

ARTICLE

Influence of increased voltage on the nitriding zone during plasma nitriding

Einfluss erhöhter Spannung auf die Nitrierzone beim Plasmanitrieren

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Abstract

Plasma nitriding is an established process for increasing the corrosion and wear resistance of steel. However, the possibilities of modern developments in the field of high-voltage plasma power supplies have been hardly investigated. For example, modern plasma generators allow improved arc management, which enable plasma nitriding at higher voltages.

In the present work, the influence of increased voltage (up to 800 V) on the nitriding of a ferritic steel X38CrMoV5-1 was investigated. It was found that the thickness of the compound layer increases with increasing voltage. Especially at short process times the increased voltage leads to increased growth. An increase in the nitriding depth was also observed.

Furthermore, the increased voltage has an effect on the composition of the compound layer too. A moderate increase in ϵ -nitride in the compound layer was observed.

One explanation for the observed behavior is the over proportional increase in power with increasing voltage, indicating an increased ionization rate of the plasma. Due to this, more diffusible species would be available for nitriding. The presented results could be used to reduce process times, particularly where the formation of a compound layer is the aim of the process. An example of such a process is oxy-nitriding.

KEYWORDS

compound layer, increased voltage, plasma nitriding, short-time process

Abstract

Das Plasmanitrieren ist ein etabliertes thermochemisches Verfahren zur Verbesserung der Korrosions- und Verschleißbeständigkeit von Stählen. Moderne technologische Entwicklungen auf dem Gebiet der Hochspannungsplasma-strom-Versorgung und die Erforschung ihres Potenzials sind kaum

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untersucht worden. So ermöglichen moderne Plasmageneratoren ein deutlich verbessertes Arc-Management, das Plasmanitrierprozesse bei höheren Spannungen ermöglicht. In der vorliegenden Arbeit wurde der Einfluss einer erhöhten Spannung (bis zu 800 V) auf das Nitrieren eines ferritischen Stahls (X38CrMoV5-1) untersucht. Es wurde festgestellt, dass die Dicke der Verbindungsschicht mit steigender Spannung zunimmt. Insbesondere bei kurzen Prozesszeiten führt die erhöhte Spannung zu einem deutlich erhöhten Wachstum. Darüber hinaus wurde auch eine Zunahme der Gesamtnitriertiefe beobachtet. Darüber hinaus scheint die erhöhte Spannung einen Einfluss auf die Zusammensetzung der Verbindungsschicht zu haben. Mit zunehmender Spannung wurde eine moderate Zunahme von ϵ -Nitrid in der Verbindungsschicht beobachtet. Eine Erklärung für das beobachtete Verhalten ist der überproportionale Anstieg der Leistung mit steigender Spannung, was auf eine erhöhte Ionisierungsrate des Plasmas hinweist. Dadurch stehen mehr diffusionsfähige Spezies für die Nitrierung zur Verfügung. Die vorgestellten Ergebnisse können genutzt werden, um die Nitrierprozesszeiten zu verkürzen, insbesondere wenn die Bildung einer Verbindungsschicht das Ziel des Prozesses ist. Ein Beispiel für solche Prozesse ist das Oxy-Nitrieren.

SCHLÜSSELWÖRTER

Hochspannung, Kurzzeitprozesse, Plasmanitrieren, Verbindungsschicht

1 | INTRODUCTION

Plasma nitriding is an established thermochemical process for increasing the corrosion and wear resistance of steel and other metals. It has been successfully used in industry for decades to optimize components and tools for their intended use. Nevertheless, since its establishment, there have been limited investigations into the further development of the plasma nitriding process. Modern technological developments in the field of plasma power supplies and the exploration of their potential have hardly been investigated. For example, modern plasma generators allow significantly improved arc management. The potential of these new capabilities needs to be investigated. For example, the improved arc management can be used to enable plasma nitriding processes at higher voltages. These experiments are not a form of plasma immersion ion implantation. In contrast to it, where powerful high-voltage pulses of several 10 kV are used, no new test stand is needed. A generator is connected to an existing pulsed hot-wall plasma nitriding plant, which enables a direct current voltage of up to 1000 V during the process.

