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CHOSEN ASPECTS OF THE MODELLING OF KINETICS OF THE (CARBO) NITRIDED LAYER GROWTH

Keywords

Nitriding process, model of the process, simulation of the layer growth.

Abstract

An example of the experimental-theoretical model of the nitriding process of steel is presented. The model makes it possible to simulate kinetics of the nitrided layer growth and consequently to optimize the algorithm of the process parameters change, btaining desired phase composition and layer structure. Attention has been paid to the analysis of the growth of the surface layer of iron (carbon) nitrides (compound layer) on 4340 (AISI, PN: 40HMN) alloy steel. The basis of the experimental-theoretical model is constituted by the mathematical description of the layer growth previously presented [24], in which experiential data from the database later developed [25] were taken into account.

Introduction

In order to meet the growing demand for the extending scope of applications of surface treatment processes, with the concurrent lowering of

their costs, it appears necessary to possess intelligent tools to support these processes. These tools should make possible an optimal choice of the algorithm of the parameters changes of single processes or a suitable matching of different complementary processes, which ensure a synergic effect in the formation of complex and diversified strength properties, resistance to frictional and corrosion wear.

A vital support in the scope of the applications is constituted by the experimental-theoretical models of surface treatment processes [1–5] that are being intensively developed. In order to precisely design the structure of the surface layer with the aid of a process model, it is necessary to include in mathematical descriptions all possible mechanisms which influence the growth of the layer in successive stages of the applied process.

In the case of the nitriding process, the mathematical description of the kinetics of the nitrided layer growth is subject to a continuous evolution. Commencing with attempts to describe selected stages of this process [6–12], attempts are made at present to mathematically represent phenomena occurring in a gas atmosphere, on the boundary gas-metal and in a nitrided material, together with a description of mutual dependencies between these phenomena [13–20].

For the mathematical representation of the phenomena accompanying the growth of the nitrided layer, Cranc-Nicholson's finite difference method [16] is used, as well as the finite element method [1], and intelligent computational methods, i.e. neural networks (NNs), fuzzy logic (FL) and genetic algorithms [21, 22, 23].

A mathematical description of the layer growth, useful for the process simulation, can be appropriate if in the mathematical formulae suitable experimental data (e.g. nitrogen concentration on the layer boundaries) are taken into account. For this aim, it is necessary to possess a database including data sets concerning the relations between the parameters of the process and its results.

In the case of the nitriding process, which has been used in the industry for many years now, such data sets already exist. However, it is necessary to conduct further complementary research to include both the issues from metal physics and engineering materials, because some data can (and do) indicate new mechanisms in the layer growth kinetics. For example, in the modelling of the nitriding process, and in particular in the predicting of the development of hardness profiles, the influence of the phase structure of the layer of (carbo)nitrides on the diffusion layer growth kinetics has not been taken into account so far.

In this reasearch the experimental-theoretical model of the growth of the nitrided layer as well as the results of a simulation analysis of the layer growth conducted with its aid have been presented. Attention has been paid to the analysis of the growth of the surface layer of iron (carbo)nitrides (compound layer) on 4340 (AISI, PN: 40HMN)

alloy steel. The basis of the experimental-theoretical model is constituted by the mathematical description of the layer growth presented in previous research [24], in which experiential data from the database later developed [25] were taken into account.

1. Mathematical description of layer growth kinetics

The creation process of a nitrided layer comprises many stages, which include the following:
- transport of ammonia in the gas phase and an adsorption of gas molecules at the solid surface;
- chemical reactions at the surface (ammonia dissociation), which depend on the pressures of the partial components of the atmosphere;
- desorption of reaction products (N_2, H_2), which is influenced by the general rate of the gas flow;
- transport of nitrogen atoms through the surface and diffusion in the material; and,
- creation of a multi-phase nitrided layer.

The kinetics of the course of the process depends on the rate of the above-mentioned partial stages, and the kinetic equation which describes its slowest stage is, at the same time, the basic equation describing the kinetics of the whole process. The rate of particular stages of the creation and growth of the nitrided layer changes with the duration of the process. The slowest stage in the initial stadium of the formation of the layer is the ammonia dissociation on the surface of the nitrided material. After the formation of the layer in the conditions of a quasi-equilibrium of the diffusion, the transport of nitrogen in the material becomes the slowest. This makes the kinetics of the whole process a complex function of time.

