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NITROGEN AVAILABILITY OF NITRIDING ATMOSPHERE IN CONTROLLED GAS NITRIDING PROCESSES

ROZPORZĄDZALNOŚCI AZOTU ATMOSFERY AZOTUJĄCEJ W PROCESACH REGULOWANEGO AZOTOWANIA GAZOWEGO

Parameters which characterize the nitriding atmosphere in the gas nitriding process of steel are: the nitriding potential K_N , ammonia dissociation rate α and nitrogen availability m_{N_2} . The article discusses the possibilities of utilization of the nitriding atmosphere's nitrogen availability in the design of gas nitriding processes of alloyed steels in atmospheres derived from raw ammonia, raw ammonia diluted with pre-dissociated ammonia, with nitrogen, as well as with both nitrogen and pre-dissociated ammonia. The nitriding processes were accomplished in four series. The parameters selected in the particular processes were: process temperature (T), time (t), value of nitriding potential (K_N), corresponding to known dissociation rate of the ammonia which dissociates during the nitriding process (α). Variable parameters were: nitrogen availability (m_{N_2}), composition of the ingoing atmosphere and flow rate of the ingoing atmosphere (F_{In}).

Keywords: Controlled gas nitriding, Nitrogen availability, Nitriding potential, Ammonia dissociation rate, Alloyed steels

Parametrami charakteryzującymi atmosferę azotującą w procesie azotowania gazowego stali są: potencjał azotowy K_N , stopień dysocjacji amoniaku α oraz rozporządzalność azotu m_{N_2} . W artykule omówiono możliwości wykorzystania rozporządzalności azotu atmosfery azotującej w projektowaniu procesów azotowania gazowego stali stopowych w atmosferach azotujących uzyskanych z amoniaku, z amoniaku rozcieńczonego zdysocjowanym amoniakiem, azotem oraz azotem i zdysocjowanym amoniakiem. Procesy azotowania wykonano w czterech seriach. Parametrami ustalonymi w poszczególnych seriach była temperatura procesu (T), czas (t), wartość potencjału azotowego (K_N), któremu odpowiada określona wartość stopnia dysocjacji amoniaku zdysocjowanego podczas procesu azotowania (α). Parametrami zmiennymi była rozporządzalność azotu (m_{N_2}), skład atmosfery wlotowej i natężenie przepływu atmosfery azotującej wlotowej (F_w).

1. Introduction

The nitriding process takes place in conditions of forced flow of the nitriding atmosphere. The kinetics of the process and the phase composition of the nitrided layer being formed are decided by the ratio between the flux of nitrogen from the atmosphere to the steel surface and the flux of nitrogen diffusing into the steel. The first flux is described by the laws governing mass transport in atmosphere, while the second – by the laws of diffusion in steel. During the nitriding process control can be effected only on the flux of nitrogen from the atmosphere to the surface of the steel being nitrided [1-3]. Gas nitriding can be accomplished utilizing four types of ingoing atmospheres: single component atmosphere composed of only ammonia (NH_3), a two-component atmosphere composed of ammonia and pre-dissociated ammonia (NH_3-NH_{3diss}), a two-component atmosphere composed of ammonia and nitrogen ($NH_3 - N_2$) and a tri-component atmosphere composed of ammonia with nitrogen and pre-dissociated ammonia ($NH_3 - N_2-NH_{3diss}$) [4].

The basic process parameters characterizing the nitriding atmosphere are: the nitriding potential (K_N), the ammonia

dissociation rate (α), the percentage composition of gaseous components of the atmosphere and the flow rate (F_{In}) [5]. The *nitriding potential* describes the possibilities of the nitriding atmosphere, from the point of view of formation of nitrided phases α , γ' and ϵ in conditions of concentration equilibrium of the atmosphere with the nitrided surface. The algorithm of its variation vs. time and temperature of the process determines the phase composition and the growth kinetics of the nitrided layer. The *dissociation rate* is a parameter describing which part of the ammonia have to decomposed to provide nascent nitrogen, essential to the formation of the nitrided layer and to attain equilibrium, described by the nitriding potential. The nitriding potential is universally used to control the kinetics of the nitriding process. Its value uniquely characterizes atmospheres comes from the single component atmosphere of ammonia (NH_3), as well as two-component atmospheres, comes from ammonia diluted by pre-dissociated ammonia (NH_3-NH_{3diss}) or by hydrogen ($NH_3 - H_2$) [6-8]. In such atmospheres, the nitriding potential can be utilized to control not only the growth kinetics of the solution layer but also the thickness and phase composition of the iron nitride layer. On the other hand, in the case of atmospheres diluted by

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nitrogen, information about the value of the nitriding potential is not sufficient for full control of the growth kinetics of the nitrided layer, especially of the iron nitride layer. In this case, the significant supplementary parameter characterizing the nitriding atmosphere is nitrogen availability (m_{N_2}). This parameter links the ammonia dissociation rate with the flow rate of the ingoing atmosphere (that, introduced into the furnace in the nitriding process) and contains information about the amount of nitrogen (in grams per minute) obtained in the given process conditions [9].

