

Technical Paper

Development of Manufacturing Technology for Nitriding Processes Using Nitriding Potential Control

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Nitriding is used on main component parts of construction machinery because it provides excellent sliding properties and smaller deformation under thermal treatment. These parts are processed under specific conditions that are appropriate for their various requirements. On the other hand, conventional nitriding processes had technical issues in controlling atmospheres and setting conditions. These issues, however, can now be solved because the method of determining nitriding conditions using Lehrer phase diagram has been established thanks to the recent advances in the instrumentation technology such as H_2 sensors. This paper describes the determining procedure of the optimum nitriding conditions when introducing the nitriding potential control to mass production processes and reports the resulting reduction in the amount of gasses used.

Key Words: Nitriding, Potential, K_N , H_2 sensor, Compound layer, Diffusion layer

1. Introduction

Gas nitriding is a thermal treatment process for diffusing nitrogen into steels by introducing ammonia (NH_3) gas in a furnace and heating to 500 to 580°C. The diffused nitrogen forms a very hard compound layer that consists of an iron-nitrogen compound and a diffusion layer where nitrogen is dissolved, thus improving the fatigue strength and wear characteristics of steels.

Nitrided parts have two basic features: excellent sliding characteristics provided by the compound layer, and a small amount of deformation from thermal treatment due to low process temperatures below the transformation temperature. The latter, in particular, gives the benefit of simplified processes when processing thin-walled parts because it eliminates the process of correcting distortions, etc., after heat treatment, which is required in carburizing processes that are conducted above the transformation temperature (**Fig. 1**).

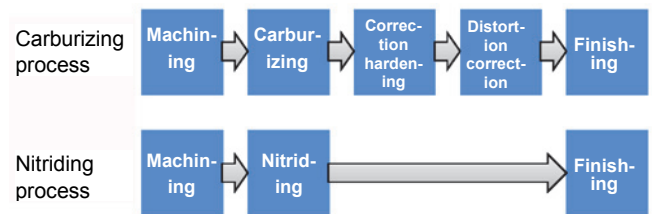


Fig. 1 Comparison between carburizing and nitriding processes

Taking advantage of the above features, Komatsu uses nitriding processes on hydraulic pump pistons (**Fig. 2**) for hydraulic excavators that require good sliding characteristics, and on transmission gears (**Fig. 3**) for bulldozers that are thin-walled and require high dimensional precision.

However, the nitriding process poses more technical challenges as compared with the carburizing process, such as controlling the treatment atmosphere (gas composition in the furnace) and setting the process conditions. This paper reports on determining procedure of the optimum nitriding conditions by introducing nitriding potential control, and the resultant reduction in the gas consumption.



Fig. 2 Hydraulic pump piston for hydraulic excavators



Fig. 3 Transmission gear for bulldozers

2. Phases Produced in the Nitriding Process

Fig. 4 shows a photo of the structure of a nitrided part, and Fig. 5 shows a binary phase diagram¹⁾ of Fe-N. Nitriding is conducted at temperatures lower than 592°C, or the eutectoid temperature of Fe-N. This process produces a 5 to 20µm thick compound layer consisting of the ε and γ' phases, and an approximately 0.5 mm thick diffusion layer.

The ε phase produced in the outermost surface of the compound layer is composed of Fe_{2.3}N and contains 7.7-11.1 mass% nitrogen. This phase, also called a porous layer, has a structure of fine and brittle pores that are connected like a chain. There are two different opinions as to its properties. One says that this phase forms a conforming surface in the initial stage of use, while the other insists that delamination accelerates wear. Therefore, its thickness is controlled in an atmosphere that is appropriately controlled according to the properties required for the part. This phase is removed by machining in some cases. The γ' phase, which is formed at the inside of ε phase, is composed of Fe₄N and contains 5.9 mass% nitrogen. Since this phase has a dense structure, it exhibits good sliding characteristics.

At the temperature of 592°C, up to 0.1 mass% nitrogen is dissolved in the α phase of the diffusion layer, causing solid solution hardening, and also precipitation hardening occurs due to the formation of fine nitride compounds by alloy elements contained in the steel. The hardening depth is greater

than the compound layer thickness, and the depthwise hardness is primarily provided by the diffusion layer.

The compound and diffusion layers generated in nitriding vary in the formation state depending on the nitriding conditions, which results in significant variations in the hardness and sliding characteristics of parts. Therefore, it is necessary to process parts under specific conditions that are appropriate for the required properties.

