CONTROLLED NITRIDING USING A ZEROFLOW PROCESS

Traditional nitriding has very limited control over the growth of the nitrided layer. Now, a new economical, environmentally friendly version of the gas nitriding process allows a substantial reduction in the consumption of industrial gases compared with currently used processes and allows maintenance of full control over the kinetics of the layer growth.

Leszek Maldziński
University of Technology
Poznan, Poland

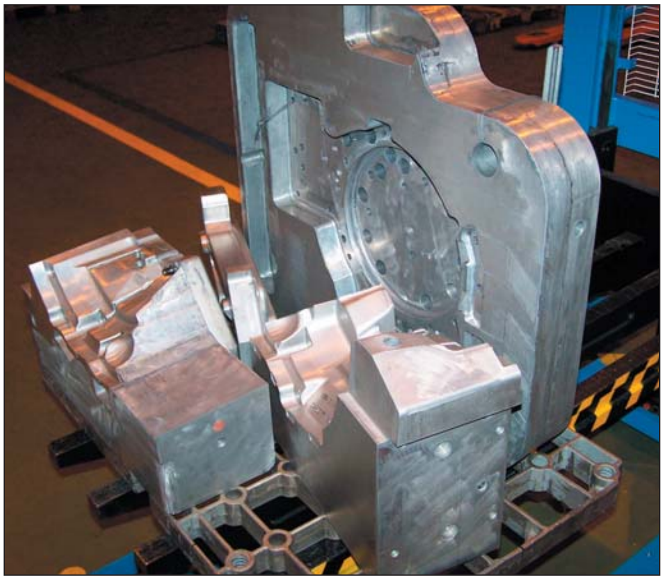
Traditional nitriding, which has limited control of the growth of the nitrided layer, is still very much in use worldwide[1]. The process is carried out using only ammonia, and the resulting layer is composed of superimposed ε + γ′ + α (epsilon plus gamma prime plus alpha) phases. In industrial practice, the superficial zone of iron nitrides ε + γ′ (as a rule exceedingly thick and brittle) is usually removed by grinding[2,3], which substantially adds to the cost of the manufacturing process. This process involves a high consumption of ammonia (NH_3).

Controlled gas nitriding, performed for more than 60 years, represents an advancement over the (but still used today) traditional method using 100% ammonia atmospheres. Two-component atmospheres consisting of ammonia and dissociated ammonia (NH_3 and dissociated NH_3)[4,5], as well as ammonia and molecular nitrogen (NH_3 and N_2) came into use about 50 to 60 years ago[6-8]. Through proper selection of atmosphere composition and adjustment of its flow rate through the retort, it is possible to form layers of the required phase composition (consisting of ε + γ′ + α, γ′ + α, or α zones) having the required thickness of individual zones, together with a limited nitrogen concentration at the surface. These processes allow the elimination of final grinding, thus reducing the cost of the entire manufacturing process. However, nitriding using two-component atmospheres involves considerable consumption of gases as well. In addition, both processes have other disadvantages. Because of the nonequilibrium characteristic of nitriding in a $NH_3 + N_2$ mixture, control of kinetic growth of the nitrided layer is less accurate than in a NH_3 and NH_3 + dissociated NH_3 mixture (nitriding in these two atmospheres exhibits equilibrium characteristics). In addition, the need for an ammonia dissociator when using the NH_3 + dissociated NH_3 mixture adds to the cost of the installation.

Controlled Nitriding Using a ZeroFlow Process

This concept assumes carrying out the process of controlled nitriding using NH_3 alone. This is a simpler process than that using two-component mixes of ammonia diluted with

Horizontal furnace for nitriding using ZeroFlow process. Photo courtesy of Seco/Warwick Group, Swiebodzin, Poland.



Nitrided aluminum extrusion dies.

