

# The Effect of Sputtering on Kinetics of Compound Zone Formation in the Plasma Nitriding of 3% Cr-Mo-V Steel

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**Kinetic studies of compound zone formation in plasma nitriding of 3% Cr-Mo-V DIN 39CrMoV13.9 steel were performed at 538 °C in a mixture of 30% N<sub>2</sub> and 70% H<sub>2</sub>. It was found that the process could be described by a half-order polynomial equation and that the TableCurve®2D software can be used to analyze the effect of sputtering on the kinetic. The sputtering rate (SR) was found to be about 0.03 μm/h. The short nitriding cycles (up to 24 h) produced a mixture of the γ' and ε nitrides and the longer cycles (up to 400 h) produced the γ' single-phase layer. The presence of the ε phase resulted in faster sputtering as well as faster diffusional growth of the compound zone.**

**Keywords** 3Cr-Mo-V steel, compound growth rates, mechanisms of compound growth, nitrogen-hydrogen plasma, plasma nitriding

## 1. Introduction

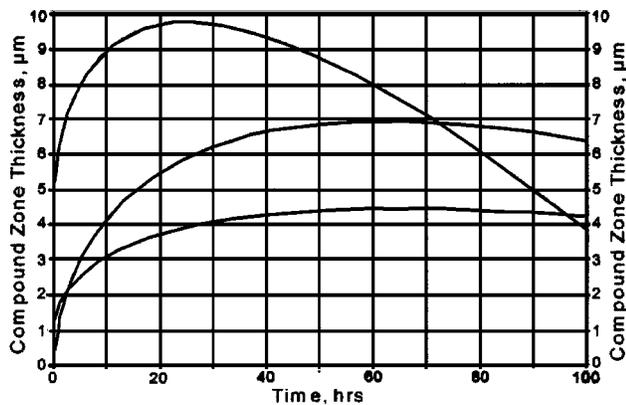
The role of sputtering in plasma nitriding has been a subject of many studies in the last 35 years.<sup>[1–15]</sup> A qualitative approach to analysis of the sputtering rate (SR) in plasma nitriding has been proposed by Keller,<sup>[2]</sup> who concluded that the parabolic growth of the compound zone (zone containing a mixture of Fe<sub>4</sub>N and Fe<sub>2–3</sub>N nitrides) is affected by a linear removal rate of the surface atoms due to sputtering. The first numerical analyses of these processes were done by Marciniak<sup>[9,10]</sup> and Sun and Bell.<sup>[15]</sup> The calculated and experimentally verified SR for samples plasma nitrided at 520 °C were about 0.6 g/m<sup>2</sup> h (it corresponds to 0.1 μm/h) for iron and 0.6 to 0.8 g/m<sup>2</sup> h for 0.38% C-1.6% Cr-Al-Mo steel.<sup>[9]</sup> The model developed by Sun and Bell<sup>[15]</sup> allowed precise calculations of the compound layer growth for a specific steel, the specific nitriding conditions, and the assumed SR. The assumed values of SR were between 0.1 and 0.5 μm/h.<sup>[15]</sup> If the assumptions of Keller<sup>[2]</sup> and Marciniak<sup>[10]</sup> are correct, then the kinetic of the compound zone growth  $y$  in plasma nitriding can be described by the half-order polynomial equation:

$$y = a + bx + c\sqrt{x} \quad (\text{Eq 1})$$

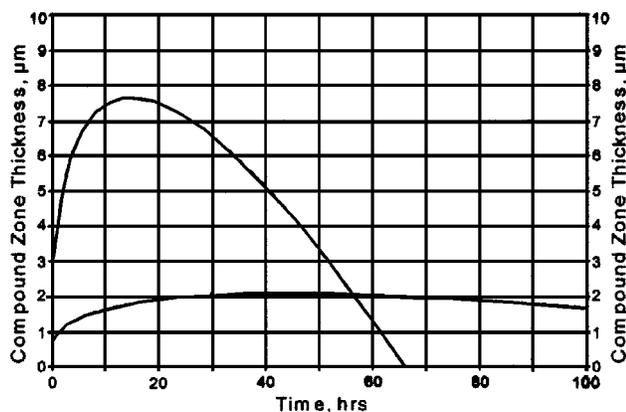
where  $a$  is a compound zone thickness formed during the ramp-up time,  $b$  is an SR,  $c$  is a coefficient of compound zone growth due to diffusion, and  $x$  is a nitriding time. The experimental results of Edenhofer<sup>[4]</sup> for the kinetics of the compound zone formation on En 9 (AISI 4142) steel plasma nitrided at 450, 530, and 570 °C were fitted to Eq 1 using the TableCurve®2D software<sup>[16]</sup> and are presented in Fig. 1. The fit of the data for the available 45 h range is very good, since the coefficient of

determination,  $r^2$ , is high: 0.993, 0.995, and 0.962, respectively. The calculated SR is 0.057 μm/h for 450 °C, 0.124 μm/h for 530 °C, and 0.427 μm/h for 570 °C. The graph extrapolated to 100 h of nitriding time shows the curves' tendency; the maximum, respectively, at approximately 65, 50, and 35 h of nitriding and the diminishing values thereafter. At the same time, the growth due to diffusion (the coefficient  $c$ ) is larger for higher temperatures and smaller for lower nitriding temperatures. Similar graphs based on the experimental data of Marciniak<sup>[10]</sup> for 36 H3M (0.36% C-3% Cr-0.6% Mo-0.6% Mn-0.27% Si) steel nitrided at 530 °C are presented in Fig. 2. The curve with a well-distinguished maximum at about 16 h drawn for nitriding with 50% nitrogen and 50% hydrogen represents a growth of a compound zone consisting of a mix of the epsilon and gamma prime type nitrides.<sup>[9]</sup> The SR is about 0.425 μm/h. Nitriding with 15% nitrogen and 85% hydrogen produced a gamma prime type compound zone and an SR of about 0.036 μm/h. The "diffusion" fraction of the kinetic equation, which represents a nitriding potential, is higher for the samples nitrided with 50% nitrogen and 50% hydrogen than for samples nitrided with 15% nitrogen and 85% hydrogen. However, all of the above predictions for the range of time exceeding the experimental data range may not be accurate since extreme caution is advised in relying on polynomials for extrapolations and forecasts beyond the range of the dataset.<sup>[16]</sup> The diminishing value of the compound zone thickness during a long nitriding time may have important practical meaning; the compound zone could eventually disappear completely and therefore the nitriding rate would drop down and/or a denitriding of the steel could take place.<sup>[5]</sup> Wells and Strydom suggested that the compound zone growth might also be affected by redeposition of the sputtered material.<sup>[12]</sup> This phenomenon could be enhanced by oxygen, which may always be present in a small quantity in industrial systems, and, therefore, the compact portion of the compound zone can be significantly reduced by formation of the oxynitride.<sup>[12]</sup> Consequently, in our studies, we researched the actual kinetics of compound zone formation in long nitriding with an aim to establish the SR in such a cycle. The 3% Cr-Mo-V steel we investigated is used in the gear industry to achieve an exceptionally deep case. It was then very important to verify

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**Fig. 1** Compound zone thickness vs nitriding time for 42Cr Mo4 (AISI 4142 steel) plasma nitrided 3.3 mbar in the atmosphere of 25% nitrogen + 75% hydrogen at 570 °C (upper curve), 530 °C (middle curve), and 450 °C (bottom curve) based on the experimental data of Edenhofer.<sup>[4,21]</sup> The graph is extrapolated over the original limit of 45 h. The fit equations are  $y = 3.8722 - 0.236x + 2.361\sqrt{x}$ ,  $y = -0.789 - 0.124x + 1.958\sqrt{x}$  and  $y = 0.758 - 0.057x + 0.918\sqrt{x}$  and  $r^2 = 0.993, 0.995, \text{ and } 0.962$ , respectively



