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. <https://doi.org/10.3390/coatings12050618>

Received: 7 April 2022

Accepted: 28 April 2022

Published: 2 May 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 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

The nitriding of steels is a well-known thermochemical process. Depending on both the thickness and hardness of the compound and diffusion layer achieved after nitriding, the stress behaviour under tribological, corrosive, and/or fatigue loading can thus be improved. This has led to a wide range of industrial applications of nitrided steel components. Gas and plasma nitriding are the main processes used for this purpose.

The nitriding of Al materials can only be carried out by means of a plasma-based process due to the natural passive layer (aluminium oxide). Al nitriding presents a number of challenges in terms of process technology [1–4] and material-specific properties [5], which currently limit industrial application. Primary issues include the lack of hardness and local cavity formation in the area near the surface as a result of the exclusively external nitriding mechanism involved (element diffusion) [6,7]. Nitriding leads to the formation of a compound layer, but without a diffusion layer, leading to the absence of a support for the thin hard AlN layer, which is very unfavourable in the case of loading.

It is well known that the formation and growth of the AlN layer are material-dependent [5,6,8]. In addition to the chemical composition, the nature and size of the microstructural constituents are decisive in determining the material's nitriding behaviour. For example, previous works by the present authors have shown that conventional hypereutectic Al cast alloys (>12 wt.% Si) are difficult to nitride [2,9], whereas similar alloys produced by spray compacting processes exhibit good nitriding behaviour [10,11]. The differences result from the process-specific rapid solidification, the features associated with the formation of the microstructure, and, in particular, the size of the precipitates.

The main component of the nitride layer is hexagonal AlN, which has predominantly covalent and 45%–47% ionic bonds [12,13]. The high binding energy of 2.88 eV [13] is responsible for the material's high melting point (2490 °C), its good thermodynamic and chemical stability as well as its high electrical resistance (i.e., semiconducting behaviour) [14,15]. Oxygen is the most common impurity in AlN, leading to crystal disorder (voids) [16] and the typical dark colouration [14,17,18]. The incorporation of 4% oxygen almost halves the material's thermal conductivity [16]. Cationic impurities, such as Mg, Fe, and Si, can be incorporated into the AlN lattice, and the resulting voids also reduce conductivity [12].

Due to oxygen leakage during plasma nitriding, the nitride layer may contain oxygen in the form of lattice defects [19], Al₂O₃, and MgO (which has not been sputtered off) [20,21]. Both oxides are characterized by high melting temperatures (Al₂O₃: 2050 °C; MgO: 2852 °C). The hardness of MgO is only about half that of Al₂O₃. Both oxides are electrical insulators, but good conductors of heat [18,22,23].

Furthermore, it is suspected that Mg₃N₂ can occur in the nitride layer [21,24]. Unlike AlN, Mg₃N₂ is chemically unstable and decomposes at temperatures as low as $T \geq 800$ °C. Studies by Yang et al. [25] prove that when nitrogen is injected into a Mg–Al melt (750–800 °C), Mg₃N₂ and AlN are produced.

Mg-enrichment is detectable at the nitride layer–substrate interface [26]. It is assumed that the diffusion of other alloying elements through the layer is possible, though difficult to detect due to potential sputtering [2].

The current limitations in the load-bearing capacity of nitrided aluminium surfaces due to the above-mentioned layer structure prevent a broad industrial applicability as known for steels. In order to improve this, a novel duplex technology for plasma nitriding and subsequent surface remelting by means of an electron beam was developed [27]. The basis for further developments of a load-related surface composite was a profound understanding of the initial microstructure after plasma nitriding, and especially at the interface between the AlN layer and Al substrate. In the case of the spray-compacted Al alloy used, the main concern is that of possible differences in the layer bonding on the different microstructural constituents, such as the Al matrix, the primary silicon precipitates, and the intermetallic phases. This was investigated using different high-resolution imaging and analytical methods, such as a transmission electron microscope (TEM), X-ray induced photoelectron spectroscopy (XPS), and hardness measurements via nanoindentation in the scanning electron microscope (SEM). These results are essential for understanding the impacts of a duplex treatment consisting of plasma nitriding and electron beam surface remelting on the microstructural changes (cf. [28]).

2. Materials and Methods

2.1. Material

The spray-formed hypereutectic Al alloy DISPAL S232[®] was used as the base material (Table 1). Due to the typical high cooling rates of the spray-forming process, the microstructure of the hypereutectic spray-formed Al alloy consisted of oversaturated Al solid solution (α -Al), exclusively primary precipitated silicon (Si_p) and different intermetallic compounds (IC), such as Al₇Cu₂Fe, Al₉Fe₂Si₂, Al₃FeSi₂, and Cu₅Zr—as determined by means of XRD analysis (see [27]). Compared to conventional casting alloys, the high cooling rates and thus fine precipitations during the spray compacting process also allow the addition of exceptionally high Fe contents (>1 wt.%) (cf. Table 1).

Table 1. Chemical composition and hardness (F state) of the base material.

	Element Concentration [wt.%]						Hardness
	Al	Si	Fe	Mg	Cu	Zr	H _{IT} 20 mN [GPa]
DISPAL S232 [®]	Bas.	16.4	5.2	0.4	2.6	0.5	2

2.2. Surface Treatment Technologies and Parameters

Nitriding was carried out in a commercial DC plasma nitriding facility by ELTROPULS Anlagenbau GmbH (Baesweiler, Germany). The samples (diameter: 40 mm, height: 10 mm) were ground before treatment with silicon carbide abrasive paper (1200 grit size). Very complex physical processes and chemical reactions, which are not yet understood in detail, take place during this process. The plasma nitriding process of aluminium alloys is very challenging in terms of temperature–time control and this has been investigated in numerous of our own studies in the past and will not be discussed in more detail here. A comprehensive description of the overall nitriding process, including the influence of and relationships between parameters, is given by Dalke et al. [4].

Parameters for plasma nitriding used were selected by means of previous examinations and are given in Table 2. The aim of these settings was to generate different nitride layer thicknesses t_{AlN} in the range of 1.5–4.3 μm .

Table 2. Parameter sets of plasma nitriding (T_N ... nitriding temperature; p ... pressure; t_{plasma} ... plasma-on-time; $t_{N, \text{eff}}$... effective nitriding time; τ ... pulse-pause ratio) and important values for characterizing the AlN layer generated (t_{AlN} ... layer thickness; R_a ... mean roughness; R_z ... the average surface roughness).

Set	Nitriding Parameters					Layer Characteristics		
	T_N [°C]	p [Pa]	t_{plasma} [h]	$t_{N, \text{eff}}$ [h]	τ	t_{AlN} [μm]	R_a [μm]	R_z [μm]
PN1	465	150	6	1.53	0.30–0.39	1.5	0.36 ± 0.015	3.1 ± 0.19
PN2			5	2.30	0.25–0.33	3.0	0.28 ± 0.07	2.6 ± 0.01
PN3	475		8	2.57	0.25–0.35	4.3	0.48 ± 0.03	4.3 ± 0.25

2.3. Characterization Methods

Glow discharge optical emission spectroscopy (GDOES) was used to determine the depth-dependent element concentration profiles after nitriding. On the basis of the element curves, initial statements could be made about the AlN layer thickness and the diffusion processes in the area near the surface of the Al base material.

The microstructure was analyzed by means of metallographic cross sections using light optical microscopy (LOM) and scanning electron microscopy (SEM). Furthermore, the topography and morphology of the nitrided surfaces were evaluated by means of SEM.

X-ray induced photoelectron spectroscopy (XPS) experiments were carried out on a PHI Quantum 2000 attached with a 15 kV X-ray gun using monochromatic Al $K\alpha$ radiation. The spot size was approximately 100 μm and the pass energy 117.4 eV. Additionally, argon ions (4 keV) were used to etch the samples. The sputter rate used was approximately 7 nm/min for a total sputtering time of 411 min ($\approx 2.9 \mu\text{m}$). The spectra were evaluated using Multipak V. 6.2 software and the Handbook of Photoelectron Spectroscopy, Physical Electronics Inc.