The influence of increased voltage (up to 800 V) on the nitriding result of ferritic-martensitic steel 1.2343 (X38CrMoV5-1) was investigated. The compound layer

thickness increases with increasing voltage. Especially at short process times leads the increased voltage to significantly increased nitriding results. In addition to a significant growth in the compound layer thickness, an increase in the total nitriding depth was also observed.

2 | MATERIAL AND METHODS

2.1 | Sample material

The ferritic-martensitic hot work tool steel 1.2343 (X38CrMoV5-1) were used. The samples were round specimens with a diameter of 35 mm and a thickness of 4 mm. Before the tests, the round specimens were prepared to a polishing level of 3 μm .

2.2 | Experimental procedure

The experiments were performed in a modified hot-wall plasma nitriding system. A direct current pulse physical vapor deposition plasma generator was used, these generators have a better arc control management and thus the experiments with increased voltage became possible.

During the experiments, the voltage and the process time were varied, while the remaining parameters were kept constant. The voltage was varied from 500 V to 800 V in 100 V steps and the process time between 0.5 h, 2 h and 16 h, Table 1.

In order to keep the sample temperature constant as the voltage increased, the temperature of the wall heating had to be adjusted. This was necessary because the higher voltage causes the plasma to introduce more power and thus heat into the process. Accordingly, the heat input through the wall heating had to be reduced, Table 2.

2.3 | Test methods

The following properties of the nitrided zone were investigated:

- Hardness – depth profile by micro-indenter,
- Compound layer thickness by scanning electron microscope,
- Composition of the compound layer by x-ray diffraction (Siemens D9000).

The hardness-depth profile and the compound layer thickness were determined at the cross-section. For this purpose, the samples were separated, embedded, ground and polished. To determine the compound layer thickness, the samples were additionally etched with Oberhoffer (10 s wipe etch).

The compound layer thickness was determined by scanning electron microscope. Each sample was measured at 5 different points and the average value was calculated.

TABLE 1 Constant parameters of high voltage processes.

Process parameters	Steel samples
Temperature	565 °C
Pressure	300 Pa
Pulse-pause ratio	100 μ s–400 μ s
Gas-mixture	80 % Nitrogen, 20 % Hydrogen

TABLE 2 Setting of the heating for constant specimen temperature of 565 °C.

Voltage (V)	Heating temperature (°C)
500	660
600	620
700	350
800	off

The hardness-depth profile was determined with the aid of a micro-indenter. The hardness was determined according to Vickers. The surface hardness and the total nitriding depth were also determined.

The composition of the compound layer was determined by x-ray diffraction. The measurement was performed in detector scan at a fixed angle of 5° and were taken between 20° and 100° with an increment of 0.2° and a scan speed of 5 s per increment.

3 | THEORY

3.1 | Plasma nitriding

Nitriding is a thermochemical process for surface modification of metallic materials (e.g. steel, aluminum, titanium) in order to harden the surface layer and reduce corrosion and wear on the surface [1]. Complex component geometries as well as internal contours can be treated without special precautions. A distinction is made between salt bath nitriding, gas nitriding and plasma nitriding [2].

Plasma nitriding has the advantage that the formation of the nitrided zone can be adjusted within a wide range and the process can be easily integrated into the coating process for diamond like carbon layers [2]. By means of a plasma, a nitrogen-hydrogen atmosphere is energized and atomic nitrogen is made available at the material surface, which can diffuse into the work piece [3]. In the work piece, the nitrogen causes a transformation of the original tool surface by forming a nitrided zone. This can consist of a compound layer on the surface and a precipitation zone called a diffusion zone. The formation of a compound layer can be prevented by selecting appropriate process parameters [4].

In steels, a complete transformation of the original material surface occurs in the compound layer by forming iron nitrides. After the nitriding process, γ' - and ϵ -nitrides have been determined [5, 6]. They have a ceramic character with increased hardness and brittleness, whereby there are differences between the nitrides [7].