Starting from attempts to describe selected stages of the process, efforts have been made to mathematically combine the phenomena occurring at particular stages. Due to a variety of phenomena accompanying the growth of the layer this task is difficult. However, through an appropriate selection of parameters (i.e. high temperature, a proper nitriding atmosphere composition, relatively high flow rate of the gases), a situation can be achieved where, in the whole process, the main role is played by the transport of nitrogen in the material [20]. Experimental data collected in such cases and concerning the growth of particular monophase zones in the nitride layer [25], as well as concerning the growth of such zones in other diffusion systems, e. g. metal-metal [26], point to the parabolic law of the phase growth:

$$\Delta x_i = k_i \sqrt{t} \tag{1}$$

where Δx_i is the thickness of i-th phase in n-phase layer after time t of the process (for the nitrided layer, the maximum value is $n = 3$), and k_i is the kinetic growth parameter of i-th phase, the so-called parabolic growth constant.

Equation (1), with empirically determined constants k_i, describes the growth kinetics of phases in the given temperature.

From a practical point of view, this is sufficient in most cases because the k_i value at different temperatures for all the phases of the diffusion systems allows the determination of the change of the given phase thickness Δx_i as a time function in accordance with Eq. (1).

However, this is a simplified description of kinetics, which makes it impossible to determine, e. g. in the case of the nitrided layer, the coefficients of nitrogen diffusion in individual phases of the layer or nitrogen concentrations on phase boundaries. Also, one cannot foresee, on the basis of this equation, the influence of the growth speed of a given phase of the remaining phases creating the layer. Hence, it has become necessary to develop general mathematical dependencies between the growth parameters k_i and the diffusive parameters, which would enable one to design diffusion coefficients in the mono-phase zones of the layer, as well as to predict the growth of the layers in the time function of the process.

While generalising the above mentioned function for the n-phase layer case and at the same time assuming that the growth speed of a given phase is also influenced by the remaining phases existing in this system, the following is obtained:

$$k_i^2 = \phi_i\left(D_1......D_{n,}, \Delta c_1, \Delta c_2,.....\Delta c_n, T\right) \qquad (2)$$

It is only the knowledge of the explicit form of the above mentioned expression which enables a full description of the kinetics of the phase growth in a multiphase binary system. As a starting point, a quality analysis of the growth of the i-th phase in an n-phase metal-metal system was considered [26].

A change of the thickness of a given phase in this system results from (analogous to the case of the growth of a given layer in a three-phase nitrided layer) both the processes of an internal diffusion in this phase and an interaction between the phases ("phase-jostling"). Consequently, in paper   [24] the following system of equations has been obtained:

$$\sum_{j=1}^{n} \beta_{i,j} k_i k_j = \left(D_i^c\right)_{ef} \Delta c_i \qquad (3)$$

This is a system of non-linear n equations, which can be solved with the use of e.g. the method of successive approximations (iterations). For this purpose, Eq. (3) can formally be presented in the following form:

$$k_i = \frac{2\left(D_i^c\right)_{ef} \Delta c_i}{\sum\limits_{j=1}^{n} \beta_{ij} k_j} \quad i = 1,2,3 \quad 1-\varepsilon,\ 2-\gamma',\ 3-\alpha \tag{4}$$

In the method of successive approximations, for example for zone ε, the following is obtained:

$$k_\varepsilon^{(1)} = \frac{2\left(D_\varepsilon^c\right)_{ef} \Delta c_\varepsilon}{\sum\limits_{j=1}^{3} \beta_{ij} k_j^{(0)}},\ \dots\ ,\ k_\varepsilon^{(2)} = \frac{2\left(D_\varepsilon^c\right)_{ef} \Delta c_\varepsilon}{\sum\limits_{j=1}^{3} \beta_{ij} k_j^{(1)}},\ \dots \tag{5}$$

The equations obtained combine the kinetic growth parameter of a given phase k_i with the difference of concentrations on the phase boundaries and an effective diffusion coefficient in the phase. Moreover, they bind the growth rate of a given phase with the kinetic parameters of the remaining phases in the system in question. From the system of equations obtained it is evident above all that the greater growth parameters are, the greater the difference of concentrations on the boundaries of phases Δc_i is, in accordance with the diagram of the phase equilibrium, as well as the greater the diffusion coefficient in a given phase – $\left(D_i^c\right)_{ef}$ is.