Transmission electron microscopy (JEOL JEM 2200FS) was used for spatially resolved (AlN layer, interface, near-surface influenced base material) detailed microstructural characterization. For this purpose, two strips with a thickness of 1.5 μm were cut out of each of the relevant sample areas with a diamond saw, before the strips were embedded face-to-face, ground and finally thinned to a final thickness of approximately 100 nm using an ion beam. The imaging for the microstructural examination was carried out using the two TEM modes bright field (bf) and dark field (df), as indicated in each case by the caption. Within the TEM, different tools were used for quantitative and qualitative analysis. Energy dispersive spectroscopy (EDS) or energy dispersive X-ray spectroscopy (EDX) was first used to determine the element concentrations of the exposed areas. It should be noted that these tools are not suitable for the detection of light elements (without N and O). The concentration curves shown can therefore be evaluated qualitatively, but not quantitatively.

Furthermore, electron energy loss spectroscopy (EELS) was used. Based on the spectra, the electronic structure of the solid and its bonding character could be determined [29].

For characterization of the nitride layer, both the low-loss range and the core-loss range were considered.

Selected area electron diffraction (SAED) was used to determine the structure and orientation relationships.

For instrumented hardness measurement (Fisherscope 2000), the sample surfaces were polished up to 1 μm . To procure sufficient statistics, 5 indentations were measured per sample. The test procedure was force-controlled with a maximum load of $F_{\text{max}} = 20 \text{ mN}$. The evaluation of the recorded force-indentation depth curves from the loading and unloading cycle was carried out according to ISO 14577 [30] with the so-called Oliver–Pharr method, from which the indentation hardness H_{IT} and the modulus of elasticity E_{IT} were determined. Instrumented indentation hardness H_{IT} correlates to traditional forms of hardness, as it is a measure of the material's resistance to plastic deformation. The modulus of elasticity was determined from the slope of the unloading line dF/dh [30].

The nanoindentation was performed inside a scanning electron microscope (SEM) using a Picoindenter (PI 87, Hysitron) mounted on the SEM stage. Hardness–depth curves were recorded in the nitride layer starting from the surface and extending up to the Al substrate. The indentations were performed using a Berkovich indenter in displacement-controlled mode with a maximum depth of $z_{\text{max}} = 60 \text{ nm}$. The specimen was tilted at an angle of 70° relative to the electron beam during the measurement process. Since the hardness values determined were load-dependent due to their elastic material behaviour or surface effects, the measurements only exhibit a comparative character [31].

3. Results and Discussion

3.1. Characterization of the Base Material

Light microscope images (Figure 1a) show the general microstructure of the spray compacted Al base material already described in Section 2.1.

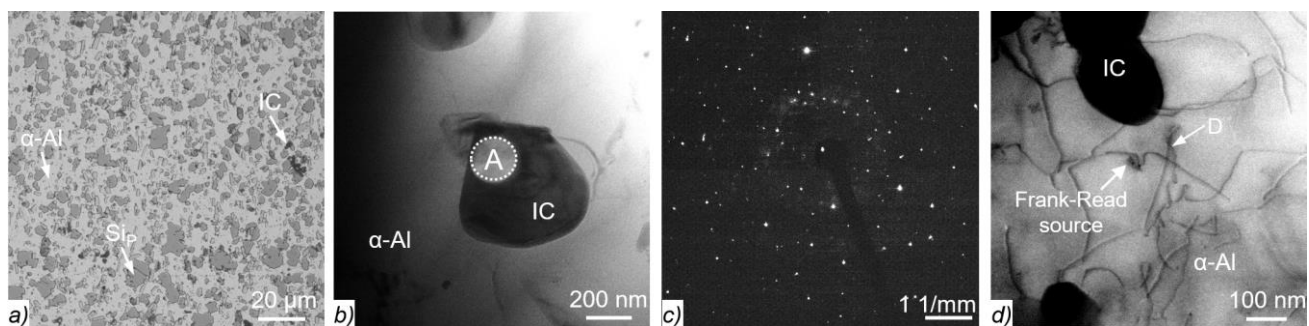


Figure 1. Microstructure of the base material: (a) light optical micrograph overview (Al solid solution ($\alpha\text{-Al}$), primary precipitated silicon (SiP), intermetallic compounds (IC)); (b) bf-TEM image of intermetallic phase with SAED analysis area A; (c) diffraction pattern from area A; (d) bf-TEM image of Al matrix with precipitations IC and dislocations D.

Using TEM examinations, it could be observed that most of the intermetallic phases IC in the Al matrix were spheroidal and $<1 \mu\text{m}$ in size (Figure 1b,d). The plate-like precipitate A (Figure 1b) was identified as β -phase (Al_3FeSi_2) by SAED measurements, as it is seen by means of the diffraction pattern shown in Figure 1c. The other phases mentioned above (see Section 2.1) could not be detected in the TEM analysis.

Diffraction contrast shows that the face centered cubic (fcc) Al solid solution had a low dislocation density (Figure 1d). The bonding ratios of Al and Si were analysed in the base material by means of plasmons. It was shown that characteristic plasmons occurred in the Al matrix at approximately 14.8 eV (vs. 15.0 eV [32]) and in SiP at approximately 17.0 eV (vs. 16.5 eV [32]), which were used as reference values for the further investigations.

3.2. Influence of the Process Parameters on the Results of Plasma Nitriding (PN)

The nitriding behaviour and the influence of the nitriding conditions on the layer formation have already been investigated at a fundamental level for spray-compacted Al-Si alloys [3,4,6,33]. Within the scope of this work, different nitride layer thicknesses (for parameters see Table 1) were specifically set for the subsequent remelting experiments (see [28]). The thicker the nitride layer, the more complete the surface coverage with AlN (I. in Figure 2a–c). However, as a result of the outward diffusion of aluminium and magnesium (from the bulk material toward surface) during the nitriding process, cavity formation (see C in Figure 2c) occurred below the nitride layer (cf. II in Figure 2a–c). This fact further limited the material's already poor supporting behaviour due to the low hardness of the Al base material.

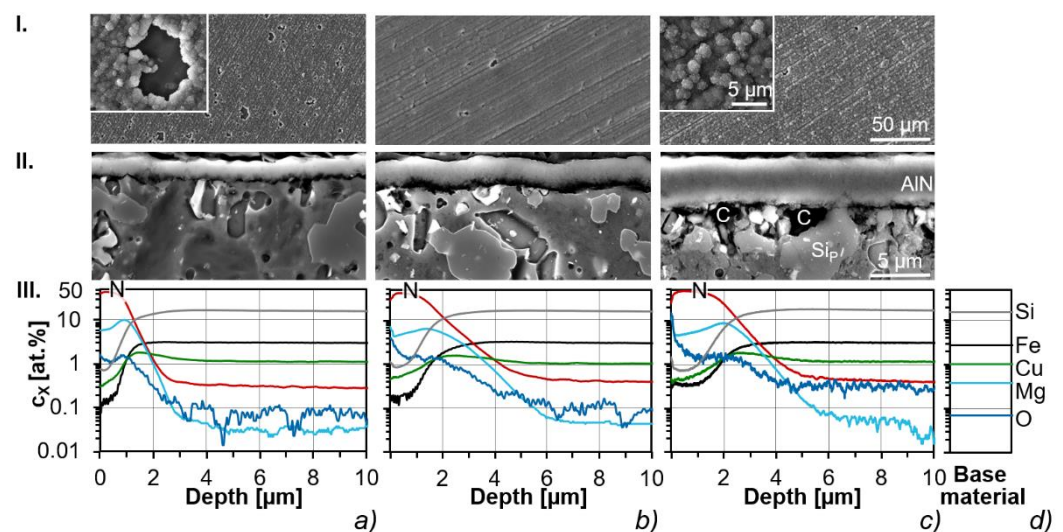


Figure 2. Characterization of AlN layers with different thicknesses t_{AlN} (effective nitriding times): (a) $t_{\text{AlN}} = 1.5 \mu\text{m}$; (b) $t_{\text{AlN}} = 3 \mu\text{m}$; (c) $t_{\text{AlN}} = 4.3 \mu\text{m}$; (d) Al base material by means of I. surface topography; II. cross sections (C ... cavities; SiP ... primary silicon) and III. element concentration–depth profiles measured by GDOES (without illustration of Al content).