2. Nitrogen availability of the nitriding atmosphere

As a result of the dissociation reaction, one mole of ammonia gives 0.5 mole of nitrogen and 1.5 moles of hydrogen. Knowing the volume of ammonia which dissociates, mass of the nitrogen mole (28.016 g) as well as its volume (22.414 dm³) it is possible to calculate the mass of nitrogen m_{N_2} obtained from the reaction of dissociation:

$$m_{N_2} = \frac{0.5 \cdot V_{NH_3}^*}{22.414} \cdot 28.016 \quad (1)$$

where: $V_{NH_3}^*$ – volume of ammonia which dissociates in the process of nitriding

The volume of the ingoing atmosphere can be expressed by:

$$V_{In} = V_{NH_3}^* + V_{NH_3}^{**} \quad (2)$$

where: V_{In} – volume of ingoing atmosphere, $V_{NH_3}^{**}$ – volume of ammonia which does not dissociate

Since:

$$V_{NH_3}^* = s \cdot V_{In} \quad (3)$$

where: s – volume content of ammonia in the ingoing atmosphere which does not dissociate.

The mass of the nitrogen obtained from the dissociation reaction can be calculated by the formula:

$$m_{N_2} = \frac{1}{1.6} s \cdot V_{In} \quad (4)$$

By inserting the flow rate F_{In} (l·min⁻¹) in the place of volume V_{In} it is possible to calculate the mass of nitrogen obtained in unit time, in g·min⁻¹:

$$m_{N_2} = \frac{1}{1.6} \cdot s \cdot F_w \quad (5)$$

The dissociation rate of ammonia in the nitriding atmosphere α , in turn, expresses the ratio of the doubled part s of ammonia to the volume of the effluent atmosphere [10]:

$$\alpha = \frac{2 \cdot s}{1 + s} \quad (6)$$

Transformation of equation (6) yields the relationship binding the content of ammonia in the ingoing atmosphere which undergoes dissociation during nitriding, with the dissociation rate of ammonia:

$$s = \frac{\alpha}{2 - \alpha} \quad (7)$$

By the insertion of expression (7) into equation (5) is obtained by the formula used for calculation of nitrogen availability

m_{N_2} , depending on atmosphere flow rate and ammonia dissociation rate. Formula (8) is a measure of nitrogen availability in g·min⁻¹:

$$m_{N_2} = \frac{1}{1.6} \cdot \frac{\alpha}{2 - \alpha} \cdot F_{In} \quad (8)$$

The indication of the correlation of growth kinetics of the nitrided layer with the nitrogen availability of the nitriding atmosphere and nitriding potential, depending on the type of ingoing atmosphere was the subject of the present paper.

2.1. Nitrogen availability in an atmosphere of the NH_3 and $aNH_3 - cNH_{3diss}$ type

The NH_3 type atmosphere has many common features with type $aNH_3 - cNH_{3diss}$ where a – percentage content of NH_3 and c – percentage content of NH_{3diss} . The value of the nitriding potential uniquely characterizes each of the atmospheres from the point of view of nitriding intensity. In these atmospheres, same values of the nitriding potential correspond to same nitrogen availabilities (Fig. 1).

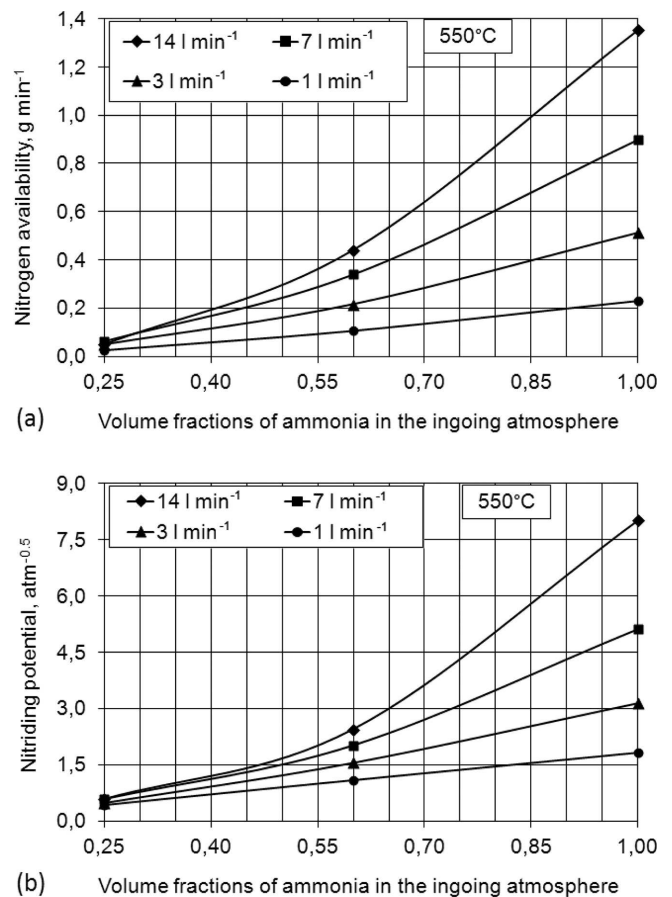


Fig. 1. Variation of nitrogen availability m_{N_2} (a), and the nitriding potential K_N (b) vs. content of ammonia in a two-component ingoing atmosphere with pre-dissociated ammonia [8]

Knowing the value of the dissociation rate to obtain the required value of the nitriding potential in the $aNH_3 - cNH_{3diss}$ – type atmosphere, as well as the flow rate of that atmosphere, it is possible to use formula (9) to calculate what flow rate of

a single component atmosphere is needed to obtain the same value of the nitriding potential:

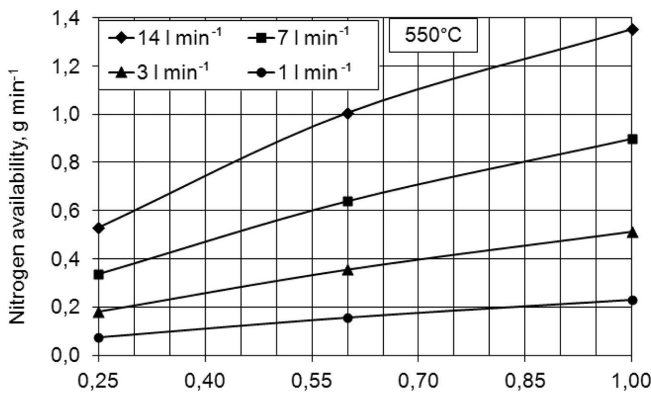
$$F_{In}^{NH_3} = \frac{(2 - \alpha) \cdot \alpha_{NH_3-NH_{3diss}}}{(2 - \alpha_{NH_3-NH_{3diss}}) \cdot \alpha_{NH_3}} F_{In}^{NH_3-NH_{3diss}} \quad (9)$$

Where: $F_{In}^{NH_3}$ is the flow rate of the single component atmosphere, comprising ammonia only, α_{NH_3} is the dissociation rate of the nitriding atmosphere obtained from the single component ingoing atmosphere, $F_{In}^{NH_3-NH_{3diss}}$ is the flow rate of the two component atmosphere NH_3-NH_{3diss} , $\alpha_{NH_3/NH_{3diss}}$ is the ammonia dissociation rate of the nitriding atmosphere obtained from the two-component ingoing atmosphere NH_3-NH_{3diss} .

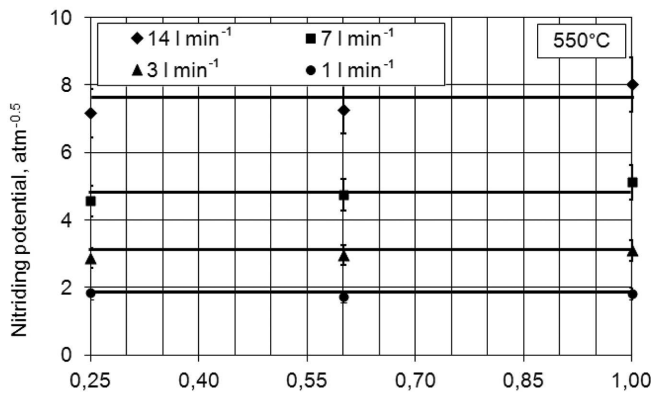
Expression (9) can be utilized to optimize ingoing atmospheres from the point of view of reduction of ammonia consumption in the designed nitriding process.

2.2. Nitrogen availability of the $aNH_3 - bN_2$ atmosphere

In terms of design possibilities of forming the desired nitriding potential, the aNH_3-bN_2 atmosphere (where a – percentage content of NH_3 , b – percentage content of N_2) is similar to the NH_3 atmosphere. In this atmosphere, the value of the nitriding potential depends on temperature and on the flow rate of the ingoing atmosphere, but is independent of its composition (Fig. 2b). Nitrogen availability varies with changes of the atmosphere composition (Fig. 2a) [11].



(a) Volume fractions of ammonia in the ingoing atmosphere



(b) Volume fractions of ammonia in the ingoing atmosphere

Fig. 2. Variation of nitrogen availability m_{N_2} (a), and the nitrid-

ing potential K_N (b) vs. content of ammonia in an atmosphere of 60% NH_3 -40% N_2 at 550°C [8]

If the ingoing atmosphere is of the two - component type, with a composition of aNH_3-bN_2 , then the function describing the dependence of the nitriding potential on the rate of dissociation can be written as:

$$K_N = \frac{a - 0.5 \cdot \alpha \cdot (1 + a)}{(0.75 \cdot \alpha)^{1.5}} = \frac{1 - b - 0.5 \cdot \alpha \cdot (2 - b)}{(0.75 \cdot \alpha)^{1.5}} \quad (10)$$

Solving equation (10) for ammonia dissociation rate α we obtain the expression: $\alpha(K_N, a)$:

$$\begin{aligned} \alpha(K_N, a) &= u(a) \cdot (K_N - v(a))^w \\ u(a) &= 1.0431486 \cdot (0.94520694)^a \cdot a^{0.69755645} \\ v(a) &= \frac{-4.5036713 - 37.397396 \cdot a}{1 + 56.823968 \cdot a - 15.439232 \cdot a^2} \\ w &\approx -0.59211735 \end{aligned} \quad (11)$$

By inserting equation (11) into equation (8), we obtain the dependence of nitrogen availability on the dissociation rate and on the nitriding potential:

$$m_{N_2} = \frac{1}{1.6} \cdot \frac{u(a) \cdot (K_N - v(a))^w}{2 - u(a) \cdot (K_N - v(a))^w} \cdot F_{In} \quad (12)$$

The value of nitrogen availability depends on the nitriding potential, as well as on the content of ammonia in the two-component, aNH_3-bN_2 - type ingoing atmosphere.

In the next part of the paper presents examples of utilization of nitrogen availability for the purpose of designing nitriding processes.

3. Experimental methods

Steel grades 42CrMo4 (AISI: 4140) and 18HGT (per Polish Specifications), as well as X37CrMoV5-1 (AISI: H11) were subjected to gas nitriding processes. The chemical compositions of steels used in the investigations are put together in Table 1.

TABLE 1
Chemical composition of steels used in investigations, in weight %

Steel grade	C	Mn	Si	P max.	S max.	Cr	Ni	Mo	V
42CrMo4	0.41	0.50	0.21	0.01	0.01	1.10	0.12	0.23	-
18HGT	0.20	1.0	0.23	0.02	0.02	1.12	0.21	-	0.02
X37CrMoV5-1	0.40	0.35	0.1	0.01	0.02	5.10	0.19	1.3	0.4

Nitrided layers were formed by the NITREG[®] controlled gas nitriding process, in an Nx609 - type furnace supplied by Nitrex. This equipment has the regulation and control of the nitriding atmosphere by the nitriding potential, ingoing atmosphere component ratio, as well as by the atmosphere flow rate. Process parameters are shown in Table 2.