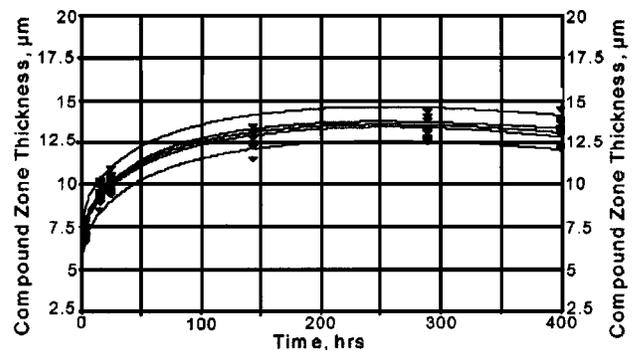
**Fig. 2** Compound zone thickness vs nitriding time for 36H3M 3% Cr-Mo steel plasma nitrided at 530 °C in the atmosphere of 50% nitrogen + 50% hydrogen (upper curve) and 15% nitrogen + 85% hydrogen (bottom curve) based on the experimental data of Marciniak.<sup>[10]</sup> The graph is extrapolated over original limits of 16 and 36 h, respectively. The fit equations are  $y = 1.275 - 0.425x + 3.295\sqrt{x}$ ,  $y = 0.5 - 0.036x + 0.479\sqrt{x}$ , and  $r^2 = 0.994 \text{ and } 0.986$ , respectively

if the thickness of the compound zone would become thinner to the point of disappearing completely with prolonged nitriding.

## 2. Experimental

### 2.1 Material and Processing

A quenched and tempered 3% Cr-Mo-V (DIN 39CrMo V13.9) nitriding steel was used for these studies. The Brinell hardness was 321 to 363. The test samples were  $1 \times 1 \times 6$  in. bars with a ground surface finish of Ra 1.6  $\mu\text{m}$  or better. All samples were blasted with 180-grit aluminum oxide before nitriding. The equipment and processing details were described



**Fig. 3** Compound zone thickness vs nitriding time for 3% Cr-Mo-V steel plasma nitrided at 538 °C. The fit equation is  $y = 6.158 - 0.0294x + 0.933\sqrt{x}$  and  $r^2 = 0.952$ . Confidence and prediction intervals represent normal distribution and standard error (small interval) at 95%