The chemical composition and/or microstructure of the substrate played an important role in the diffusion-controlled nitriding process. The concentration–depth profiles measured by means of GDOES show the strong enrichment of nitrogen, magnesium, and oxygen in the area of the nitride layers (III. in Figure 2a–c) compared to the initial nominal composition of the Al base material (III. in Figure 2d). While nitrogen was deliberately added during nitriding to form AlN, the enrichment with other elements (except oxygen) resulted from diffusion processes within the Al base material.

The oxygen enrichment resulted from unavoidable oxygen leakage despite pressure reduction ($p_{\text{N}} = 1.5 \text{ mbar}$), as well as from nitrogen gas impurities. While the maximum oxygen enrichment for a depth of $z > 0.5 \mu\text{m}$ (exclusion of surface effects due to roughness) was approximately $1.4 \pm 0.2 \text{ wt.\% O}$ for all three variants, the diffusion depth, starting from the low layer thickness ($t_{\text{AlN}} = 1.5 \mu\text{m}$) with $z_{\text{O}} \approx 2.5 \mu\text{m}$, increased to values of $z_{\text{O}} \approx 6 \mu\text{m}$ for higher layer thicknesses ($t_{\text{AlN}} \geq 3 \mu\text{m}$). The latter was promoted by the increasing degree of cavity formation mentioned above (cf. Figure 2c).

Within the three nitriding variants investigated, the maximum Mg content in the AlN layer was between 6.5 and 10 wt.% Mg. This corresponded to an increase of 15–25 times compared to the nominal Mg content (0.4 wt.% Mg) in the Al base material. From the concentration–depth profiles, it could be estimated that the Mg content reached a minimum at the interface between the AlN layer and the base material, and then successively increased in the direction of the base material. The area influenced in terms of the transport of Mg

from the base material reached a depth of $z \approx 15\text{--}23\text{ }\mu\text{m}$ and correlated with the Al concentration–depth profile.

Based on the X-ray phase analysis, only AlN could be identified clearly [34]. Due to the possibly amorphous structure or the small proportion, the existence of the phases Al_2O_3 , MgO, or an Al-Mg mixed oxide could neither be ruled out nor proven beyond doubt. Indications for an aluminium oxy-nitride phase or magnesium nitride, as already proven for wrought alloys containing Mg [35], could not be determined. More detailed information on the structural composition of the AlN layers was obtained by XPS analysis.

Starting from the maximum content (25 at.%) at the surface, the oxygen content decreased successively with increasing distance from the surface or with increasing sputtering time (Figure 3a). The nitrogen, however, exhibited exactly the opposite course. As a result, both AlN and AlO_x were detected down to a depth of $z = 1.7\text{ }\mu\text{m}$ ($t_N = 251\text{ min}$) by peak shape fitting of the Al2p-peak (Figure 3b–d). While the nitrogen profile at the interface showed an abrupt drop, the oxygen and magnesium profiles showed a steep local maximum (Figure 3a). The Mg2p-peak fit (not shown) proved the formation of MgO in this area.

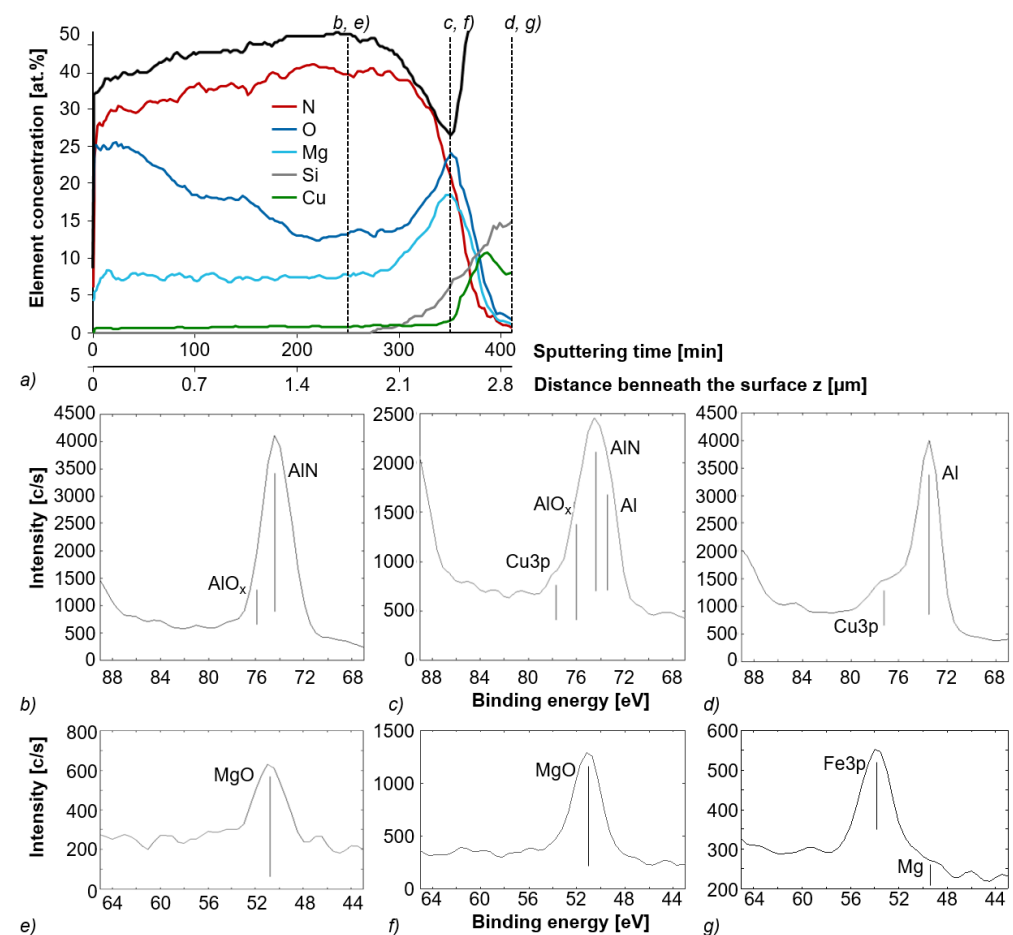


Figure 3. XPS analysis of a nitride layer with a thickness of approx. $2.2\text{ }\mu\text{m}$ (measuring area: $1 \times 1\text{ mm}^2$; spot size: $100\text{ }\mu\text{m}$; Al-K α radiation): (a) element concentration–depth profiles with indication of the 3 defined analysis depths z (dashed lines) based on the binding energies measured: (b,e) $z \approx 1.7\text{ }\mu\text{m}$ (AlN-layer); (c,f) $z \approx 2.5\text{ }\mu\text{m}$ (interface); (d,g) $z \approx 2.9\text{ }\mu\text{m}$ (substrate).

Furthermore, Cu fractions bound in CuO were also detected directly below the interface by means of the Cu2p $_{3/2}$ -peak fit. The elements bound in the nitride layer as nitrides or in oxides, such as Al, Mg, and Cu, were also identified as metallic components (see Figure 3b–d).