Nitriding process parameters

Series No.	No.	α	T (°C)	t (h)	Type of ingoing atmosphere	F_{In} (l·min ⁻¹)	m_{N_2} (g·min ⁻¹)	K_N (atm ^{-0.5})	Steel grade
I	1	0.56	570	8	100%NH ₃	1.5	0.36	1.62	42CrMo4
	2	0.08	570	8	50%NH ₃ -50%NH _{3diss}	14	0.36	1.62	42CrMo4
II	3	0.27	550	2.5	100%NH ₃	14	1.35	7.6	42CrMo4
	4	0.20	550	2.5	60%NH ₃ -40%N ₂	14	1.01	7.4	42CrMo4
	5	0.11	550	2.5	25%NH ₃ -75%N ₂	14	0.51	7.5	42CrMo4
III	6	0.05	560	2	44%NH ₃ -16%NH _{3diss} -40%N ₂	14	0.22	6.7	18HGT
	7	0.21	560	2	60%NH ₃ -40%N ₂	3	0.22	6.9	18HGT
IV	8	0.29	540	10	NH ₃	7	0.76	6.5	X37CrMoV5-1
	9	0.29	540	4	stage 1 NH ₃	7	0.76	6.5	X37CrMoV5-1
		0.14	540	6	stage 2 30%NH ₃ -70%N ₂		0.33		X37CrMoV5-1

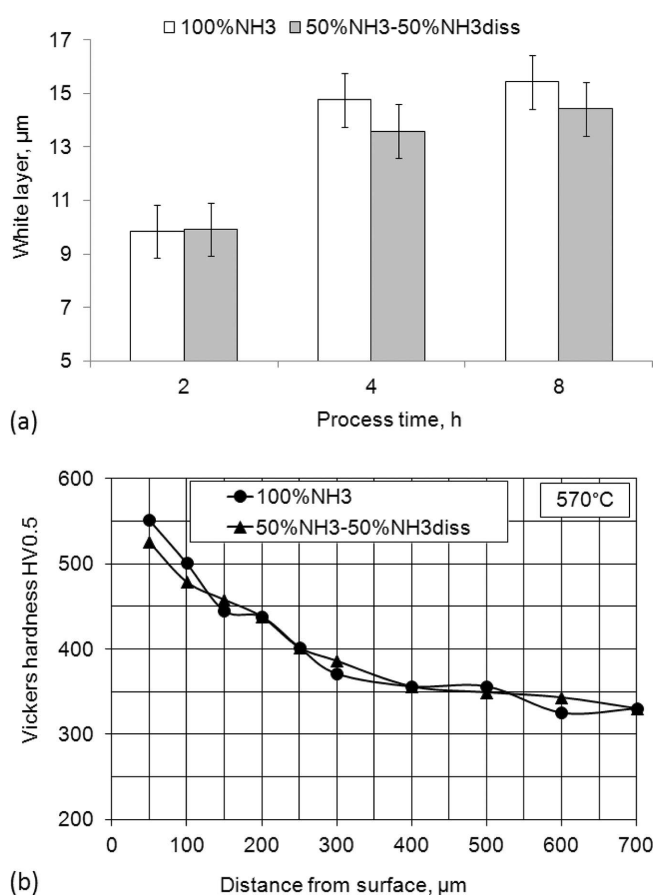


Fig. 3. Compound layer thicknesses (a) and microhardness traverses across nitrided cases (b), obtained on 42CrMo4 grade steel, nitrided in an atmosphere derived from a two-component ingoing atmosphere with pre-dissociated ammonia: 50%NH₃-50%NH_{3diss} (process 2) and single component ingoing atmosphere: NH₃ (process 1)

The nitriding processes were accomplished in four series. The parameters selected in the particular processes were: process temperature (T), time (t), value of nitriding potential (K_N), corresponding to known dissociation rate of the ammonia which dissociates during the nitriding process (α). Variable parameters were: nitrogen availability (m_{N_2}), composition of the ingoing atmosphere and flow rate of the ingoing

atmosphere (F_{In}). After completion of the processes, metallographic evaluations were carried out, as well as microhardness traverses across nitrided cases, in order to assess the effects of nitriding.

4. Results and discussion

4.1. Two-component ingoing atmosphere NH₃ – NH_{3diss}

Fig. 3 shows the thicknesses of the compound layers, as well as the microhardness profiles obtained in the process of series 1, on 42CrMo4 grade steel. In this case, the same value of the nitriding potential $K_N = 1.62 \text{ atm}^{-1/2}$ and the same value of nitrogen availability $m_{N_2} = 0.36 \text{ g} \cdot \text{min}^{-1}$ in two different types of atmospheres (ammonia and ammonia with pre-dissociated ammonia), ensured the formation of the same thickness of the compound layer, as well as same diffusion case depth. In order to obtain the same value of the nitriding potential, the two-component ingoing atmosphere with pre-dissociated ammonia (process 2) required a higher flow rate than the single component atmosphere (process 1). In order to calculate the flow rate of the single component atmosphere (NH₃) guaranteeing the same nitriding potential for both processes, expression (8) was used.