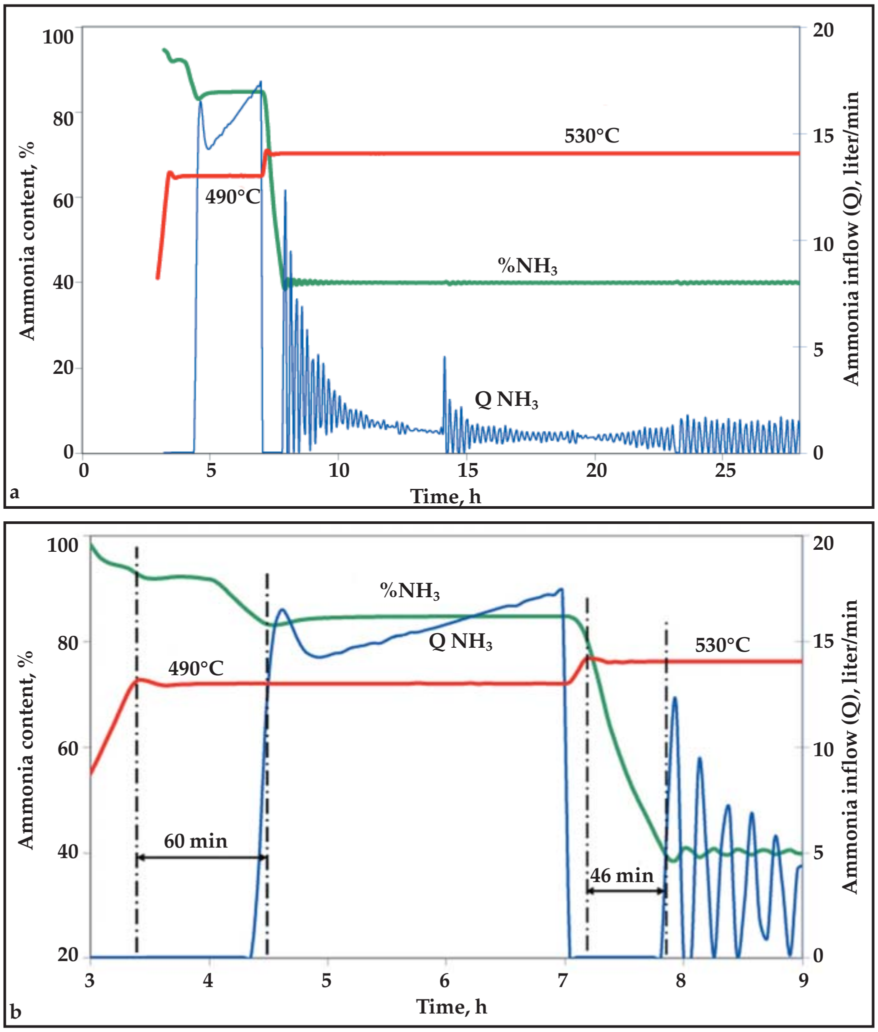


Fig. 1 — Variations of temperature, flow rate of NH_3 into the retort, and NH_3 content in a retort during two-stage nitriding (a); enlargement of left side of Fig. 2a between 0 and 9 hours (b).

N_2 or dissociated NH_3. The regulation of the chemical composition of the atmosphere in the retort, and, therefore, the regulation of the nitriding potential K_N, is obtained through the variation of the flow rate of NH_3 into the retort. What makes this process unique is that the flow of NH_3 into the furnace is at times reduced to zero, which widens the range of the gas composition in the retort (and K_N as well). The amount of NH_3 introduced into the furnace is regulated (controlled) with the aid of a gas analyzer (for example an infrared analyzer). The gas analyzer opens and closes the NH_3 inlet valve periodically at a frequency required to maintain the desired gas composition (as well as the desired K_N) in the retort.

The concept is based on experimental and theoretical investigations in terms of the thermodynamics and kinetics of gas nitriding. Investigations were carried out in a laboratory furnace using a quartz tube and also in an industrial furnace using a steel retort and a circulating fan. Nitriding was performed using NH_3, NH_3+ H_2, NH_3+ dissociated NH_3 mixtures. In the industrial furnace, the supply of NH_3 into the retort was periodically stopped though with an operating circulation fan.

The studies demonstrated that the growth rate of the nitrided layer depends only on the composition of the atmosphere or K_N in the retort. It does not depend on either the type of atmosphere introduced into furnace (NH_3, NH_3 + dissociated NH_3 or NH_3 + H_2) or the type of furnace (e.g., laboratory with a quartz tube or industrial with steel retort and fan). The results also prove that stopping the supply of NH_3 to the retort does not affect the growth rate of nitrided layer. A detailed analysis of the results is given in Ref.[9].

ZeroFlow Process under Industrial Conditions

A special horizontal furnace suitable for nitriding was used to investigate the ZeroFlow process. The furnace was fitted with an NH_3 inlet valve and an H_2 gas analyzer. The regulation of the chemical composition of the atmosphere in the retort, and, therefore, the regulation of K_N, was obtained as mentioned above by means of occasionally stopping the flow of NH_3 into the furnace. The process was a two-stage nitriding process similar to that used in industrial practice.

Figure 1a shows the variations of temperature, ammonia in flow rate, and NH_3 content in the retort during two-stage nitriding. Operating parameters were: Stage I - 490°C (915°F) and 85% NH_3 content in retort, Stage II - 530°C (985°F) and 40% NH_3. The flow rate of NH_3 into the retort was periodically closed both at the beginning of first and second stage of nitriding, which caused a relatively fast drop of NH_3 content in the retort atmosphere up to the fixed values. Reaching a fixed gas composition takes up around 1 hour during the first stage and 46 minutes during the second stage (Fig. 1b). By comparison, in other processes, depending on the area of the charge, NH_3 content reached a fixed value from 20 to 50 minutes.