3.3. High-Resolution Analysis of the Nitride Layer ($t_{\text{AlN}} \sim 4.3 \mu\text{m}$)

The TEM investigations focused initially on the area of the nitride layer in general (Section 3.3.1), and then locally on the interface between the nitride layer and the substrate (Section 3.3.2). The reason for this is the importance of the interface for bonding after nitriding and, as shown in further investigations (part II), for subsequent local short-term remelting by means of an electron beam. In order to understand the complicated processes involved, an analysis of the initial nitrided state was essential.

3.3.1. Characterization of the Nitride Layer

(A) Depth-dependent chemical composition

Due to the relatively large diameter of the GDOES measuring spot ($d_m = 4 \text{ mm}$), the depth-dependent values of the element concentrations corresponded to an average value (cf. Figure 2). For more precise local assignment of the elements, qualitative EDS measurements were carried out on TEM samples. A complete quantitative analysis was not possible by means of EDS because the elements nitrogen and oxygen could not be analysed reliably. For this reason, the fraction data in Figure 4c–e are given only in a normalized manner (relative fraction).

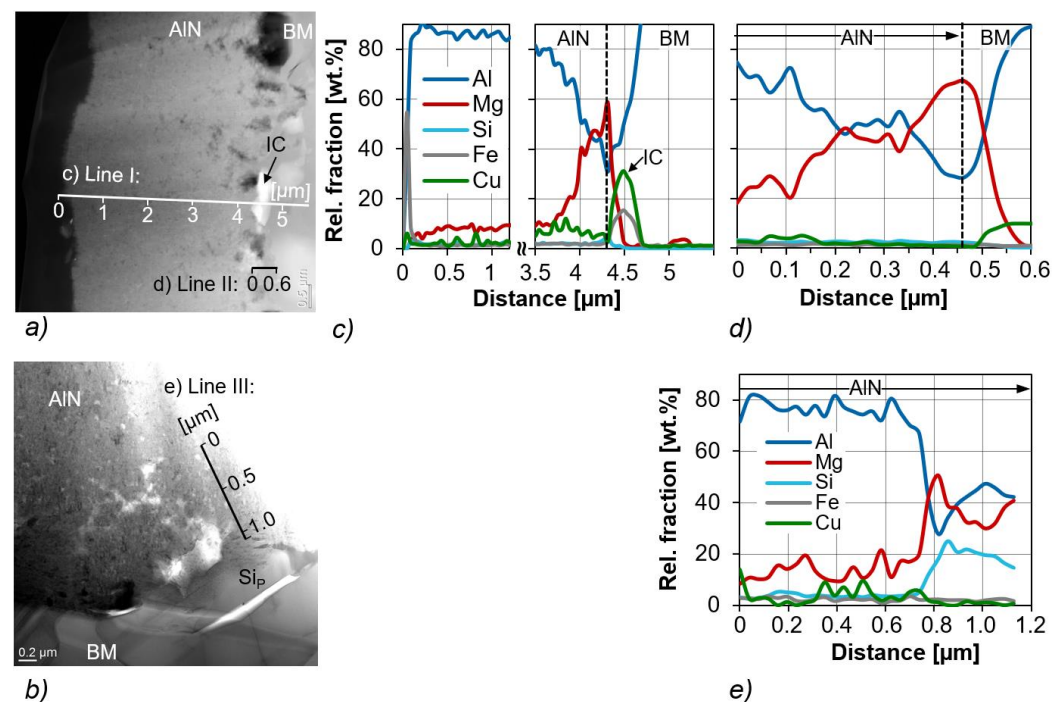


Figure 4. TEM investigations by means of a nitride layer with a thickness of $t_{\text{AlN}} \approx 4.3 \mu\text{m}$: (a,b) overview of the cross sections (df) investigated with the positions of the EDS measuring lines, and EDS profiles measured without nitrogen and oxygen (dotted line: interface) for: (c) EDS line I: over the total nitride layer thickness with an intermetallic compound (IC) at the interface; (d) EDS line II: at the interface area without intermetallic compounds; (e) EDS line III: at the interface area with primary silicon Si_P in the base material BM.

Figure 4 shows EDS line profiles measured within the AlN layer starting from different microstructural constituents of the substrate at the interface (cf. Figure 4a,b):

- Line I: The entire AlN layer thickness of $l_{\text{total}} = 5.5 \mu\text{m}$ (step size: 40 nm) with an intermetallic phase at the interface (Figure 4c).
- Line II: A small area at the interface of $l_{\text{total}} = 0.6 \mu\text{m}$ (step size: 20 nm) without the intermetallic phase (Figure 4d).
- Line III: A small area at or close to the interface of $l_{\text{total}} = 1.1 \mu\text{m}$ (step size: 40 nm) above a primary silicon precipitation (Figure 4e).

For EDS line I, the intermetallic compound at the interface consisted of copper, iron, and aluminium (cf. IC in Figure 4c). Furthermore, EDS measurements revealed that the majority of the nitride layer was primarily characterised by Al, smaller but notable amounts of Mg, and traces of Si, Fe, and Cu (Figure 4c). In a small area of approximately $z = 0.8 \mu\text{m}$ beneath the interface between AlN and the base material, a clear degree of Mg enrichment with somewhat less Cu was detectable in the AlN layer (Figure 4c). The Mg maximum was reached directly at the interface and exceeded the nominal Mg concentration in the substrate by 1–2 orders of magnitude.

Comparative measurements at an interface without intermetallic compounds (line II, Figure 4d) or above a primary Si precipitation (Si_p) (line III, Figure 4e) confirmed the Mg enrichment, but not the Cu enrichment. It was concluded from this information that during nitriding, Cu diffusion only occurred locally and over short distances around the Cu-containing intermetallic phases.

In the case of primary silicon precipitation at the interface (line III, Figure 4e), the Mg enrichment was the lowest in terms of both maximum and depth. This meant that the Si precipitates blocked or limited the long-range diffusion of Mg from the substrate.

The Cu concentration profile showed only individual peaks whose maximum corresponded with those in the Al profile, possibly indicating minor precipitation. These can also be recognised in Figure 4b by the white strips within the AlN layer. This may have resulted from diffusion processes.

(B) Identification of the phase composition

By means of both EELS and SAED, AlN and Al were identified within the nitride layer (Figure 5d,e). The additional Al present in the nitride layer produced strong single-crystal reflections in the SAED analysis region (Figure 5c), which were presumably due to the strongly diffractive dark regions of the bright-field image (Figure 5a).

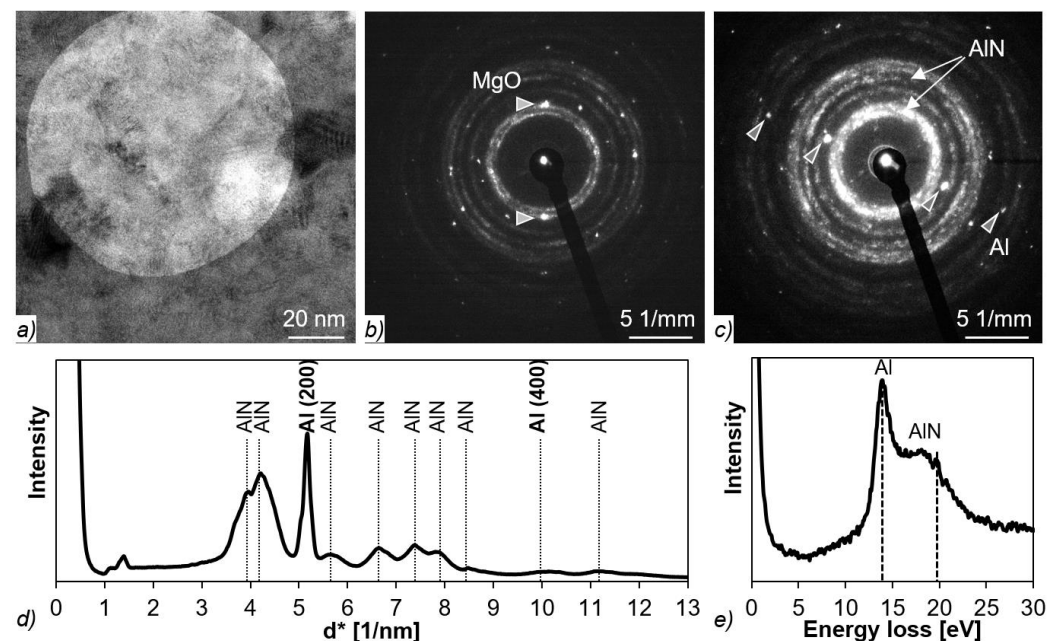


Figure 5. Phase analysis in the upper part of the AlN layer: (a) TEM image (bf) with area of SAED analysis and associated diffraction patterns of (b) AlN, and (c) Al; (d) radial intensity distribution of the diffraction pattern from (b,c); (e) energy loss spectrum.