4.2. Two-component ingoing atmosphere NH₃ – N₂

The second series processes were carried out utilizing same flow rates, differing, however by the degree of dilution of the ingoing atmosphere. The compound layers formed on 42CrMo4 grade steel in an atmosphere obtained from a single component NH₃ ingoing atmosphere, and a two-component ingoing atmosphere containing nitrogen 60%NH₃-40%N₂ are of the same thickness, while those obtained in an atmosphere comprising 25%NH₃-75%N₂ (process 5) are clearly thinner (Fig. 4a). On the other hand, the obtained microhardness profiles across diffusion cases are the same for all three processes (Fig. 4b).

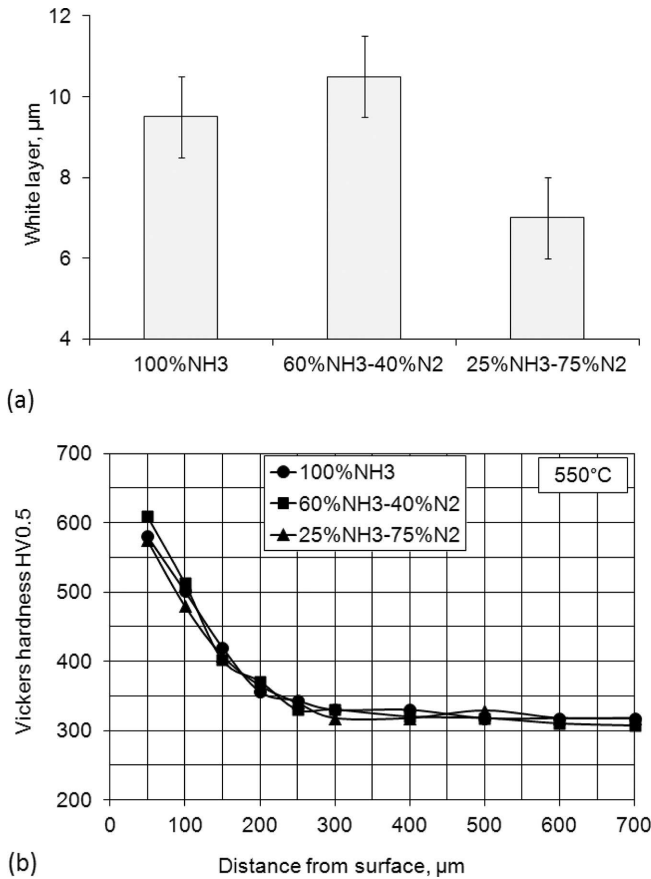


Fig. 4. Compound layer thicknesses (a) and microhardness traverses across nitrided cases (b), obtained on 42CrMo4 grade steel, nitrided in an atmosphere derived from a single component ingoing atmosphere NH_3 (process 3) with pre-dissociated ammonia: $50\%NH_3$ - $50\%NH_{3diss}$ (process 2) and single component ingoing atmosphere: NH_3 (process 3), two-component atmosphere with nitrogen $60\%NH_3$ - $40\%N_2$ (process 4), and $25\%NH_3$ - $75\%N_2$ (process 5)

The fourth series comprised two processes: 1) single stage with a single component atmosphere of ammonia only 10 h duration (process 8), and 2) double stage process with Stage 1 of 4 h duration in a single component atmosphere of ammonia only and Stage 2 of 6 h duration in a two-component atmosphere comprising $30\%NH_3$ - $70\%N_2$ (process 9). Parameters common to both processes were temperature and flow rate of ingoing atmosphere which caused both processes to be characterized by the same value of the nitriding potential (Fig. 5a). Dilution of the ingoing atmosphere by nitrogen during Stage 2 of process 9 caused a drop in the nitrogen availability but did not affect the value of the nitriding potential.

Fig. 6 shows thicknesses of compound layers formed after 4, 8 and 10 h, as well as microhardness profiles in diffusion cases after a process of 10 h duration on X37CrMoV5-1 grade steel.

The thickness of compound layers formed in Process No. 8 grows with time, attaining $9.9 \mu m$ after 10 h of nitriding. On the other hand, the thickness of compound layers formed in process No. 9 grows with time for the first 8 h, whereupon it begins to decrease, attaining $4.6 \mu m$ after 10 h, almost half of the thickness of the compound layer obtained in the process with a constant nitrogen availability. The microhardness profiles across the diffusion cases, obtained in processes belonging to series IV are same.

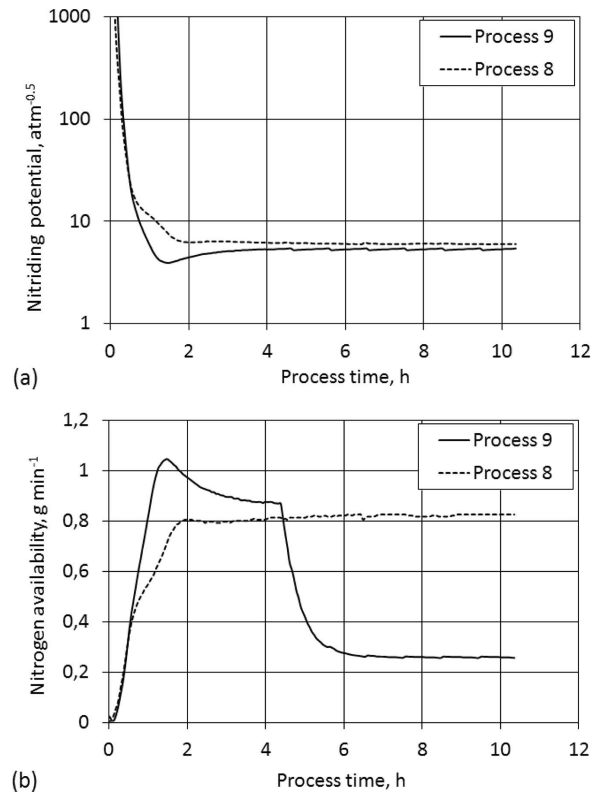


Fig. 5. Variations of nitriding potential (a) and corresponding variations of nitrogen availability of the nitriding atmosphere (b), for a single stage process (Process. 8) and a double stage process (Process 9)