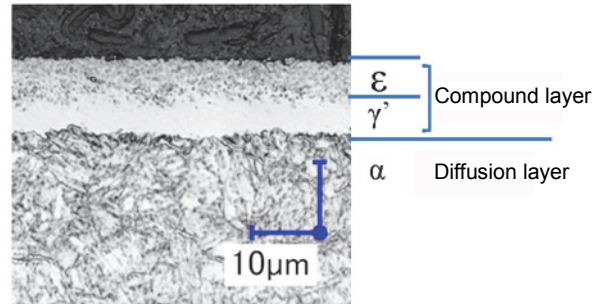


Fig. 4 Structure of nitrided part

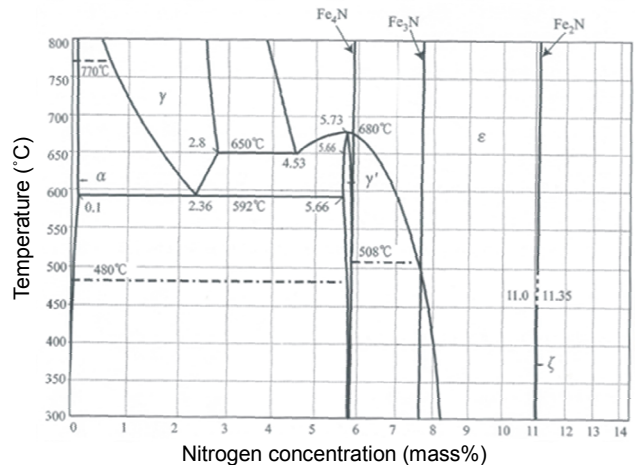
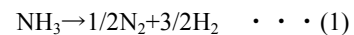


Fig. 5 Binary phase diagram of Fe-N

3. Atmosphere Control

In gas nitriding, NH₃ is used as a nitrogen source to steels. Two types of reaction occur in the furnace. The first is the thermal decomposition of NH₃, expressed by formula (1), and the second is the generation of nitrogen by dissociation caused by the catalytic reaction of iron, expressed by formula (2).



At the process temperature, NH₃ is thermally decomposed as in formula (1), and the generated nitrogen atoms quickly become nitrogen molecules, and therefore do not diffuse in steels. On the other hand, the nascent nitrogen generated by catalysis of steel, shown in formula (2), is

diffused into the steel²⁾.

Since the above two reactions occur simultaneously in the furnace, NH₃ is constantly introduced in the furnace so that the nitriding atmosphere containing NH₃ is maintained to supply nitrogen to the steel.

The atmosphere in the furnace needs to be maintained at a required value to obtain stable nitriding quality. However, since the atmosphere changes during the treatment depending on the furnace temperature and the diffusion state of nitrogen in the workpiece, the amount of introduced NH₃ needs to be constantly adjusted.

In the past, desociometers were used to measure and adjust the amount of NH₃ to be introduced since NH₃ in the atmosphere easily dissolves in water (Fig. 6). However, this method allowed only intermittent measurement, and the process could not be automated because the introducing amount had to be adjusted manually.

In recent years, infrared absorption type NH₃ concentration analyzers³⁾ capable of automatic measurement of NH₃ concentration and heat conduction type H₂ sensors⁴⁾ that allow automatic measurement of H₂ concentration by directly inserting the sensor in the furnace have been developed. It is now possible to continuously measure the atmosphere and automatically control the introducing amount by combining these sensors with computers and mass flow controllers (MFC) (Fig. 7).

Advances in these instrumentation technologies have enabled highly accurate control of atmosphere that was not possible before.



Fig. 6 Desociometer

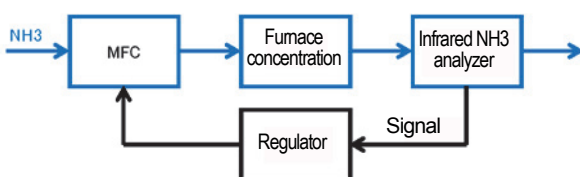


Fig. 7 Control schematic

4. Setting the Conditions Using the Lehrer Phase Diagram

In the past, NH₃ concentration has been used as an index of furnace atmospheres. The ASM Metals Handbook⁵⁾ shows a two-stage nitriding process that changes temperature and NH₃ concentration during the process with the conditions of 500 to 525°C/NH₃ 70 to 85% in the first stage and 550 to 565°C/NH₃ 15 to 35% in the second stage. Temperature is increased and NH₃ concentration is decreased in the second stage to promote nitrogen diffusion into the material and to restrict the thickness of the ε phase. However, the correlation between NH₃ concentration and generated phases was not clear.