The AlN produced strong ring patterns in the diffraction image (Figure 5c). It was concluded from this that the nitride layer consisted of a great number of very small stochastically distributed AlN crystallites. Assuming that the aperture diameter was approximately 100 nm and the sample was significantly thinner, the grain size could be estimated to be $<10 \text{ nm}$, which is confirmed by data in the literature [36,37].

While Niessner [38] gives an energy loss of 21 eV for AlN, the AlN plasmon detected by EELS was 19.8 ± 0.9 eV (Figure 5e). The shift and peak broadening could probably be explained by the contamination of the AlN with oxygen, which changed the electron structure of the material.

However, there were also local differences in chemical composition within the nitride layer. An additional Al plasmon was formed by diffusion of the Al to the surface, which was probably to be expected and to occur preferentially along the interspaces of the AlN columns. After nitriding, unbound metallic Al remained in the AlN layer. The double plasmon of Al and AlN (Figure 5e) occurred when both AlN grains and Al-rich grain boundaries were captured by the primary beam in the excited volume.

3.3.2. Characterization of the Interface between Nitride Layer and Base Material

As previously shown, the chemical composition of the interface after nitriding depended on the local microstructural constituents in the Al base material. The resulting structural effects at the interface (Figure 6a) were investigated using high-resolution phase contrast of the TEM (HRTEM) in combination with EELS and SAED measurements.

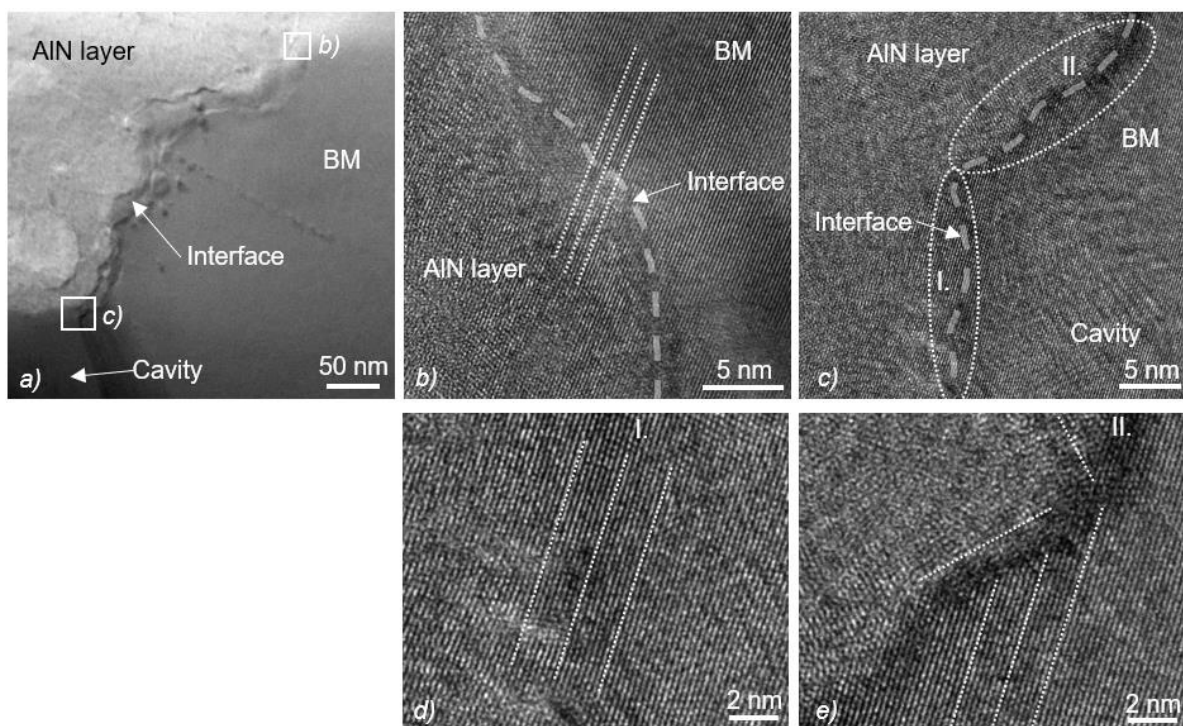


Figure 6. HRTEM images focussed on the interface (dotted line) between the AlN layer and the Al base material: (a) overview, (b) without, and (c) with diffusion-induced cavity after nitriding; higher resolution images of interfacial areas I, II: (d) area I. with coherent bonding, and (e) area II. with incoherent bonding (dotted lines: exemplary lattice planes).

The interface was not smooth, and a heavily disturbed area was visible due to the dark shadows (Figure 6b,c). The nitride layer was predominantly coherently bonded to the Al matrix, i.e., the lattice planes of the Al matrix continued within the layer (cf. Figure 6b, I. in Figure 6c,d). Due to epitaxy, nucleation on fcc Al grains began in crystallographically favourable orientations to reduce interfacial energy. On the other hand, there were also areas with incoherent bonding at the interface (II. in Figure 6c,e).

As already shown by light-optical images, larger cavities ($\leq 10 \mu\text{m}$) can form underneath the nitride layer at the interface (cf. C in Figure 2c). They were generated by the outward diffusion of Al and Mg during nitriding. As can be seen in Figure 6c (I), the transition between the cavity wall (in the cross section) and the AlN layer was also a

coherent interface, which meant that the inward diffusion of oxygen or nitrogen for the formation of the cavity can be ruled out. Cavity formation in the area of other microstructural components, such as primary Si or the intermetallic phases, was not observed.

A. Interface between Al matrix and AlN layer

A targeted EDS point analysis (see A–C in Figure 7a) in the area of the interface proved the strong Mg enrichment already found by means of GDOES (III. in Figure 2) and XPS investigations (Figure 3a). This had a size of approximately 600 nm on both sides of the interface for the examined nitrated layer (cf. point B, C in Figure 3b). The EEL spectrum recorded in this region (see Figure 3a) showed plasmons of Al and AlN (Figure 3c). It could thus be concluded that this part already belonged to the nitride layer. Furthermore, metallic Al was detected that had resulted from outward diffusion, as already described.

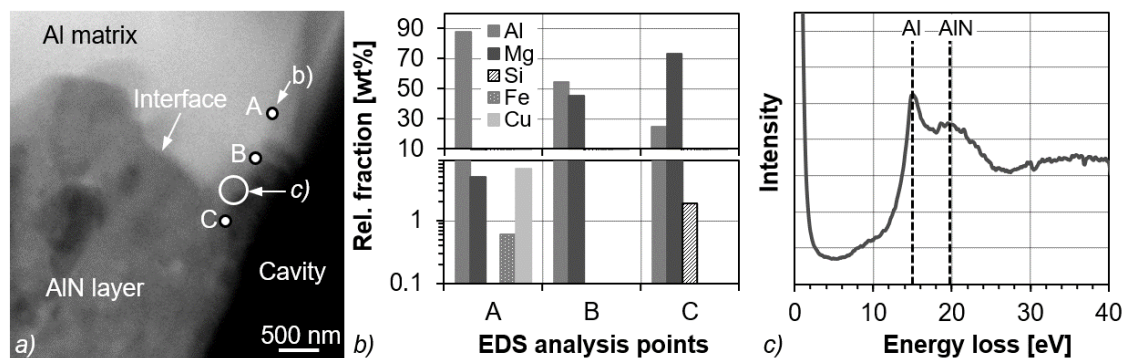


Figure 7. Analysis of the interface between the AlN layer and the Al base material: (a) TEM image (df) with measuring points of: (b) EDS analysis (point A–C); (c) low-loss area of the EEL spectrum.