2. The experimental-theoretical model of kinetics of the nitrided layer growth.

The formation of the nitrided layer on iron and low-carbon steels always occurs in the following order:

$$\alpha \to \gamma' \to \varepsilon .$$
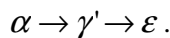
Therefore, the nitrided layer begins to form from the saturation of the alpha iron lattice with nitrogen (α) until its maximum surface concentration for a given process temperature is obtained. Then the nitride γ' (Fe_4N_{1-x}) begins to form the nitride ε (Fe_2N_{1-x}). This process later continues after a suitable time. In the nitrided layer created in this manner, which is composed in the process temperature of two mono-phase zones (ε and γ') forming the surface nitride layer (compound layer) and of diffusion layer (α), an equilibrium of nitrogen concentrations is obtained.

A simulation analysis of the growth of such a layer on 1010 (AISI) steel was made by directly applying the system of equations (3-5) for this purpose.

The values of the nitrogen diffusion coefficients in the phases and nitrogen concentration values on their boundaries were assumed in accordance with the values presented in previous research [19]. In order to verify the model, samples of processes (i.e. time-dependent parameters of these processes and their results) were selected from the database created [25] (Fig. 1).
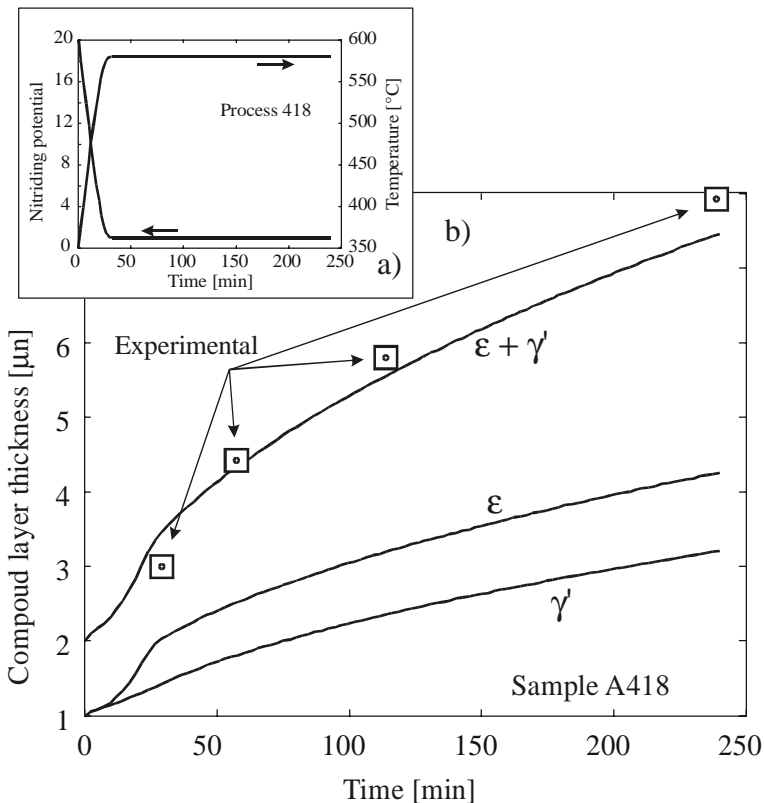

Fig. 1. The changes of process parameters taken from the database [25] (a) and results of the simulation analysis and experiential data (b). Steel 1010

The results presented indicate the correctness of the model developed; relatively small differences appear between the calculated values of the thickness of the compound layer and those measured experimentally after the process. The successful verification constitutes the basis to accept the model as a tool for the construction of the software for the control systems of the nitriding process, e.g. with respect to obtaining specific proportions of the thicknesses of

the monophase zones in this compound layer within as short a duration of the process as possible. The phase structure of the layer is decisive for the anticorrosive properties of materials nitrided. In the case of other grades of steel than low-carbon steels and Armco iron, there is no such explicit picture of the formation of the layer nitrided as the one presented above. In previous research [27], it was shown that the formation of a nitride layer occurs in accordance with two sequences:

$$\alpha \to \gamma' \to \varepsilon_1$$

and

$$\alpha(\Theta) \to \varepsilon_2 \to \gamma' \to \varepsilon_1 \,,$$
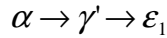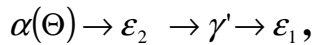
where: α – nitrogen solution in iron lattice α-Fe(N, γ' – iron nitride (Fe_4N_{1-x}), ε_1 – iron nitride (Fe_2N_{1-x}), ε_2 – iron (carbo)nitride ($Fe_2(N,C)_{1-x}$).

