A kinetic aspects of low-pressure nitriding process

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ABSTRACT

The purpose of this work was to theoretically and experimentally study the reactions that occur during low-pressure nitriding. A series of specimens made of 42CrMo4 and 41CrAlMo7 and C22 steels were low-pressure nitrided. The structure of the materials, the hardness and the thickness of the nitride layers, as well as any reactions that occurred in the gas and solid phases were tested. The process kinetics were discussed. The findings showed that a build-up of the nitrided layer from a low-pressure process depends on the kinetics of surface processes. However, a characterization of the process with nitriding potential is not justified and should be replaced with a rate of ammonia dissociation in low-pressure processes.

1. Introduction

Nitriding is used in order to increase the hardness and resistance to abrasion of part surfaces as well as generate residual stresses field, what improves their fatigue and pitting strength [1–4]. Nitriding considerably extends the lifetime of heavy-duty machine parts [5–9]. Nitrides are the main steel hardening factors, and since iron nitrides themselves harden the material to a minor extent, the role of alloy additives, such as chromium, molybdenum, aluminum, and vanadium, all of whose nitrides and carbonitrides make it possible to harden materials to 1000–1400 HV, becomes very important. Hence, the properties of a nitrided layer depend on its structure, i.e., the thickness of the surface layer of nitrides and its chemical and phase composition as well as the effective case depth [10–14]. The kinetics of a nitriding process and the reactions that occur within it have been studied by many researchers but usually address gas and plasma nitriding [5,8,15–23]. Low-pressure nitriding (LPN) is a relatively new and unexplored variation of the process.

Nitriding processes use the thermal decomposition of ammonia to form a nitrided layer, and the decomposition process occurs during continuous flow [24–26]. Ammonia is a metastable compound in the presence of iron and in temperature above 400 °C. It dissociates according to the reaction of $NH_3(g) \leftrightarrow 0{,}5 \cdot N_2(g) + 1{,}5 \cdot H_2(g)$. As a result, the closed system endeavor to establish a stable equilibrium of $Fe-N_2$, manifested by the decomposition of ammonia on the iron until it is exhausted. Under these conditions, only very low concentrations of nitrogen on iron at atmospheric pressure can be obtained. In order to obtain higher nitrogen concentrations, nitriding processes are performed in an open system, the chemical composition of the atmosphere is forced by its flow through the retort, supplementing ammonia losses due to dissociation reactions [27]. The phenomena that occur during nitriding are shown in Fig. 1. The main atmosphere streams are the boundary zone and the steel surface being nitrided, where unit stages occur in sequence. Atomic nitrogen, produced on the steel surface as a product of the decomposition of ammonia, diffuses into the material only when the chemical potential of nitriding in the nitriding atmosphere is higher than that of the steel. The formation of a nitrided layer during the process of steel saturation with nitrogen follows the general rules of diffusion. From the moment that a compact layer of iron nitrides forms, the kinetics of the solution layer build-up depends on the phase (chemical) composition of the nitride layer [28]. During steel nitriding between the layer of iron nitrides and the surface layer of iron nitrides, the quasi-balance of the nitrogen concentration is determined. In the diffusion layer, the total nitrogen content is the sum of nitrogen bound elements in nitrides, nitrogen dissolved internally in the iron network and the so-called excess nitrogen, the presence of which is caused by elastic dilation of the network around nitrides forming alloy elements [29]. Only nitrogen bound in nitrides of alloy elements and nitrogen dissolved in an interstitial way, contribute to the increase of strength properties [30].

To summarize, the most important parameters affecting the kinetics of the nitrided layer's growth and its phase composition during gas nitriding process include the nitriding potential, temperature, the composition and flow rate of the nitriding atmosphere, the composition of the steel being nitrided and the preparation of the surface to be nitrided, which has been confirmed in Refs. [13,31,32].

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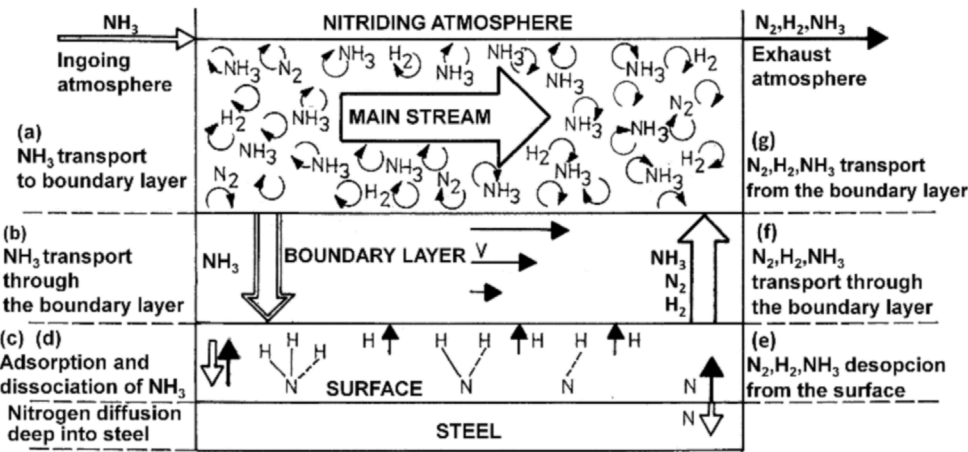
Fig. 1. Phenomena that occur during gas nitriding of steel in a nitriding atmosphere. Stages a, b, f, and g supply substrates to form the nitrided zone and remove gaseous reagents resulting from the process. Stages b and f transport of gaseous reagents through the boundary zone between the main atmospheric stream and the steel surface. Stages c, d and e include adsorption, gradual dissociation of the ammonia and desorption of the gaseous reagents.