Later, Lehrer studied the equilibrium of iron and NH₃, revealing the correlation between the nitriding potential K_N derived from NH₃ concentration and the generated phases at equilibrium using the Lehrer phase diagram^{6,7)} (Fig. 8).

The nitriding potential K_N defined by formula (3) is used to replace NH₃ concentration as an index of the nitriding capability of atmospheres.

$$K_N = \frac{P_{NH_3}}{P_{H_2}^{\frac{3}{2}}} \cdot \cdot \cdot (3)$$

K_N : Nitriding potential

P_{NH_3} : Partial pressure of ammonia

P_{H_2} : Partial pressure of hydrogen

For example, applying formula (3) to the 500°C/NH₃70% shown as the condition in the first stage of the two-stage nitriding process produces the nitriding potential K_N of 6.7, which is expected to form ε in the outermost layer based on the Lehrer phase diagram. If the amount of ε generation needs to be restricted, we can expect that the desired phase can be obtained by lowering the nitriding potential K_N to close to K_{N2} at the ε/γ' boundary.

By using the Lehrer phase diagram, it is now possible to examine in advance the conditions, i.e., the temperature and K_N (NH₃ concentration), for obtaining generated phases as desired. It has also become possible to set the optimum conditions by determining the lowest K_N for obtaining the desired phase based on the Lehrer phase diagram.

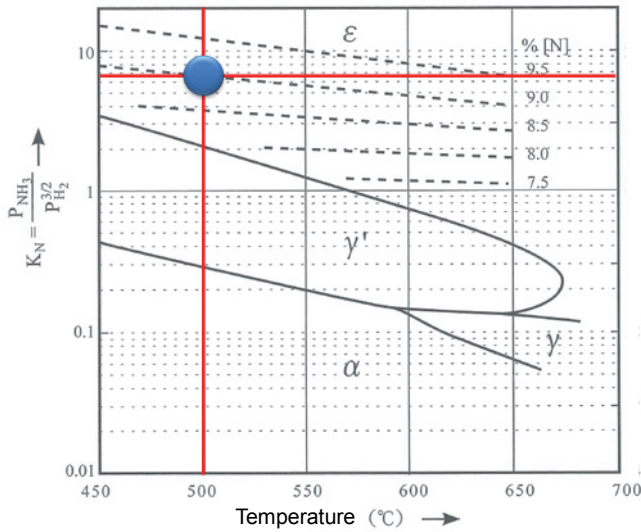


Fig. 8 Lehrer phase diagram

5. Forecasting Required Gas Flow Rate Due to Change in K_N

We forecasted the required flow rate of NH_3 gas due to the change in K_N ⁸⁾. The NH_3 concentration in the furnace is modeled in Fig. 9.

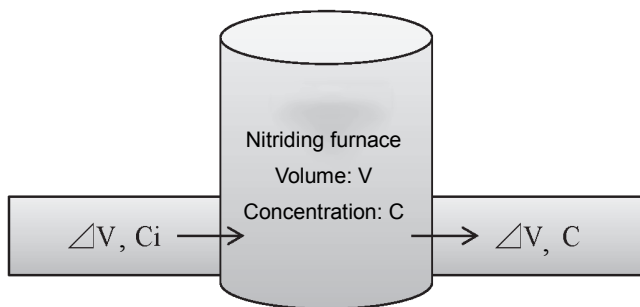


Fig. 9 NH_3 concentration in the furnace

The change in NH_3 concentration due to gas substitution is expressed by formula (4).

$$\frac{dC}{dt} = \frac{C_i - C}{V} \frac{dV}{dt} \dots (4)$$

- C_i : Concentration of introduced NH_3
- C : Concentration of NH_3 in furnace
- V : Furnace volume

The change in NH_3 concentration due to the gas decomposition reaction of formula (1) is expressed by formula (5).

$$\frac{dC}{dt} = -k \frac{P_{NH_3}}{P_{H_2}^{3/2}} = -k \frac{C}{\left[\frac{3}{4}(1-C)\right]^2} \dots (5)$$

k : Reaction speed constant

$$P_{H_2} : \frac{3}{4}(1-C)$$

By adding formulas (4) and (5), we obtained formula (6) for determining the NH_3 concentration in the furnace.

$$\frac{dC}{dt} = \frac{C_i - C}{V} \frac{dV}{dt} - k \frac{C}{\left[\frac{3}{4}(1-C)\right]^2} \dots (6)$$

The NH_3 concentration, or the nitriding potential K_N , can be determined by calculating the reaction speed constant k , specific to each furnace, in advance from a known NH_3 concentration obtained for a certain flow rate and then successively calculating formula (6) for each Δt .