The rapid drop in NH_3 is a favorable phenomenon from the standpoint of regulating the kinetics nitrided layer growth. During the drop of K_N, the possibilities of regulation of the growth of the nitrides are suspended until the gas composition reaches a level programmed for a given process stage. Beyond this point, gas composition is regulated through an intermittent flow of NH_3 into the retort. The drop of K_N depends on surface area and catalytic properties of retort and charge. Simulations of the growth of nitrides on 4140 were performed to estimate the influence of the rate of stopping the flow of NH_3 (Fig. 2). The variation in changing rate of NH_3 content (from 1 and 2.5 h) exhibits a small effect on the growth rate of nitrides ($\varepsilon + \gamma'$), and can practically be neglected. How-

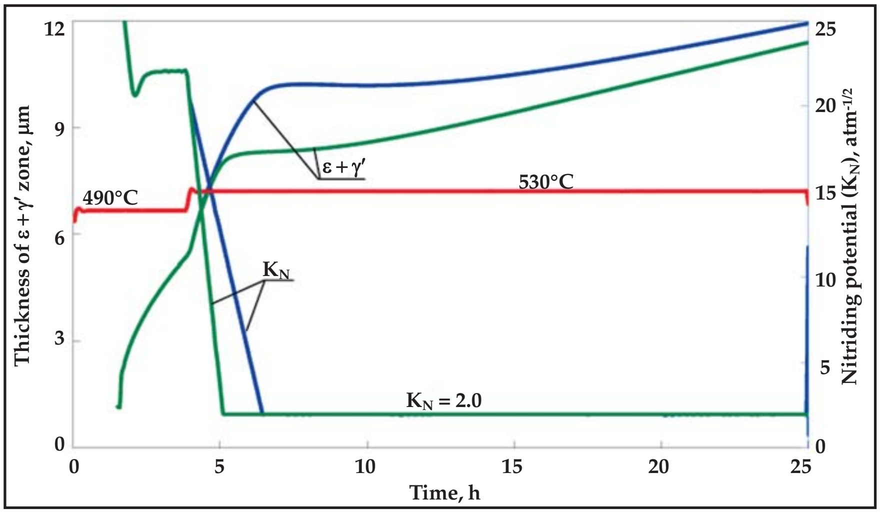


Fig. 2 — Comparison of growth rate of nitrides (ε + γ′) on 4140 steel at a fast drop of K_N (green) and slow drop of K_N (blue).

ever, it must be noted that the dropping rate does not influence a growth of nitrided layer. Further, similar phenomenon also occurs during nitriding using two-component atmospheres.

The investigation included a comparison between the nitrided layer obtained in a controlled standard process (using an NH_3 + dissociated NH_3 mixture) and that using ZeroFlow process. Figure 3 shows an example of a nirtrided layer and iron nitrides obtained using the ZeroFlow process.

Study Results

The results of the investigation indicate that by performing the ZeroFlow process using NH_3 alone, it is possible to produce nitrided layers identical to those obtained using standard processes in two-component atmospheres. In such a process, the control of composition of the atmosphere in the retort is carried out by occasionally stopping NH_3 flow into the furnace, thereby obtaining precise control of the kinetic growth of the nitrided layer similar to that available using NH_3 + dissociated NH_3 atmospheres.

The ZeroFlow process offers practical, economical, and environmental benefits over processes using two-component atmospheres including:

- Low consumption of gas (up to 8 times less than in processes using NH_3 + dissociated NH_3 and NH_3 + N_2 atmospheres.
- Easier, less expensive nitriding installation for the zero-flow process. Only one simple gas inlet valve and a gas analyzer is required to precisely regulate and control the chemical composition of the atmosphere obtained from NH_3 compared with two inlet valves, a high quality gas flow meter, and a gas analyzer required for processes using NH_3 + dissociated NH_3 and NH_3 + N_2 atmospheres. In addition, a dissociater is required for the dissociated ammonia.
- The ZeroFlow process can be carried out in furnace fitted with a steel retort, which is significantly cheaper than that made of a Ni-base heat resistant alloy required for processes using a two-component atmospheres.

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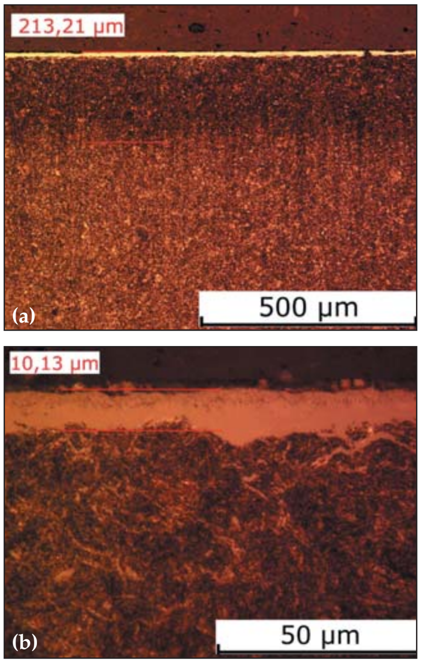

Fig. 3 — Photomicrographs of the nitrided layer (a) and iron nitrides (b) on 4140 steel nitrided using the ZeroFlow process at stage I (490°C, K_N = 22 atm$^{-1/2}$, and 3 h) and stage II (530°C, K_N = 1.3 atm$^{-1/2}$, and 22 hours).

For more information:
Prof. Dr. Hab.Inz. Leszek Maldziński
University of Technology
Poznan, Poland
and scientific adviser
of Seco/Warwick Group
mobile phone: +48692434340
e-mail: leszek.maldzinski@op.pl.