In contrast to compound layer, no complete transformation of the material is carried out in the diffusion zone. Depending on the number of alloying elements and composition of the steel, nitride precipitations are formed. In the case of low-alloyed steels, precipitations of γ' -nitride predominate in the diffusion zone [2]. In the case of high-alloyed steels containing special nitride formers such as chromium, aluminum, molybdenum, tungsten, vanadium or silicon, small, finely distributed, hard and very temperature-resistant nitride precipitates of these elements are formed [2, 8]. These are responsible

for particle hardening and thus for an increase in hardness and strength [2]. Further effects of the special nitrides are partly massive volume changes, which lead to large lattice distortions and residual compressive stresses [9]. These lead to an increase in fatigue strength [10, 11].

3.2 | Developments in the field of plasma nitriding

In one paper, the influence of various adaptations of a plasma nitriding system on the nitriding result on C45E was investigated [12]. There were three different modified installations. First, the samples were nitrided conventionally with pulsed plasma. Second, a bias voltage was applied to the samples and third, the samples were nitrided passively. In this third installation, the sample is electrically isolated and a grid-shaped cathode near the samples provides the diffusible nitrogen for nitriding. There was no significant difference in the properties of the nitrided zone of the samples of these three modifications. Neither the surface hardness nor the total nitriding depth differed significantly. A reduction in the compound layer thickness was observed in the passively nitrided samples.

In another paper, the possibility of using the hollow cathode for nitriding austenitic steel was investigated [13]. The process can be used for the continuous nitriding of steel strips, but is consequently limited to very simple geometries.

Out-of-the-ordinary investigations include nitriding with the aid of an ion beam, and nitriding with the aid of a laser in a nitrogen atmosphere [14–16]. Materials that are difficult to nitride with conventional methods, such as aluminum or titanium, are usually studied here. However, austenitic steels are also examined. Successful nitriding is possible with the help of these methods, but is usually limited to a low total depth. Furthermore, it is difficult to nitride more complex components in this way

and simpler geometries such as cutting inserts were investigated.

This brief overview is intended to show that research is being carried out in the area of further development of the plasma nitriding process, but not all possibilities, such as increasing the voltage in the process, are being exploited for better technological development.

4 | RESULTS

4.1 | Influence of voltage on hardness-depth profile and compound layer thickness

The results are presented separately according to the process time. Starting with 16 h of treatment time.

At the 16 h tests, the increased voltage has hardly any influence on the hardness depth profile, Figure 1. There is no influence on the surface hardness and the total nitriding depth varies between 200 μm and 216 μm . A slight increase in the total nitriding depth can be assumed, but cannot be clearly confirmed. The compound layer thickness increases from 7.8 μm to 12.1 μm between 500 V and 800 V, Figures 1, 2. The effect was noticeable at a voltage of 700 V and higher.

At a treatment time of 2 h, a significant increase in the total nitriding depth from 79 μm to 119 μm can be observed with increasing voltage. An increase in surface hardness is not visible, Figure 3. Likewise, an increase in the compound layer thickness from 1.8 μm to 8.4 μm can be observed, Figures 3, 4. In this case, a significant change was already measurable from 600 V onwards.

With a further reduction of the treatment time to 0.5 h, there is a difference between 20 μm and 60 μm in the total nitriding depth, whereby at 500 V concrete values were difficult to measure due to the weak nitriding, Figure 5. At 500 V, a significantly lower surface hardness was measured and no compound layer could be detected. At 600 V, the surface hardness was in the range