While no copper nor iron were detected in the nitride layer (point C in Figure 3b), these elements were detected together with Mg at the interface. A Cu signal from the pole shoes of the TEM can thus be ruled out. It is therefore assumed that nitriding caused Cu to diffuse from the Al matrix to the interface, and to accumulate there. Since the solubility of Cu in Al is already clearly exceeded at room temperature [39], an Al_2Cu phase or Mg-containing phases (Mg_2Cu or MgCu_2) were most likely formed.

In addition, weak reflections that can be assigned to Mg_3N_2 were observed at the interface by means of fine-range diffraction, along with pronounced single-crystal reflections from Al in the region of low-indicated lattice planes $d^* \leq 4 \text{ nm}^{-1}$ (Figure 8a). Since these reflections did not occur in a ring, it could be concluded that they originated from only a single grain. However, the detection of this phase was confirmed by a number of measurements.

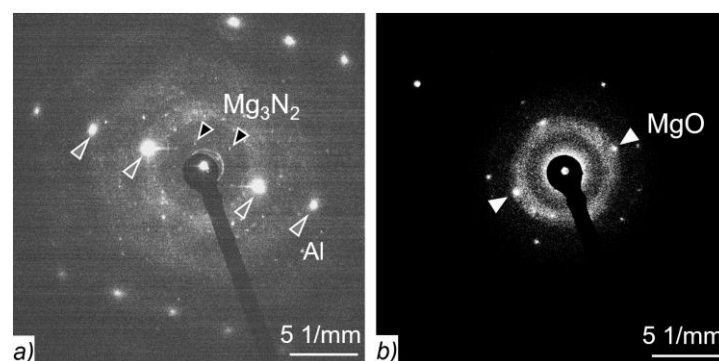


Figure 8. Diffraction patterns of: (a) Mg_3N_2 , and (b) MgO from analysis in the upper part of the AlN layer.

At another representative location, MgO was also detected by means of fine-range diffraction, which produced pronounced single-crystal reflections in the diffraction pattern (Figure 8b). These Mg compounds presumably formed at the beginning of the nitriding process, with their formation favoured by the higher diffusion coefficient of Mg in Al compared to the self-diffusion of Al in Al [40] and the high affinity of oxygen for Mg.

Other phases such as Al_2O_3 were not identified. However, it has to be assumed that they were indeed present, as indicated by means of both XPS data (see Figure 3) and references in the literature [4]. However, their local content was too low for analysis by means of SAED.

B. Interface between primary silicon particles and the AlN layer

As already described in Section 3, the process-specific high cooling rates during spray compacting led to the exclusive precipitation of primary silicon particles, so that the Al solid-solution matrix was Si-free in the initial state. On the primary silicon precipitates, the nitride layer was, in principle, well bonded, but cracks could also be found in isolated cases. These were either due to shrinkage cracks during cooling or to preparation-related effects. No cracks were found on other microstructural constituents. Compared to the local interface between the Al matrix and AlN (cf. Figure 7c) described previously, the EEL spectrum measured above the primary silicon precipitates contained only a single peak for AlN (Figure 9b).

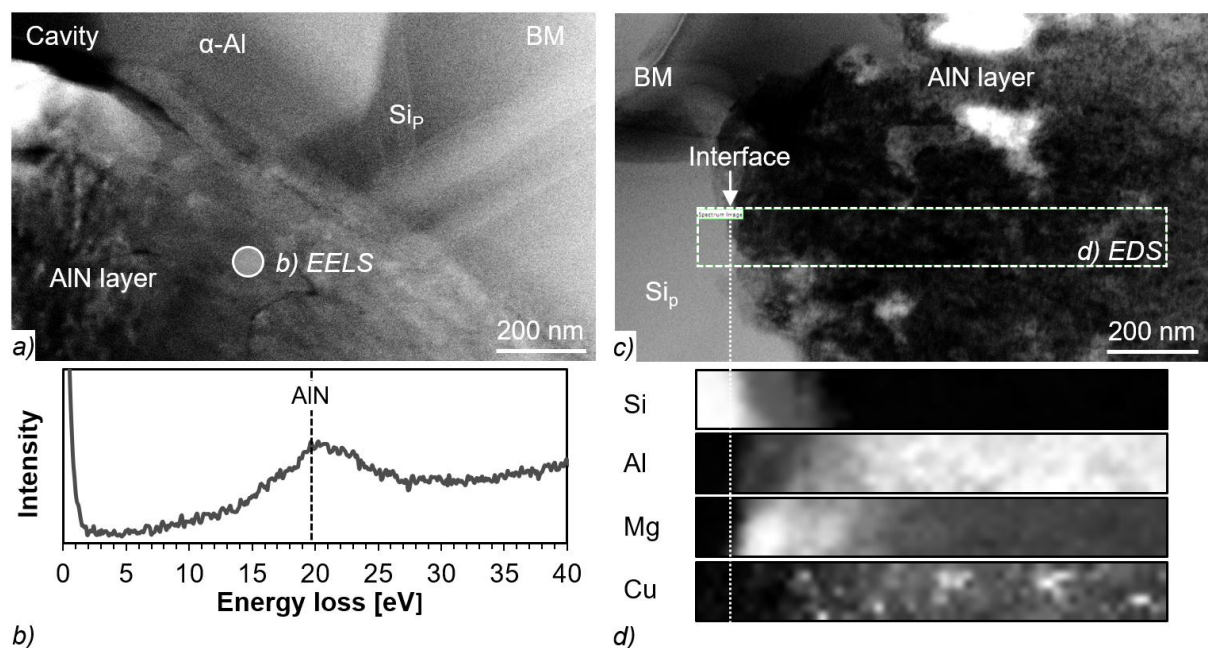


Figure 9. Analysis of the interface between primary silicon Si_p and the AlN layer: (a) TEM image (df) of a cross section with point of EELS measuring, (b) low-loss spectrum; (c) TEM image (bf) of a cross section with an EDS measuring field; (d) EDS mapping for the elements Al, Mg, Si, Cu.

Using an EDS mapping process that started on a primary silicon precipitate (100% Si) and measured into the AlN layer (cf. dotted rectangle in Figure 9a), it could be seen that a graded Si content existed in the AlN layer in the region of the interface down to a distance of approximately 200 nm (cf. Si in Figure 9b). Roughness effects could be ruled out as a cause for this measurement signal, since Si reflections in the diffraction pattern would have had to appear at the same position as in the underlying Si_p crystallite. It could be assumed that Si diffused into the nitride layer or was sputtered during nitriding before being redeposited there, as long as no closed nitride layer had grown over the Si. If the Si had been metallic, the concentration could have been too low to have produced a pronounced plasmon. Presumably, however, the Si was bound as SiO_2 or Si_3N_4 . To

determine this, further SAED investigations need to be carried out on a thinner area of the sample in order to be able to detect the phases with a low volume fraction.

3.3.3. Characterization of Layer Hardness

Hardness measurements by means of load-controlled indentation testing with a maximum load of $F_{\max} = 20 \text{ mN}$ resulted in an average indentation hardness of $H_{IT} (20 \text{ mN}) = 9.6 \pm 0.5 \text{ GPa}$ for the nitride layer (cross section). The indentation modulus of the nitride layer determined from this was $E_{IT} (20 \text{ mN}) \approx 110 \text{ GPa}$.