Estimating the flow rate of NH_3 when the nitriding potential in the first stage of the two-stage nitriding would be reduced from K_N 6.7 to close to the ϵ/γ' boundary, we anticipated that the hourly flow rate could be reduced by 80%, which indicated that the reduction of K_N would be effective for restricting the gas flow rate.

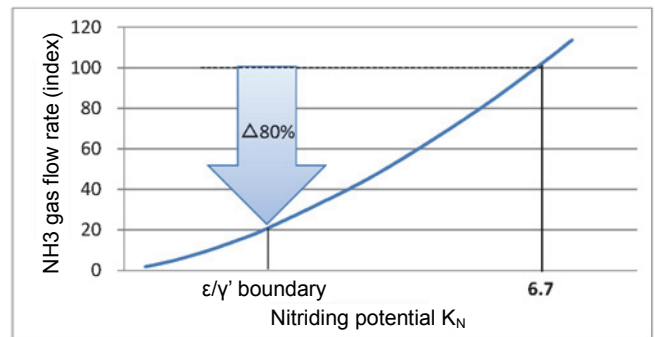


Fig. 10 Hourly change in gas flow rate

As described above, we are able to predict the condition of the compound layer produced on the surface of a workpiece in advance by introducing the potential control of nitriding that combines atmosphere control using new instrumentation technology and the condition setting method using the Lehrer phase diagram. Based upon this, we conducted quality examinations using a production furnace. The aim was to determine the optimum nitriding conditions required for achieving the target quality and to reduce gas consumption.

6. Examination of Quality

We processed test pieces of a round bar shape with a 30 mm diameter using the nitriding potential control. The test pieces are made of steel for nitriding based on SCM435H added with nitride generating elements, and a pit type gas nitriding furnace with an effective dimension of 1200 dia. x 1200 was used for the treatment. The process condition consisted of changing the K_N level in the first stage of the two-stage nitriding described above between “small”, “medium” and “large” in the ϵ phase region (Fig. 11).

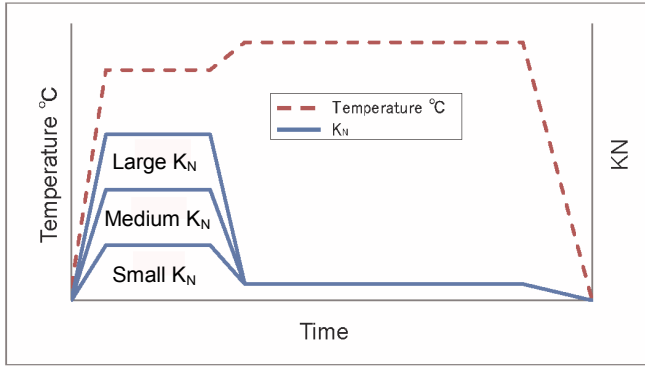


Fig. 11 Process pattern

This test resulted in a constant hardness in the 50 μm position regardless of the potential, as shown in Fig. 12, and there was no significant difference in both the hardness distribution in the diffusion layer in Fig. 13, and the nitrogen concentration distribution in Fig. 14, between different K_N levels. The compound constituent in Fig. 15 and the structure photos in Fig. 16 indicate that the ratio of the ϵ phase decreases as the K_N decreases, which is consistent with the quality expected from the Lehrer phase diagram.

From the above observations, it was confirmed that the hardness distribution in the diffusion layer does not change even if the K_N in the first stage of the two-stage nitriding decreases in the ϵ phase region, allowing the K_N to be decreased in the range where the compound thickness satisfies the specifications.