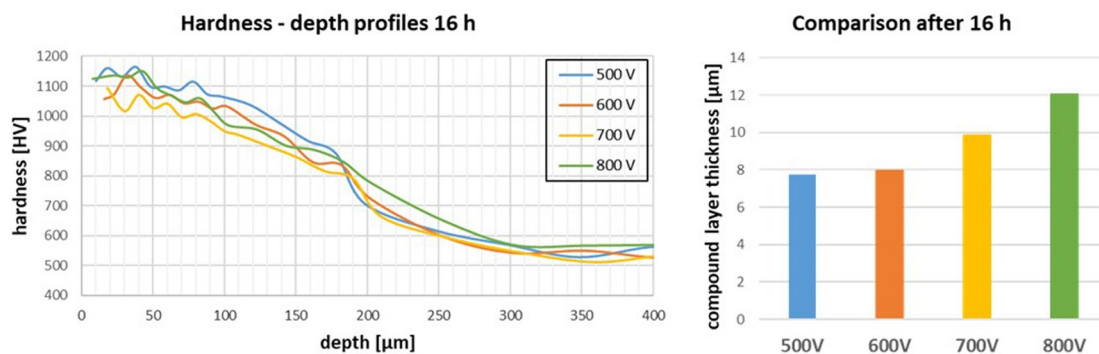


FIGURE 1 Left: hardness depth profiles, right: compound layer thickness at different voltages, 16 h.

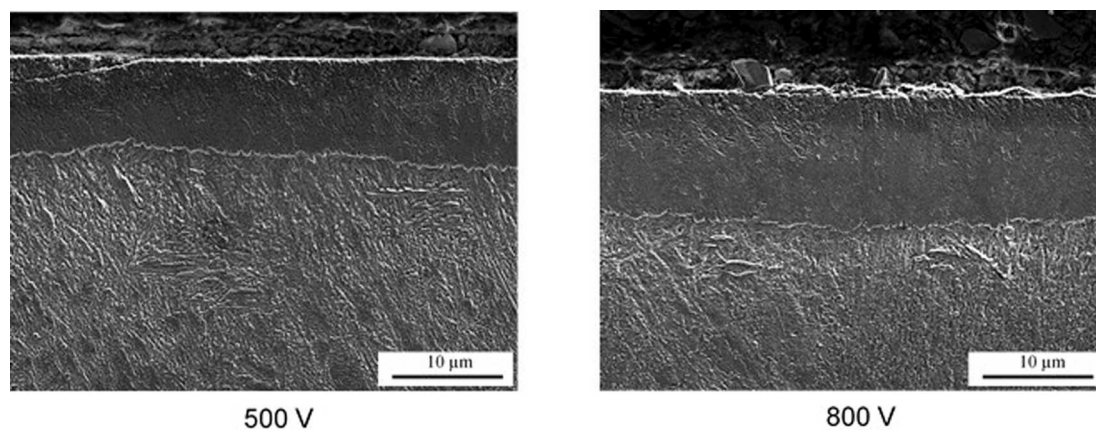


FIGURE 2 Scanning electron microscope pictures of compound layer at 500 V and 800 V, 16 h.

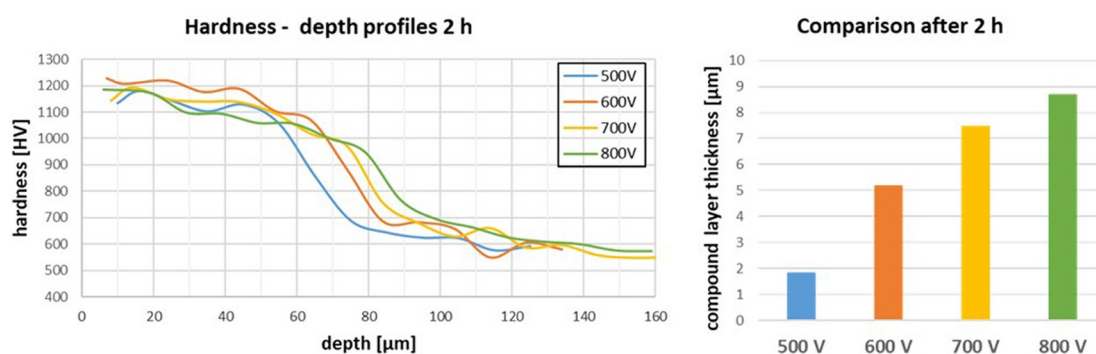


FIGURE 3 Left: hardness depth profiles, right: compound layer thickness at different voltages, 2 h.