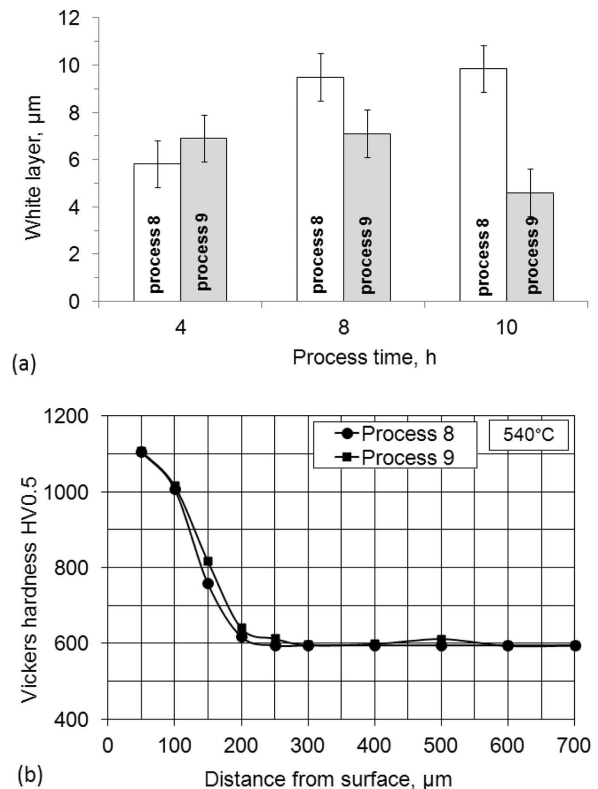
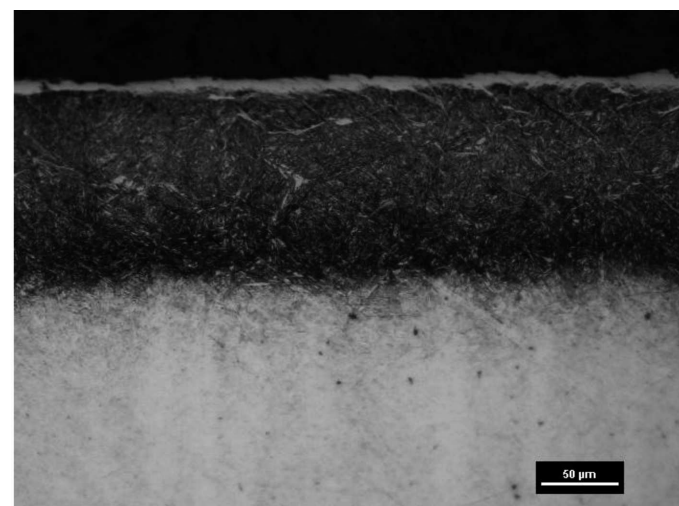


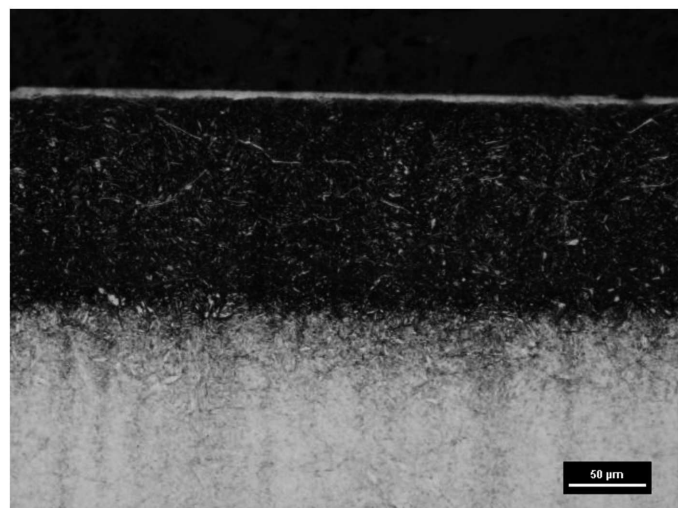
Fig. 6. Thicknesses of compound layers (a) and microhardness profiles across diffusion cases (b) obtained on X37CrMoV5-1 grade steel in a process with constant nitrogen availability value of the atmosphere (Process No. 8) and in a process with variable nitrogen availability (Process No. 9)

Fig. 7 shows the microstructures of the X37CrMoV5-1 grade steel obtained in process 8 (Fig. 7a) and process 9 (Fig. 7b).

An analysis of the microhardness profiles as well as that of compound layers thickness allows the conclusion that in single component atmospheres (NH_3) and two-component atmospheres (NH_3-N_2), employing the same value of the nitriding potential but different value of nitrogen availability, similar depths of the diffusion cases but different thicknesses of the compound layers (Fig. 7). Nitrogen availability is thus a parameter which definitely better describes the nitriding properties of the NH_3-N_2 atmosphere than the nitriding potential.