It has been observed that the domination of one or the other sequence of the layer formation depends on the chemical composition of the steel, mainly of the carbon content and the nitrogen potential in a given temperature of the process. Also, characteristic phase changes have been noted which occur in the layer in the function of the process time. For example, for 4340 steel, with the temperature of 580°C and $N_p = 3.25$, after three hours of the process, the whole compound layer is dominated by the ε_2 phase. An example of the microstructure of such layers formed in times of 3 and 10 h, together with the distribution of the volume share of the phases in the layer, obtained on the basis of X-ray examinations, was presented in Fig. 2. Additionally (Fig. 3), in order to confirm the identification of phases on the microstructures of the layers (the dark-grey shade - γ' phase, light grey shade - ε phase), diffraction images of the samples were presented after successive removal through grinding of the successive layer zones. During a longer process (over 3 hours), the share of γ' phase begins to increase in the layer by forming a characteristic profile, in accordance with which, the maximum content of γ' phase is located, not at the boundary with the diffusive layer, but a certain distance from it.

Quite differently, in comparison with iron, the phenomena accompanying the nitrided layer growth on steels, and especially its nucleation and phase evolutions occurring during the process in the surface layer of (carbo)nitrides of iron have a vital influence on the formation of the experimental-theoretical model of the layer growth. For the purpose of a suitable mapping of these phenomena in a mathematical description, it is necessary to have a rich set of experiential data [25].
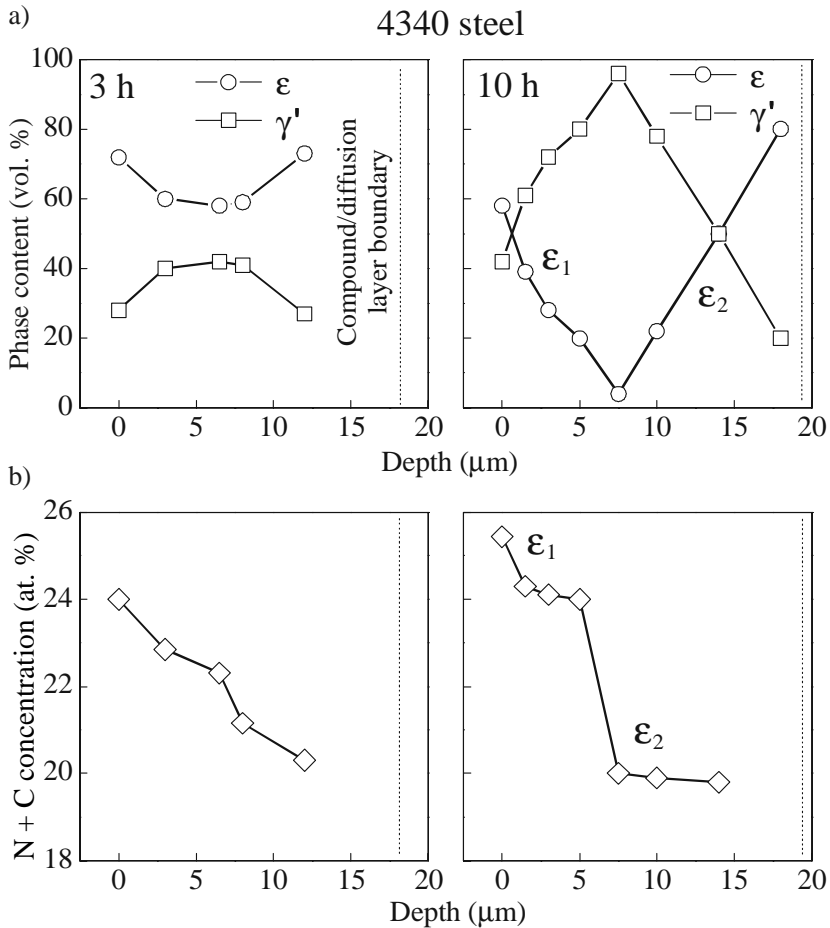
Fig. 2. Depth distributions of ε and γ' phases in the compound layer on steel 4340 (a). Total interstitial content (N+C) as a function of depth (b). Nitriding parameters: $N_p = 3.25$, $t = 3$ h and 10 h