Furthermore, hardness–depth profiles were recorded by means of nanoindentation using a Picoindenter in the SEM. Due to the phenomenon of surface rounding during sample preparation, the interface between the AlN and the Al substrate was taken as a reference point $z = 0 \text{ }\mu\text{m}$ (Figure 10a). Hardness measurements in the AlN layer, therefore, showed negative depth values ($-z$), with positive depth values (z) in the Al substrate.

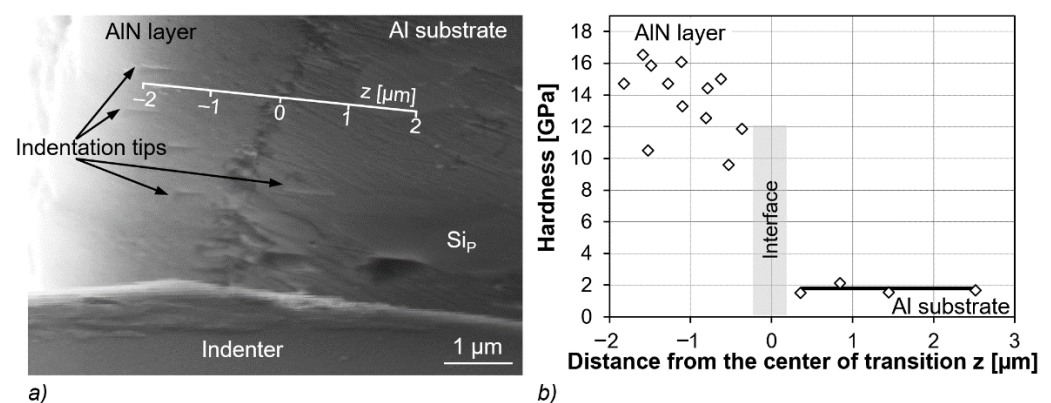


Figure 10. Nanoindentation hardness measurements in displacement-controlled mode with a maximum depth of $z_{\max} = 60 \text{ nm}$: (a) SEM image with indentation tips (exemplary); (b) hardness–depth profile.

As expected, nitriding led to the formation of a steep hardness gradient. With the base material exhibiting a mean hardness value of $1.5 \pm 0.4 \text{ GPa}$ (cf. Figure 10b), the hardness of the nitride layer was higher by a factor of approximately 10 ($14.4 \pm 1.8 \text{ GPa}$). In principle, the hardness measured within the nitride layer showed larger fluctuations. The low values (approximately 10 GPa) may have come from areas with high Al contents.

In the lower part, the nitride layer was obviously slightly softer due to the high Mg content and the associated formation of MgO or Mg_3N_2 . The interface could not be measured with confidence due to pop-in of the indenter, which occurred because of the cavities formed.

4. Conclusions

The subject of the investigations was high-resolution analysis of element diffusion as a result of the nitriding process and the bonding of the nitride layer (layer thickness: approximately $4 \text{ }\mu\text{m}$) on the microstructural components of a spray-compacted Al alloy DISPAL S232® (AlSi17Fe5Cu3Mg). The following essential findings can be summarised for the nitrided initial state:

- (1) The nitride layer consisted predominantly of AlN with small fractions of Al. This resulted from the well-known mechanism of outward nitriding, in which the Al diffuses from the substrate through the already formed nitride layer towards the surface. On cooling, unbound Al remained present in the nitride layer and probably accumulated in the region of the AlN crystallite boundaries. As a result of diffusion, localised cavities occurred beneath the nitride layer where an Al matrix was predominantly present rather than primary silicon or stable intermetallic phases.

- (2) Due to the AlN nanocrystallites (<50 nm), the proportion of grain and phase interfaces was very high, which led to very rapid diffusion, and thus to a relatively high growth rate.
- (3) The lower part of the nitride layer was characterised by a very high Mg concentration. Both oxygen and nitrogen were detected there, leading to the additional formation of MgO and Mg₃N₂.
- (4) On the primary silicon precipitates, the nitride layer was in principle well bonded, but cracks were also to be found in isolated cases. These were either due to shrinkage cracks during cooling or to preparation-related effects. No cracks were found on other microstructural constituents. Up to a distance of approximately 200 nm above the primary silicon precipitates, an increased Si concentration was detected, which could have indicated diffusion. The influence of roughness was ruled out due to the position of the reflections in the SAED measurement.
- (5) The nitride layer was mostly coherently bonded to the Al substrate.
- (6) Cu enrichment occurred in the Al matrix during nitriding, which exceeded the Cu solubility in the Al solid solution at room temperature. However, no Cu-containing phases were detected. It is conceivable that Guinier–Preston zones formed that increased the hardness in this area. It is also possible that Cu was influenced by the diffusion current of Al and Mg and accumulated at the interface.

The initial state shown here is the basis for a better understanding of the processes and changes that occur during the subsequent duplex treatment, consisting of plasma nitriding and electron beam remelting (see part II).

Author Contributions: Conceptualization, funding acquisition, project administration, supervision, writing—original draft preparation, visualization, A.B.; investigation, writing—review and editing, J.B.; investigation, methodology, investigation, review and editing, E.H.; investigation, V.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by German Research Foundation (DFG), grant number AIN-Flash-I and -II (No. BU2568/6-1; 9-1). Open Access Funding by the Publication Fund of the TU Bergakademie Freiberg.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would also like to thank A. Dalke (TU Bergakademie Freiberg, Institute of Materials Engineering) for carrying out the nitriding experiments. The TEM samples were prepared by A. Leuteritz. The authors also wish to thank G. Bittner and R. Lehnert (both TU Bergakademie Freiberg, Institute of Materials Engineering) for carrying out the nano and pico indentation hardness measurements.

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

References

1. Stock, H.-R.; Chen, H.-Y.; Mayr, R. Plasmanitrieren von Aluminiumwerkstoffen—Möglichkeiten und Grenzen eines neuen Verfahrens, Teil 1: Vorreinigung der Oberflächen. *Aluminium* **1994**, *70*, 220–228.
2. Reinhold, B. Untersuchungen zum Einfluss des Sauerstoffpartialdrucks beim Plasmanitrieren von Aluminiumlegierungen und Chromlegierten Stählen. Ph.D. Thesis, TU Bergakademie Freiberg, Freiberg, Germany, 2004.
3. 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.
4. Dalke, A.; Buchwalder, A.; Spies, H.-J.; Zenker, R. Influence of process control on nitride layer formation of spray formed Al alloys during dc pulse plasma nitriding. In Proceedings of the IFHTSE 2014, München, Germany, 12–15 May 2014.
5. Spies, H.-J. Stand und Entwicklung des Nitrierens von Aluminium- und Titanlegierungen. *HTM J. Heat Treat. Mater.* **2000**, *55*, 141–150. [[CrossRef](#)]
6. Spies, H.-J.; Dalke, A. Nitriding of Aluminum and its Alloys. In *ASM Handbook, Heat Treating of Nonferrous Alloys*; Totten, G.E., Ed.; ASM International: Geauga, OH, USA, 2016; Volume 4E, pp. 302–307. [[CrossRef](#)]