(a)



(b)

Fig. 7. Microstructures of the X37CrMoV5-1 grade steel obtained in process 8 (Fig. 7a) and process 9 (Fig. 7b) after 10 hours of nitriding

4.3. Three-component ingoing atmosphere $NH_3 - NH_{3diss} - N_2$

Fig. 8 shows the thicknesses of compound layers obtained on 18HGT grade steel in nitriding atmospheres derived from: a two-component ingoing atmosphere, comprising $60\%NH_3-40\%N_2$ and a three-component ingoing atmosphere comprising $44\%NH_3-16\%NH_{3diss}-40\%N_2$. The thicknesses of

compound layers obtained after 2 and 4 h of processing in the III rd series of tests, are of the same order (Fig. 8a). The microhardness profiles across diffusion layers are also same (Fig. 8b). The same growth kinetics of case and of the superficial compound layer formation in both atmospheres was due to equal nitrogen availability of both atmospheres ($m_{N_2} = 0.22 \text{ g} \cdot \text{min}^{-1}$). The attainment of same values of nitriding potential and nitrogen availability in a three-component atmosphere calls for a substantially higher flow rate than in the case of the two-component atmosphere with nitrogen.

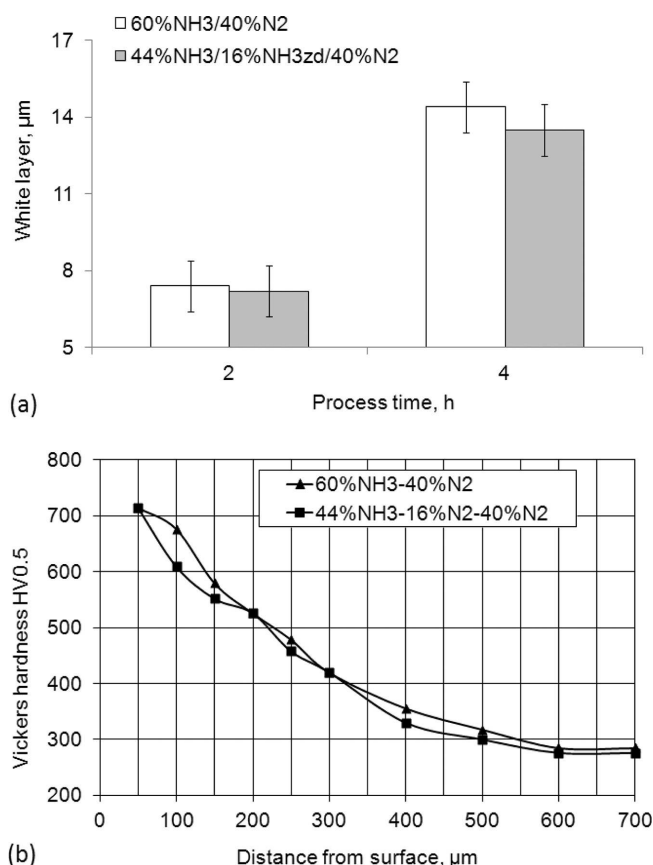


Fig. 8. Thicknesses of compound layers and microhardness profiles across the diffusion case, obtained in a nitriding atmosphere derived from a two-component ingoing atmosphere of the $60\%NH_3-40\%N_2$ type, and three-component ingoing atmosphere comprising $44\%NH_3-16\%NH_{3diss}-40\%N_2$

4.4. Discussions

As the investigations carried out show that nitrogen availability may be a parameter characterizing the flux of nitrogen from the nitriding atmosphere. A comparison of processes 1 and 2 allows the observation that the attainment of a nitriding potential of 1.62 in an atmosphere with pre-dissociated ammonia requires a flow rate of $14 \text{ l} \cdot \text{min}^{-1}$, while in a single component atmosphere comprising ammonia only, the required flow rate is only $1.5 \text{ l} \cdot \text{min}^{-1}$. The ammonia dissociation rates had values of correspondingly 0.08 for the atmosphere with pre-dissociated ammonia and 0.56 for the single component ammonia only atmosphere. The atmospheres described here are characterized by the same value of the nitriding potential, hence they also have the same nitrogen availability. If the nitriding atmospheres obtained from ingoing atmospheres

of the NH_3 and NH_3-NH_{3diss} , type are characterized by the same values of the nitriding potential, then they also have the same nitrogen availability, this availability being at its maximum. It should be emphasized that in the case of the nitriding atmosphere obtained from the single component ingoing atmosphere of ammonia only, then the maximum nitrogen availability for a given nitriding potential is attained when the flow rate is slowest. The flow rates of ingoing atmospheres in the described processes are bound by the expression (8).

The correlation between flow rates required to obtain the same values of nitriding potentials occurs also for atmospheres of the $NH_3 - N_2$ and $NH_3-NH_{3diss} - N_2$ type, on condition that the content of nitrogen in the two-component and three-component atmosphere is the same and can be described by the following equation:

$$\frac{F_{In}^{NH_3/N_2}}{F_{In}^{NH_3/NH_{3diss}/N_2}} = \frac{(2 - \alpha_{NH_3/N_2}) \cdot \alpha_{NH_3/NH_{3diss}/N_2}}{(2 - \alpha_{NH_3/NH_{3diss}/N_2}) \cdot \alpha_{NH_3/N_2}} \quad (13)$$

Where: $F_{In}^{NH_3/N_2}$ – flow rate of ingoing $NH_3 - N_2$ atmosphere, α_{NH_3/N_2} – ammonia dissociation rate of nitriding atmosphere obtained from the two-component ingoing $NH_3 - N_2$ atmosphere, $F_{In}^{NH_3/NH_{3diss}/N_2}$ – flow rate of three-component ingoing $NH_3-NH_{3diss} - N_2$ atmosphere, $\alpha_{NH_3/NH_{3diss}/N_2}$ – ammonia dissociation rate of nitriding atmosphere obtained from three-component ingoing $NH_3-NH_{3diss} - N_2$ atmosphere.