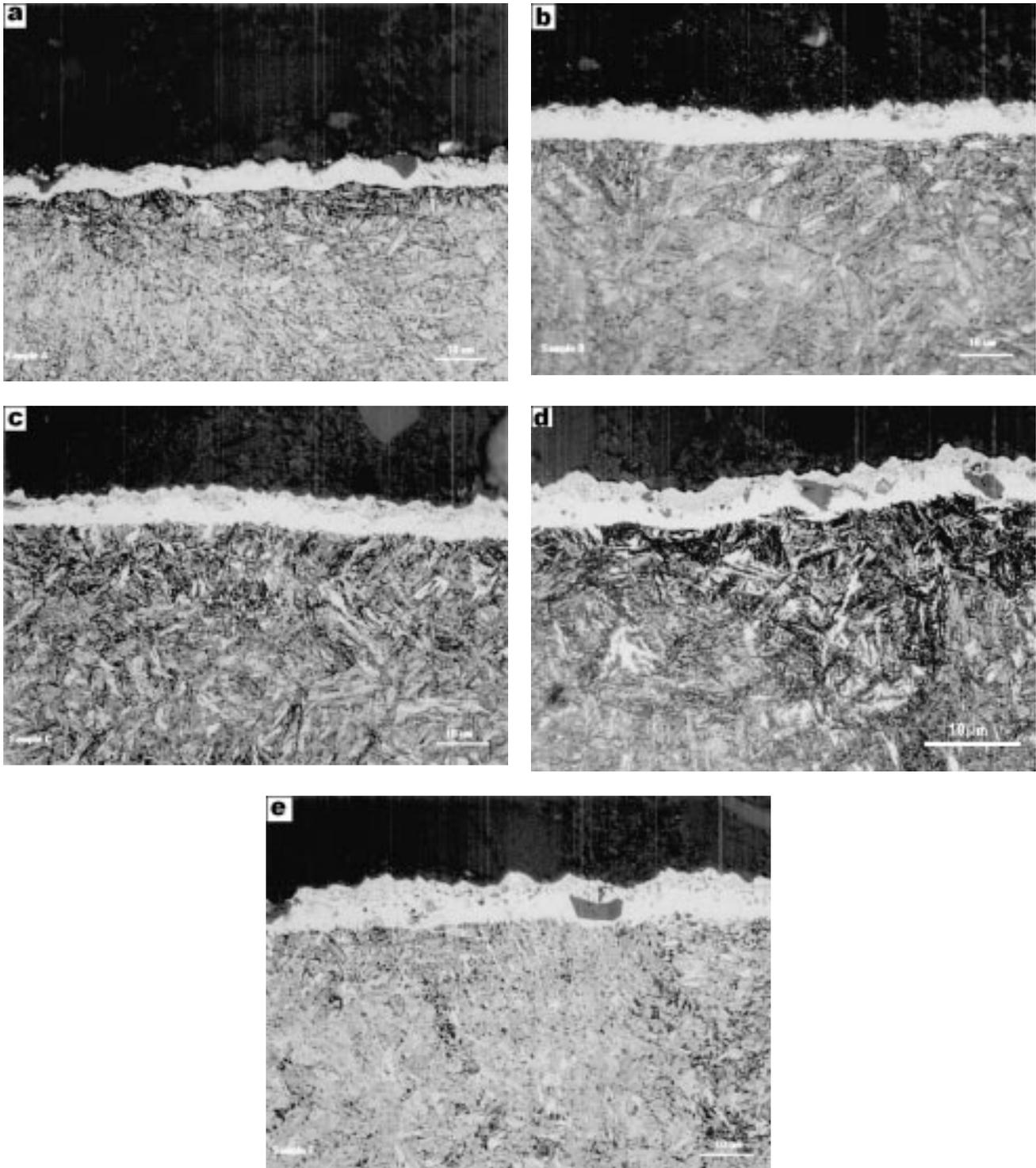
elsewhere.<sup>[17]</sup> The nitriding was carried out at 538 °C nominal temperature, and the nitriding times were from 4 to 400 hours. The samples were treated in a DC plasma in the atmosphere of 30% nitrogen and 70% hydrogen and a pressure of 3.2 mbar. The ramp-up time was 4 h.

### 2.2. Testing Procedure

The samples were cut in half and prepared for metallographic studies. The compound zone thickness was measured at 400 $\times$  using the digital filar eyepiece of the MICROMET® II microhardness tester (Buehler, Lake Bluff, IL). Each sample was tested in four different areas (four sides). The compact portion of the compound zone was measured. The local peaks appearing on the surface were ignored. The accuracy of a single measurement was  $\pm 0.1 \mu\text{m}$ . There was a minimum of five samples used in each run. The x-ray diffraction phase analysis was performed using Cr  $K_{\alpha}$  radiation.