In accordance with the above mentioned description of the phase evolution occurring during the growth of the layer of (carbo)nitrides of iron on 4340 steel in the construction of the layer growth kinetics model, two stages were distinguished: the first one to describe the growth in the case when the layer's phase structure is dominated by ε phase, and the second stage from the moment of the process time, in which in the middle area of the layer, a continuous zone of γ' phase is formed. It separates two zones of the ε phase; the upper one – composed of nitride ε_1 phase and the lower one – composed of (carbo)nitride ε_2 phase. For the experimental-theoretical model, experiential data was taken, i.e. the
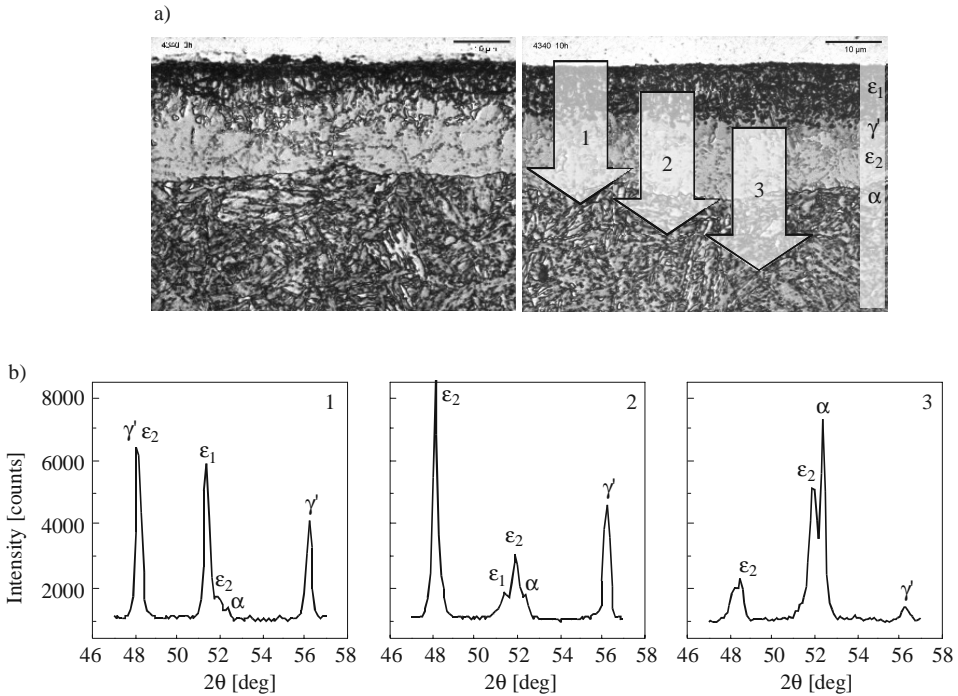
Fig. 3.　Optical micrographs of the cross-sections of the compound layer (a) – γ' appears dark grey, ε appears light grey. X-ray diffractograms (b) shown are for the entire compound layer (1) and after removal of part of the compound layer (2 and 3) by polishing