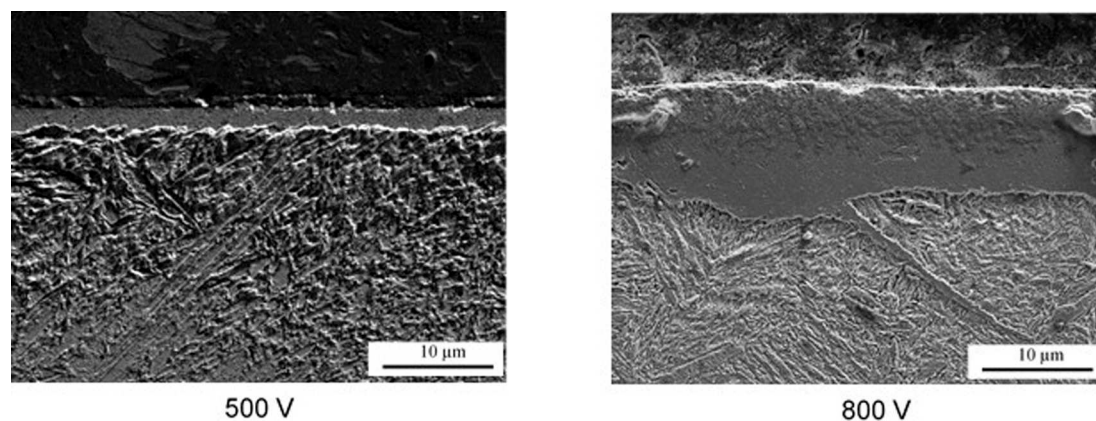


FIGURE 4 Scanning electron microscope pictures of compound layer at 500 V and 800 V, 2 h.

of the previous tests. The compound layer achieved a thickness of 5.4 µm at 800 V, Figures 5, 6.

4.2 | Influence on the compound layer composition

When analyzing the composition using x-ray diffraction, it was found that the amount of ϵ -nitride increases with

increasing voltage. This effect was detectable in all test series (16 h, 2 h, and 0.5 h). However, the effect is only moderately distinct and does not cause large transformations, Figure 7. The peaks at an angle of 38.6°; 44.0° and 57.8° (ϵ -nitride) increase and the peaks at an angle of 41.2° and 48.0° (γ' -nitride) decrease. The influence of the process time on the composition seems to be significantly higher. A strong change towards ϵ -nitride can be observed for the same peaks, Figure 8.

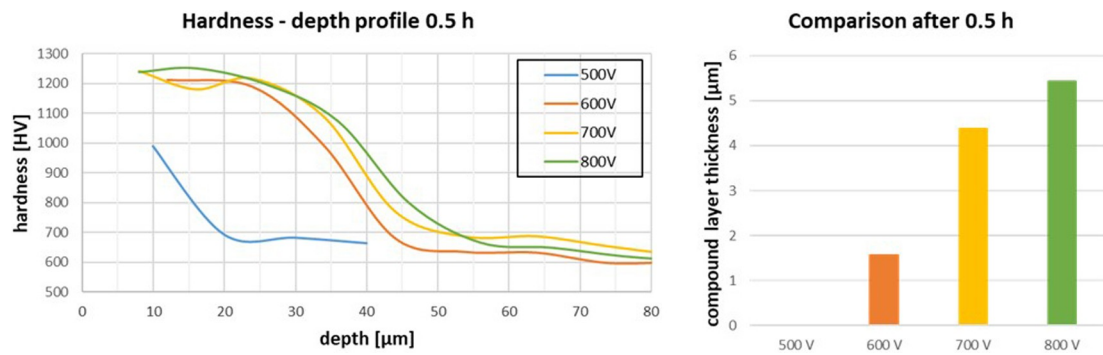


FIGURE 5 Left: hardness depth profiles, right: compound layer thickness at different voltages, 0.5 h.