## 3. Results and Discussion

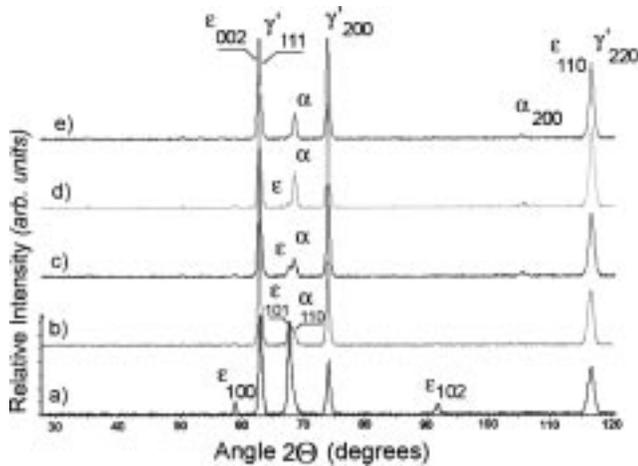
The compound zone thickness changes with the nitriding time, as shown in Fig. 3. A possible maximum value of approximately 13.5  $\mu\text{m}$  is achieved after about 250 h of nitriding, and the final value after 400 h is about 13  $\mu\text{m}$ . Photomicrographs of the compound zone are presented in Fig. 4. They do not reveal any significant presence of the vapor deposited, possible oxygen contaminated layer, as was suggested by Wells and Strydom.<sup>[12]</sup> The top portion of the compound zone contains some porosity and probably a layer of the nitrides deposited from plasma; however, its main fraction stays very compact. Optical microscopy of the microsections also revealed a presence of frequent conical structures at the surface. Similar features were also observed by others.<sup>[18]</sup> The intensity of these peaks was higher on samples nitrided longer. The x-ray diffraction showed that initially after 4 h of nitriding two iron nitrides,  $\epsilon$  ( $\text{Fe}_3\text{N}$ ) and  $\gamma'$  ( $\text{Fe}_4\text{N}$ ), were formed on the surface (Fig. 5). The intensity of the  $\epsilon$  patterns is quickly reduced and, after 25 h of nitriding, only two weak diffraction peaks from the (100) and (101) planes could be detected. The 400 h nitriding produced a single-phase gamma prime compound zone on the steel



**Fig. 4** Optical micrographs of surface layers produced on 3% Cr-Mo-V steel by plasma nitriding at 538 °C for (a) 4 h, (b) 25 h, (c) 144 h, (d) 289 h, and (e) 400 h. Bright field, etched with 2% nital

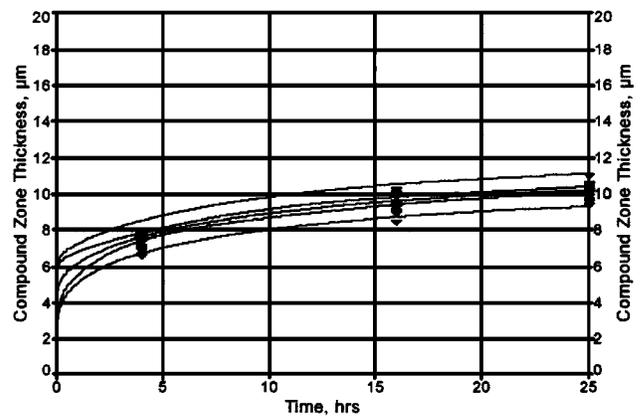
surface. It is very likely that the epsilon nitride formation was promoted by carbon present in the steel. It is known that carbon stabilizes the epsilon carbonitride and that it can diffuse outward from the steel during nitriding.<sup>[5,13,20,21]</sup> In the short nitriding processes, carbon atoms were diffused toward the surface and,

by reacting with iron and nitrogen, helped in the formation of the epsilon phase. During the long exposure to the plasma, the surface was decarburized as carbon was sputtered away and replaced by nitrogen. With a lack of carbon atoms, the nitriding potential of the plasma was shifted toward gamma prime; the