The occurrence of the said dependence of flow rates may be utilized for optimization of processing parameters in the direction of limiting ammonia consumption, i.e. making the process more environment-friendly. From the technical point of view, special significance can be attributed to the nitrogen availability parameter in the case of atmospheres diluted only by nitrogen, especially in the case of ingoing atmospheres containing more than 40% nitrogen. When dilutions of this order, the limitation of the flux of nitrogen from the atmosphere is important due to the fact that it causes, in effect, a limitation of growth kinetics of the superficial compound layer (Fig. 4a), not accompanied, however, by a limitation of growth kinetics of the diffusion case (Fig. 4b).

The causes of keeping constant growth kinetics of the diffusion case with simultaneous limited growth of the compound layer may be the following:

- 1) after the formation of the continuous uniform compound layer at the surface of the steel, it is this phase that constitutes the source of nitrogen for the growing diffusion case and the growth kinetics of this case depends, during this stage, on the average concentration of nitrogen in the compound layer
- 2) the chemical and phase composition of the compound layer depends on the value of the nitriding potential, and since that value was same in both processes, the growth kinetics of diffusion cases is the same.

A comparison of processes no. 8 and no. 9 shows the consequences of reducing nitrogen availability during the nitriding process. In process no. 8, accomplished in an atmosphere comprising 100% NH_3 , the maximum possible compound layer for the given temperature, nitriding potential and time was obtained.

Dilution of the ingoing atmosphere with nitrogen during the second stage of process no. 9 caused a reduction of nitrogen availability (Fig. 6b), while the nitriding potential

remained unaffected (Fig. 6a). In consequence, the thickness of the superficial compound layer was limited in comparison with that of the compound layer obtained in process no. 8, while maintaining the maximum possible growth kinetics of the diffusion case.

5. Conclusions

1. In a case where the nitriding atmospheres obtained from ingoing atmospheres comprising NH_3 and NH_3-NH_{3diss} , are characterized by the same values of the nitriding potential, then they also have the same nitrogen availability, this ability being at its maximum.
2. Can be achieved the same value of the nitriding potential in the two-component ingoing atmosphere containing pre-dissociated ammonia required a higher flow rate than that of the single component ingoing atmosphere.
3. In nitriding atmospheres obtained from ingoing atmospheres comprising NH_3 , or NH_3-NH_{3diss} a change of nitrogen availability is always accompanied by a change of the value of the nitriding potential
4. It is possible to change the nitrogen availability without changing the value of the nitriding potential in nitriding atmospheres obtained from ingoing atmospheres comprising $NH_3 - N_2$.
5. Lowering the nitrogen availability, while maintaining a constant value of the nitriding potential, it is possible to limit the growth kinetics of the compound layer, at the same time maintaining maximum, for given process conditions, growth kinetics of the diffusion case.

REFERENCES

- [1] J. Ratajski, R. Olik, T. Suszko, J. Dobrodziej, J. Michalski, Design, Control and in Situ Visualization of Gas Nitriding Processes, *Sensors* **10**, 1, 218-240 (2010).
- [2] J. Ratajski, Relation between phase composition of compound zone and growth kinetics of diffusion zone during nitriding steel, *Surface & Coatings Technology* **203**, 16, 2300 (2009).
- [3] P. Kochmanski, J. Baranowska, Kinetics of Low Temperature Nitriding of Precipitation Hardened Stainless Steel, *Defect and Diffusion Forum* **312-315**, 530-535 (2011).
- [4] J. Michalski, P. Wach, J. Tacikowski, M. Betiuk, K. Burdyński, S. Kowalski, A. Nakonieczny, *Contemporary Industrial Application of Nitriding and Its Modifications*, vol. 24, Materials and Manufacturing Processes **24**, 7-9, 855-858 (2009).
- [5] J. Michalski, J. Tacikowski, P. Wach, T. Babul, N. Tarfa, Attaining the steady state of the nitriding potential after a change of NH_3 atmosphere flow rate during the gas nitriding process, *Proceedings of 14th Congress of the International Federation for Heat Treatment and Surface Engineering*, 360-363 (2004).
- [6] M. Keddam, B. Bouarour, R. Kouba, R. Chegroune, Growth kinetics of the compound layers: Effect of the nitriding potential, *Physic Procedia* **2**, 3, 1399-1403 (2009).
- [7] E.J. Mittemeijer, J.T. Slycke, Chemical potentials and activities of nitrogen and carbon imposed by gaseous nitriding and carburising atmospheres, *Surface Engineering* **12**, 2, 152-162 (1996).
- [8] J. Ratajski, J. Tacikowski, M.A.J. Somers, Development of compound layer of iron (carbo)nitrides during nitriding of steel, *Surface Engineering* **19**, 4, 285-291 (2003).

- [9] J. Michalski, J. Tacikowski, P. Wach, Comparison and common characteristic of nitriding atmosphere in modern gas nitriding process, *Material Engineering* **5** (147), 459-462 (2005) (in polish).
- [10] D. Jordan, H. Antes, V. Osterman, T. Jones, Low Tor-Range Vacuum Nitriding of 4140 Steel, *Heat Treating Progress* **8**, 33-38 (2008).
- [11] J. Michalski, *Charakterystyki i obliczenia atmosfer do regulowanego azotowania gazowego stali*, Institute of Precision Mechanics, Warszawa, 2011 (in polish) (Characteristics and calculations of atmospheres for controlled gas nitriding of steel).

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