concentrations of nitrogen and carbon on the boundaries of the zones of ε_1 and ε_2 phases from the database previously developed [25], and the coefficients of nitrogen diffusion in ε phase and γ' phase from other previous research [19]. The computational results presented show, in accordance with the experiential data taken from the database, that the distinguished stages of the process are characterized by different growth rates of the iron (carbo)nitrides: I stage – quick growth compound layer which is dominated by ε phase, and II stage –a distinctive slowdown of the layer growth (Fig. 4). This is due to the formation of a compact zone of γ' phase, which is due to its characteristic homogeneity (a relatively small difference of concentrations of nitrogen on the boundaries of this phase), very slowly changes its thickness in the time of the process and becomes an effective barrier for the nitrogen stream flowing to the zone of ε_2 phase.
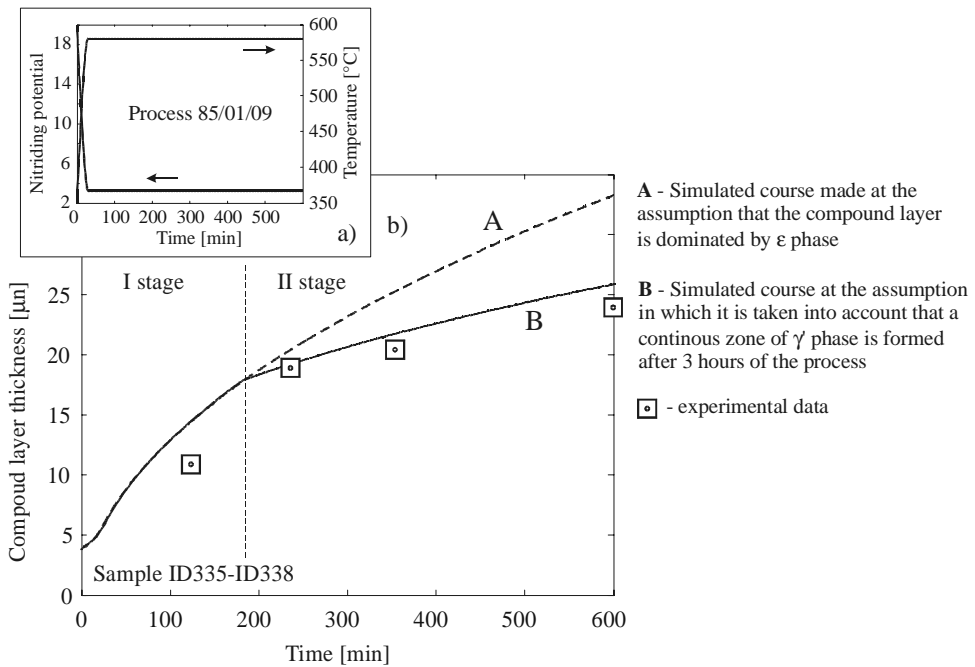
Fig. 4. The changes of process parameters taken from the database (a) and results of the simulation analysis of the compound layer growth with experiential data on 4340 steel (b)

Conclusions

1. The previously developed databases [25] allowing aggregation of gathered information constitutes the first and fundamental step to the building of experimental-theoretical models of processes.

2. The model proposed in this paper is a simple and convenient tool, which enables an execution of a comprehensive simulative analysis of the growth kinetics of a layer in conditions of a diffusion quasi-equilibrium.

3. The model developed indicates, in a direct way, the role of the main diffusion parameters, Δc^i and D_N^i, in forming the growth of particular layer zones. It enables a determination of the change of the thickness of monophase layer zones on the basis of nitrogen diffusion values in a given phase and the knowledge of the difference of concentrations on zone boundaries, – alternatively, on the basis of the model, the nitrogen diffusion coefficient in a given phase can be determined on the basis of the constant values of parabolic growth ki, determined with the use of e.g. metallographic

methods, on the basis of measurements of the changes of phase thicknesses in the function of the process.

4. The successful verification constitutes the basis to accept the model as a tool for the construction of the software for the control systems of the nitriding process, e.g. with respect to obtaining specific proportions of the thicknesses of the monophase zones in this compound layer within as short time of the process as possible.

Acknowledgements

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Wybrane aspekty modelowania kinetyki wzrostu przypowierzchniowej warstwy (węglo)azotków żelaza

Słowa kluczowe

Proces azotowania, model procesu, symulacja wzrostu warstwy.

Streszczenie

Zaprezentowano przykład eksperymentalno-teoretycznego modelu procesu azotowania stali. Model umożliwia symulacje kinetyki wzrostu warstwy azoto-wanej i w konsekwencji optymalizację algorytmu zmian parametrów procesu zapewniającego otrzymanie warstwy o założonym składzie fazowym i budowie. Skoncentrowano się na analizie wzrostu przypowierzchniowej warstwy (węglo)azotków żelaza na przykładzie stali stopowej 4340 (AISI, PN: 40HNM). Podstawę modelu stanowi matematyczny opis wzrostu warstwy zaprezentowany w pracy [24], w którym uwzględniono dane eksperymentalne z opracowanej bazy danych [25].