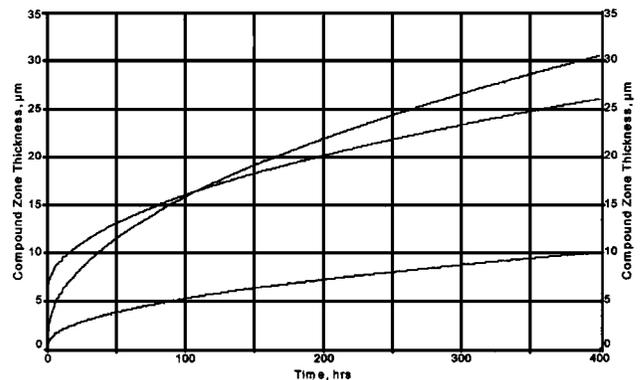


**Fig. 5** X-ray diffraction patterns of surface layers produced on 3% Cr-Mo-V steel plasma nitrided at 538 °C for (a) 4 h, (b) 25 h, (c) 144 h, (d) 289 h, and (e) 400 h. Cr  $K_{\alpha}$  radiation

lower nitrogen phase and the epsilon phase disappeared completely. The results of the compound zone thickness versus nitriding time studies clearly demonstrate the effect of sputtering; a possible maximum value at about 250 h and the diminishing values of the compound zone thereafter. The calculated SR is  $0.0295 \mu\text{m/h}$ , and the coefficient  $c$  of compound zone growth due to diffusion of nitrogen is 0.933. The total compound zone thickness  $a$ , formed during ramp-up to the final temperature is about  $6 \mu\text{m}$ . The  $a$  value depends on a growth due to diffusion of nitrogen and sputtering. Since sputtering was taken into account only from a time when the final temperature was reached, the  $a$  value was affected by an error of not counting the material removed. In fact, this value is only about  $0.06 \mu\text{m}$  if we assume that SR was the same during ramping and the final soaking. The SR of  $0.0295 \mu\text{m/h}$  from this experiment agrees very well with the value of  $0.036 \mu\text{m/h}$  calculated by us for the literature data of nitriding performed in the atmosphere of 15% nitrogen and 85% hydrogen on similar steel.<sup>[10]</sup> However, our kinetic studies as well as the studies based on the results of others<sup>[4,5,10,11]</sup> could be affected by not taking into account the fact that a phase composition of the steel surface may change during a long nitriding process. In the plasma nitriding of the 3% Cr-Mo-V steel, the equilibrium at the surface was not achieved very rapidly; in fact, it took many hours to produce a “pure” gamma prime nitride. It can then be concluded that the sputtering yield depends not only on pressure, temperature, gas composition, and the plasma power density, but mainly on the phase composition of the compound zone that formed on the surface. Some of these parameters were probably different in our experiment than in the experiments carried out by the other researchers;<sup>[4,10,15,19,21]</sup> however, as long as we consider gamma prime compound zone formation, its SR stayed low. In comparatively short nitriding cycles with a sufficiently high nitrogen content carried out by the others,<sup>[4,10]</sup> a mixture of the  $\gamma'$  and  $\epsilon$  was produced and, consequently, the SR was much higher than when the “pure” gamma prime phase was produced. This can be seen in Fig. 6, which represents the nitriding kinetics for shorter (up to 25 h) cycles. The graph is not biased by the phase composition change toward a pure gamma prime; the SR



**Fig. 6** Compound zone thickness vs nitriding time for 3% Cr-Mo-V steel plasma nitrided at 538 °C. This is a modified form of the Fig. 3 from which the data for a “pure” gamma prime compound zone were removed (144, 289, and 400 h). The fit equation is  $y = 5.438 - 0.049x + 1.221\sqrt{x}$  and  $r^2 = 0.958$ . Confidence and prediction intervals represent normal distribution and standard error (small interval) at 95%



**Fig. 7** Comparison of a hypothetical, sputtering “free” kinetic of compound zone growth in plasma nitriding of 3% Cr-Mo-V steel at 538 °C (curve with the middle final value) and 36H3M 3% Cr-Mo steel at 530 °C<sup>[10]</sup> (curve with the lowest final value) with gamma prime compound zone growth in gas nitriding of Armco iron at 550 °C with a constant nitriding potential  $K_N = 0.58 \text{ atm}^{-1/2}$  (curve with the highest final value)<sup>[22]</sup> The equations are  $y = 6.158 + 0.933\sqrt{x}$ ,  $y = 0.5 + 0.479\sqrt{x}$ , and  $y = 1.278 + 1.461\sqrt{x}$