7. Telbizova, T.; Parascandola, S.; Kreissig, U.; Günzel, R.; Möller, W. Mechanism of diffusional transport during ion nitriding of aluminium. *Appl. Phys. Lett.* **2000**, *76*, 1404–1406. [\[CrossRef\]](#)
8. Stock, H.-R.; Chen, H.-Y.; Mayr, R. Plasmanitrieren von Aluminiumwerkstoffen—Möglichkeiten und Grenzen eines neuen Verfahrens, Teil 2: Untersuchungen von plasmanitrieren Aluminiumoberflächen. *Aluminium* **1994**, *70*, 463–471.
9. Reinhold, B.; Naumann, J.; Spies, H.-J. Einfluss von Zusammensetzung und Bauteilgeometrie auf das Nitrierverhalten von Aluminiumlegierungen. *HTM J. Heat Treat. Mater.* **1998**, *53*, 329–336. [\[CrossRef\]](#)
10. Buchwalder, A.; Dalke, A.; Spies, H.-J.; Zenker, R. Plasma nitriding of spray-formed aluminium alloys. *Adv. Eng. Mater.* **2012**, *13*, 970–975. [\[CrossRef\]](#)
11. Buchwalder, A.; Spies, H.-J.; Zenker, R.; Dalke, A.; Krug, P. Plasmanitrieren von sprühkompaktierten Al-Legierungen. *HTM J. Heat Treat. Mater.* **2011**, *66*, 240–247. [\[CrossRef\]](#)
12. Klimera, A. Festigkeitssteigerung von Aluminiumnitrid-Keramiken. Ph.D. Thesis, University Würzburg, Würzburg, Germany, 2008.
13. Jinschek, J.R. Untersuchungen von Aluminiumnitrid-Schichten auf Silizium-Substraten mittels Transmissionselektronenmikroskopie. Ph.D. Thesis, University Jena, Jena, Germany, 2001.
14. Heyden, D. Nitrierung von Aluminium mit Gepulster Ionenstrahlung. Ph.D. Thesis, University Heidelberg, Heidelberg, Germany, 2001.
15. Vacandio, F.; Massiani, Y.; Gravier, P.; Garnier, A. A study of the physical properties and electrochemical behavior of aluminium nitride films. *Surf. Coat. Technol.* **1997**, *92*, 221–229. [\[CrossRef\]](#)
16. Barnikel, J. Nitrieren von Aluminiumwerkstoffen mit UV-Laserstrahlung. Ph.D. Thesis, University Erlangen-Nürnberg, Erlangen-Nürnberg, Germany, 1998.
17. Blawert, C.; Mordike, B.L. Plasma immersion ion implantation of pure aluminium at elevated temperatures. *Nucl. Instr. Meth. Phys. Res. B* **1997**, *127*, 873–878. [\[CrossRef\]](#)
18. Chen, H.-Y.; Stock, H.-R.; Mayr, P. Plasma-assisted nitriding of aluminium. *Surf. Coat. Technol.* **1994**, *64*, 139–147. [\[CrossRef\]](#)
19. Youngman, R.; Harris, J. Luminescence studies of oxygen-related defects in aluminum nitride. *J. Am. Ceram. Soc.* **1990**, *73*, 3238–3246. [\[CrossRef\]](#)
20. Dalke, A. Beitrag zur kombinierten Randschichtbehandlung von Aluminiumlegierungen: Elektronenstrahlumschmelzlegieren mit Fe-Basis-Zusatzstoffen und Plasmanitrieren. Ph.D. Thesis, TU Bergakademie Freiberg, Freiberg, Germany, 2016.
21. Chen, P.-C.; Shih, T.-S.; Wu, C.-Y. Thermally formed oxides on Al-2 and 3.5 mass% Mg alloys heated and held in different gases. *Mater. Trans.* **2009**, *50*, 2366–2372. [\[CrossRef\]](#)
22. Stock, H.R.; Jarms, C.; Seidel, F.; Döring, J.E. Fundamental and applied aspects of the plasma-assisted nitriding process for aluminium and its alloys. *Surf. Coat. Technol.* **1997**, *94–95*, 247–254. [\[CrossRef\]](#)
23. Meletis, E.I.; Yan, S. Formation of aluminum nitride by intensified plasma ion nitriding. *J. Vac. Sci. Technol. A* **1991**, *9*, 2279–2284. [\[CrossRef\]](#)
24. Bouvier, Y.; Mutel, B.; Grimblot, J. Use of an Auger parameter for characterizing the Mg chemical state in different materials. *Surf. Coat. Technol.* **2004**, *180–181*, 169–173. [\[CrossRef\]](#)
25. Yang, C.; Lü, H.; Chen, D.; Liu, F. In situ synthesis and formation mechanism of AlN in Mg-Al alloys. *Rare Metal Mat. Eng.* **2016**, *45*, 18–22. [\[CrossRef\]](#)
26. Kent, D.; Drennan, J.; Schaffer, G. A morphological study of nitride formed on Al at low temperature in the presence of Mg. *Acta Mater.* **2011**, *59*, 2469–2480. [\[CrossRef\]](#)
27. Hegelmann, E.; Jung, A.; Hengst, P.; Zenker, R.; Buchwalder, A. Investigations regarding electron beam surface remelting of plasma nitrided spray-formed hypereutectic Al-Si alloy. *Adv. Eng. Mater.* **2018**, *20*, 1800244. [\[CrossRef\]](#)
28. Buchwalder, A.; Böcker, J.; Hegelmann, E.; Jung, A.; Michler, M. Investigations on the influence of a subsequent electron beam (EB) remelting on the microstructure of an aluminium nitride layer formed on an aluminium substrate (Part II). *Coatings* **2022**, in press.
29. Linnemann, A.; Kühl, S. *Grundlagen der Licht- und Elektronenmikroskopie*; Eugen Ulmer KG: Stuttgart, Germany, 2018.
30. DIN EN ISO 14577: 01.11.2015; Metallische Werkstoffe—Instrumentierte Eindringprüfung zur Bestimmung der Härte und anderer Werkstoffparameter. Available online: <https://www.beuth.de/en/standard/din-en-iso-14577-1/190992638> (accessed on 1 April 2022).
31. Oettel, H.; Schumann, H. *Metallografie mit einer Einführung in die Keramografie*, 15th ed.; WILEY VCH Verlag: Weinheim, Germany, 2011.
32. Williams, D.B.; Carter, C.B. *Transmissions Electron Microscopy—A Textbook for Materials Science*; Plenum Press: New York, NY, USA, 1996.
33. Buchwalder, A.; Zenker, R. Pre- and Post-Surface Treatments using Electron Beam Technology for Load-Related Application of Thermochemical and PVD Hard Coatings on Soft Substrate Materials. *Surf. Coat. Technol.* **2019**, *375*, 920–932. [\[CrossRef\]](#)
34. Buchwalder, A.; Dalke, A.; Spies, H.-J.; Zenker, R. Studies of technological parameters influencing the nitriding behavior of spray-formed Al alloys. *Surf. Coat. Technol.* **2013**, *236*, 63–69. [\[CrossRef\]](#)
35. Dalke, A.; Spies, H.-J.; Biermann, H. Plasmanitrieren von Aluminiumlegierungen. *HTM J. Heat Treat. Mater.* **2011**, *66*, 116–123. [\[CrossRef\]](#)
36. Quast, M.; Mayr, P.; Stock, H.R. In situ and ex situ examination of plasma-assisted nitriding of aluminium alloys. *Surf. Coat. Technol.* **2001**, *135*, 238–249. [\[CrossRef\]](#)
37. Figueroa, U.; Salas, O.; Oseguera, J. Production of AlN films: Ion nitriding vs. PVD coatings. *Thin Solid Films* **2004**, *469–470*, 295–303. [\[CrossRef\]](#)

-
38. Niessner, W. Elektronen-Energieverlust-Spektroskopie an Gruppe-III-Nitriden und Übergangsmetall-Oxiden. Ph.D. Thesis, University Gießen, Gießen, Germany, 2000.
 39. Funamizu, Y.; Watanabe, K. Interdiffusion in the Al-Cu System. *Trans. Jpn. Inst. Met.* **1971**, *12*, 147–152. [[CrossRef](#)]
 40. Rothman, S.J. Tracer Diffusion of Magnesium in Aluminium Single Crystals. *Phys. Stat. Sol. B* **1974**, *63*, 29–33. [[CrossRef](#)]