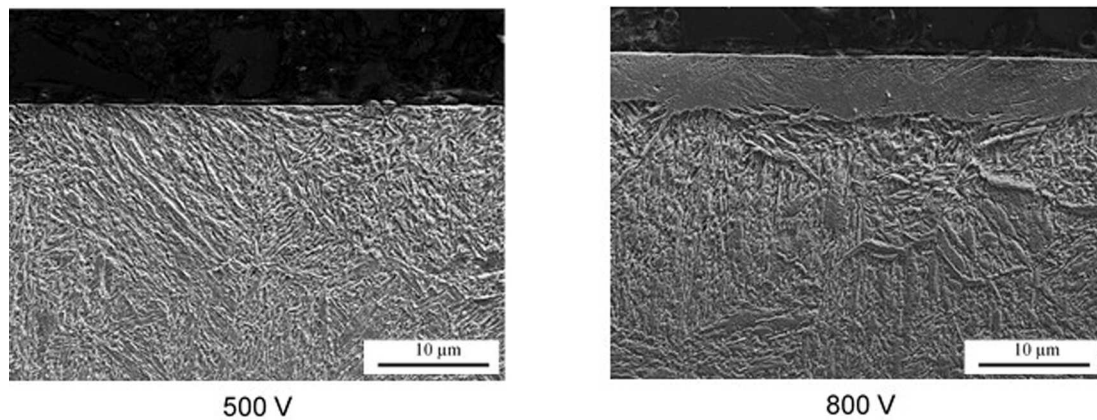


FIGURE 6 Scanning electron microscope pictures of compound layer at 500 V and 800 V, 0.5 h.

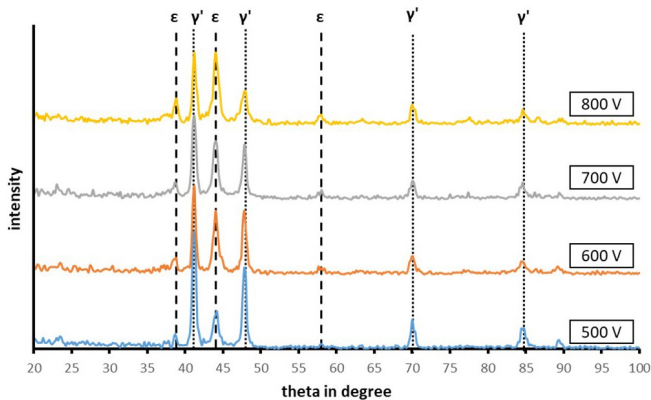


FIGURE 7 Results of x-ray diffraction measurements from 20° to 100° by 16 h process time.

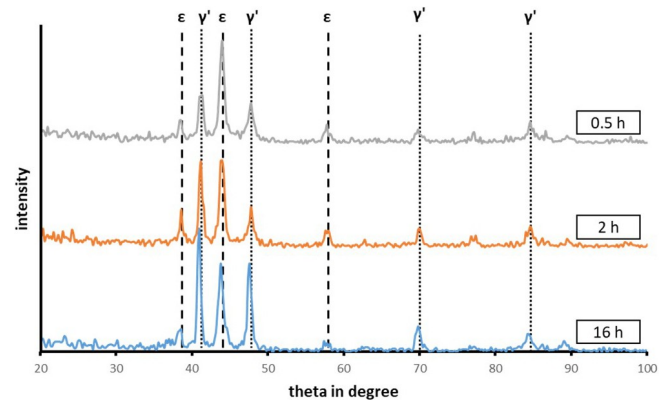


FIGURE 8 Results of x-ray diffraction measurements from 20° to 100° by 600 V.

This means that the composition of the compound layer shifts to a higher proportion of ϵ -nitride with shorter process times.

By measuring the current during the experiments, the current and thus the power of the plasma increased more with increasing voltage than had been expected. The output current was given directly from the generator. The current does not increase linearly with increasing voltage, but more strongly, Figure 9. This effect

increases with increasing voltage, and was measured up to 1000 V.

5 | DISCUSSION

Higher plasma voltage has an influence on the compound layer. With increasing voltage, an increase in the compound layer thickness can be observed in all tests.