The concept of nitriding potential was introduced by B. J. Lightfoot and D. H. Jack in 1975 as a physicochemical parameter determining the gas nitriding process, expressed by the dependence: $N_p = p_{NH_3}/(p_{H_2})^{1.5}$ where: p_{NH_3}, p_{H_2} - partial pressures of ammonia and hydrogen in the nitriding atmosphere (outlet) [33]. The nitriding potential characterizes the state of equilibrium of concentration of nitrogen between the nitriding atmosphere and the steel surface. During low-pressure nitriding, which is conducted at a low pressure (of < 30 hPa) and with a constant ammonia flow, the nitriding potential is constant and corresponds to a constant stream of nitrogen from the nitriding atmosphere to the surface being nitrided [14]. To change or limit the stream, process segmentation is applied. It is necessary to limit the stream of nitrogen supplied to the steel being nitrided for long-term processes with a goal of obtaining nitrided layers with a limited iron nitride layer depth and a relatively deep solution layer. In general, limiting the nitrogen stream can be achieved by decreasing the nitriding potential or diluting the inflowing atmosphere with nitrogen [32]. In each case, this is accompanied by a change in the degree of dissociation of the ammonia and, as a consequence, of the nitrogen stream supplied to the surface being nitrided [34]. However, low-pressure nitriding requires higher critical input ammonia contents (higher input nitriding potentials) as the nitriding pressure is reduced, which causes many issues [14].

The rate of nitrogen production by dissociation of ammonia and ammonia content changes in the outflowing atmosphere depend on the ammonia flow rate, as shown in figure (Fig. 2). Dissociation rate ω of ammonia in the nitriding atmosphere is expressed by the ratio of the doubled part of ammonia s in the ingoing atmosphere to the volume of the outgoing atmosphere: $\omega = 2 \cdot s/(1 + s)$. When the ingoing atmosphere is ammonia, the relationship between the value of the nitriding potential and the rate of dissociation of ammonia ω describes the relationship: $N_p = (1 - \omega)/(0.75 \cdot \omega)^{1.5}$. For very small flow rates (range I), the time for which an ammonia molecule remains on the steel surface is long enough for it to dissociate, and the atmospheric flow rates in the main stream and in the border zone are equal [35]. An increase in the atmosphere flow rate is followed by an increase in the amount of ammonia supplied to the steel surface. A still small but growing number of molecules are in equilibrium with the surface. The nitrogen production rate in this flow rate range is proportional to the flow rate of the inflowing atmosphere. The outflowing atmosphere contains practically no ammonia but only products of its dissociation (range I). As the flow rate of the nitriding atmosphere increases further, there is a moment (point 1) when the contact time of ammonia molecules with the surface is too short for all the molecules to dissociate. As a consequence, not all the molecules dissociate. Therefore, the outflowing atmosphere contains products of dissociation: N_2, H_2, and ammonia. From this moment on (range II), the rate of nitrogen production is determined by the ammonia supply through the border zone to the steel surface. The rate of nitrogen production increases monotonically with the increasing flow
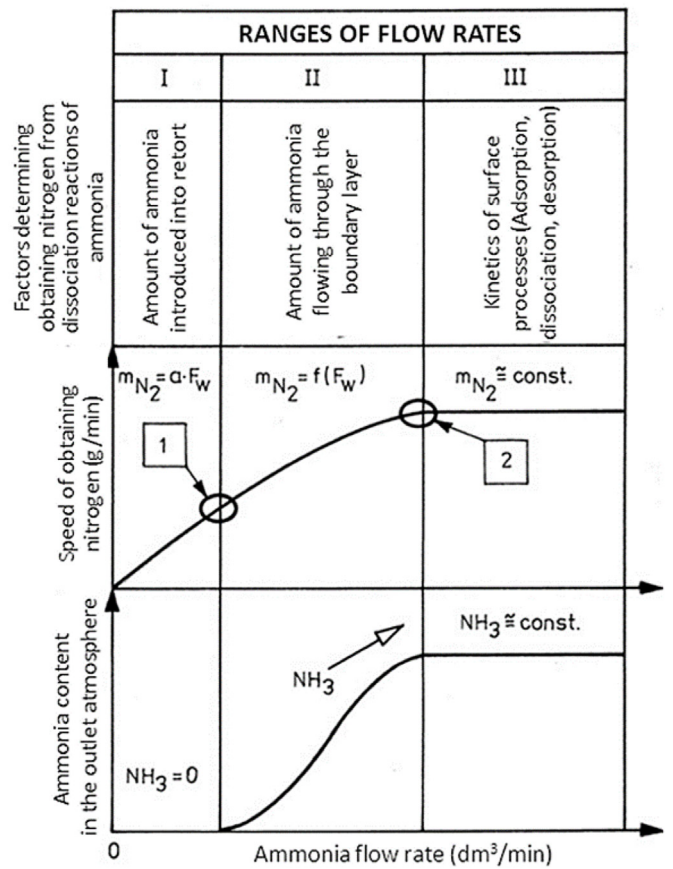

Fig. 2. The rate of nitrogen production by dissociation of ammonia and a change in the ammonia content in the outflowing atmosphere depending on the flow rate of the single-component inflow ammonia atmosphere [34].

rate of the inflowing atmosphere (ammonia), causing the rate of nitrogen production to becomes constant at point 2. A further increase in the inflowing atmospheric flow rate (range III) does not result in any increase in the nitrogen production rate, which shows a constant ammonia content in the outflowing atmosphere, and the nitrogen production rate is determined by the kinetics of the surface reactions (adsorption, desorption, chemisorption). Atmospheric pressure nitriding processes are usually conducted at flow rates within range II [34], where the nitriding potential is the crucial parameter of the process. Low-pressure nitriding processes are conducted at flow rates corresponding to range III [36], where the nitriding potential loses its