is about  $0.049 \mu\text{m/h}$  and the coefficient  $c$  about 1.221. If we hypothetically assume a “sputtering free” plasma nitriding, we can use Eq 1 with the coefficient  $b$  equal to zero to see the effect of the remaining (diffusion) fraction of the equation on the kinetic. Figure 7 presents two curves drawn for the plasma nitriding processes: one from our studies and the second one based on the work of Marciniak,<sup>[10]</sup> compared with the curve for gas nitriding with a very low nitriding potential of  $K_N = 0.58 \text{ atm}^{-1/2}$ .<sup>[22]</sup> The curves for plasma nitriding of 3% Cr-Mo-V steel and the gas nitriding of Armco iron are very similar; they achieve a final value of 25 to  $30 \mu\text{m}$  after 400 h of nitriding. The final value for the plasma nitriding curve of 36H3M steel is about  $10 \mu\text{m}$ . Regardless of the sputtering effect, the plasma nitriding process in the atmosphere of 30% nitrogen and 70% hydrogen can be considered a low nitriding potential process.

In a plasma process, activation of the cathode due to ion bombardment from the atmosphere containing sufficiently high nitrogen is very effective, and, therefore, a full coverage of the surface with the compound zone after only a few minutes of nitriding is achieved.<sup>[15]</sup> This was also evidenced in our experiments by the fact that the curve did not start at the beginning of the coordinate, but earlier (Fig. 3). In a low potential, gas nitriding process, the gamma prime phase nucleates on ferrite extremely slowly and it is only after substantial time that it becomes a continuous, compact layer.<sup>[22]</sup> The experiments showed also that the equilibrium between plasma and the steel surface was not achieved quickly when the atmosphere of 30% N<sub>2</sub> and 70% H<sub>2</sub> was used. Instead, an initially formed mixture of  $\gamma'$  and  $\varepsilon$  phases was slowly converted into a single  $\gamma'$  phase structure. The phase composition changes resulted in a reduction of the SR, as well as a reduction in the diffusional growth of the compound zone. Sputtering of the surface in plasma nitriding has then an additional effect in the process: it effectively lowers an already low nitriding potential and enhances the ability to reduce the thickness of the compound zone.

#### 4. Conclusions

The experimental data of the compound zone formation taken from the literature were analyzed and presented in graphic forms. It was found by using the TableCurve@2D software that the SR for the gamma prime (0.036  $\mu\text{m}/\text{h}$ ) was smaller than for the epsilon containing type compound zone (up to 0.425  $\mu\text{m}/\text{h}$ ). At the same time, it was confirmed that the growth of the compound zone due to the diffusion of nitrogen was also slower for the gamma prime type, which could be expected.<sup>[22]</sup> The graphs extrapolated over the experimental data range showed that the kinetic curves may achieve a maximum value and that the sputtering may cause a complete disappearance of the compound zone after long nitriding. This type of kinetic characteristics were more likely for the epsilon type compound zone than for gamma prime. The experiments carried out on 3% Cr-Mo-V steel did not show any disappearance of the compound zone, and its final value after 400 h of nitriding was still about 13  $\mu\text{m}$ . The SR calculated from our experiment was about 0.03  $\mu\text{m}/\text{h}$ . This agrees well with the value calculated for kinetic data taken from the literature for a similar steel for presumably the gamma prime type nitride.<sup>[10]</sup> The analysis limited to cycles not exceeding 25 h resulted in a higher rate of sputtering as well as a faster diffusional growth. This fact can be attributed to the presence of the  $\varepsilon$  phase in the compound zone. Based on our research, it seems to be unlikely that the  $\gamma'$  compound zone can disappear completely because of sputtering after an extremely long nitriding time. Instead, it is more likely

that it will become more porous and the specific surface area will be greater. However, this will still need to be proven by additional experimental work.

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