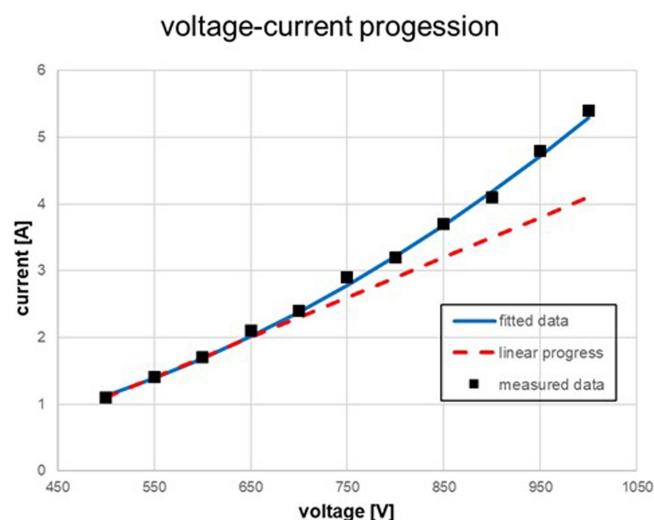


FIGURE 9 Current growth from 500 V to 1000 V.

Furthermore, an increase in the ϵ -nitride content in the compound layer was detected in all tests. From this, it can be concluded that a higher voltage favors the formation of ϵ -nitride to a moderate extent. It is interesting that the influence of time for the formation of ϵ -nitride seems to be significantly higher and shorter process times favor the formation. This might suggest, that ϵ -nitride forms at earlier stages of the process and is partially converted to γ '-nitride during longer processes.

It can also be seen from the results at shorter process times that the influence of voltage on the nitrided zone in general and on the compound layer in particular increases as the process time decreases. This can be seen at the greater difference in compound layer growth, as well as the increase in total nitriding depth with shorter process times. At 16 h, the growth of the compound layer thickness from 500 V to 800 V is approximately 50%, at 2 h, the growth is approximately 300% and at 0.5 h, no compound layer was formed at 500 V. The same is observed for the total nitriding depth at shorter process times. At 16 h, the increase between 500 V and 800 V is less than 10%, at 2 h the increase is over 60% and at 0.5 h approximately 200%.

One explanation for this behavior could be the disproportionate increase of the current at higher voltage. This observation suggests that with increasing voltage the ionization rate of the plasma increases and thus more diffusible species per time unit are available in the plasma. This increased availability could have an effect especially close to the surface, so that a thicker compound layer is formed and probably even the formation of a compound layer in general is supported. Furthermore, this increased availability of diffusible nitrogen seems to have a stronger influence on the process

for short process times than for longer process times. There, temperature-driven diffusion seems to be the greater influencing factor compared to the availability of diffusible species. As long as sufficient diffusible species are available and thus a certain saturation has occurred. This can be assumed due to the different influence of the high voltages on the total nitration depth at the different process times.

The results could be used for a shortening of economic nitriding processes, as long as the generation of a compound layer is the aim of the process. A similar compound layer thickness can be achieved at 800 V and 2 h as at 16 h and 500 V.

An example of such processes is oxy-nitriding. In this process, a compound layer is created and afterwards converted into an oxide layer (magnetite). By increasing the voltage during nitriding and possibly also during following oxidation, the process times could be massively shortened.

6 | CONCLUSION

The presented results can be summarized as follows:

- Increased plasma voltage has a great influence on the compound layer and leads to increased layer growth and increased formation of ϵ -nitride.
- The influence of high voltage on the nitrided zone is increased with short process times and affects the total nitriding depth too.
- A shortened process time also causes an increased formation of ϵ -nitride.
- With an increase in voltage, there is a disproportionate increase in current and power, which is interpreted as an increase in the ionization rate of the plasma.
- This increased ionization rate seems to be responsible for the observed effects of voltage on the nitrided zone.

Due to the possibility of massively shortening certain plasma nitriding processes in terms of time, the results offer great economic potential.

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