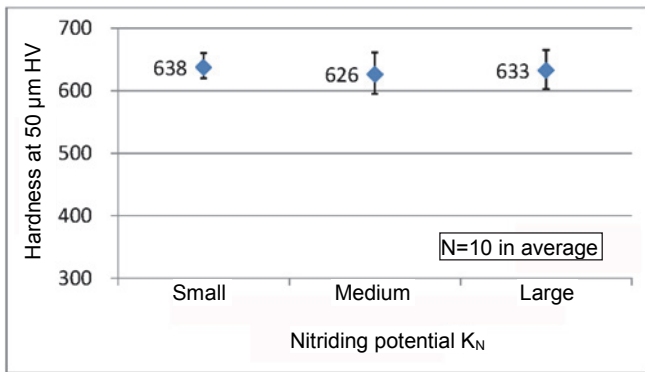


Fig. 12 Hardness at 50 μm (N=10 in average)

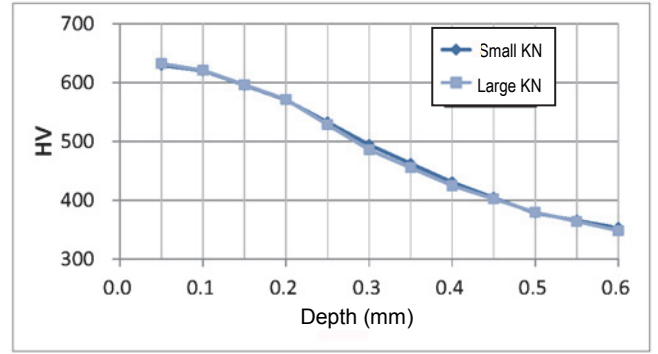


Fig. 13 Hardness distribution in diffusion layer (N=10 in average)

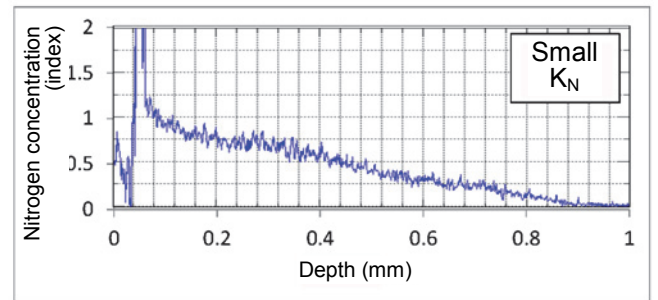
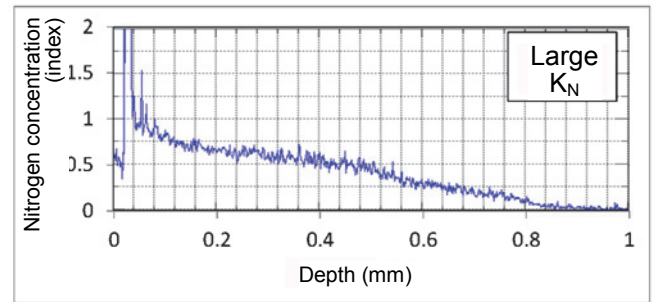


Fig. 14 Nitrogen concentration distribution

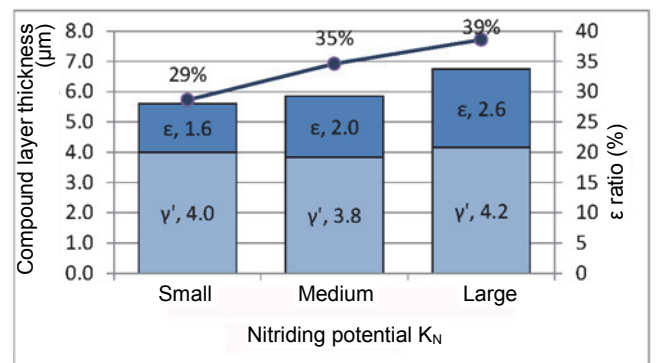


Fig. 15 Compound layer constitution (N=3 in average)

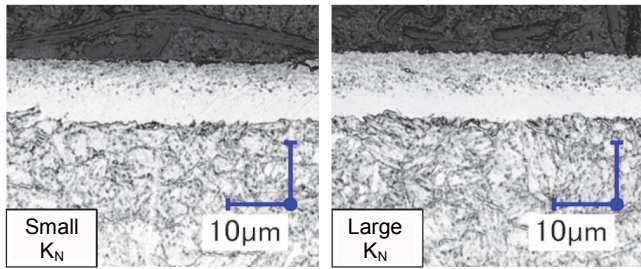


Fig. 16 Structure photos

7. Considerations

We consider the reason why there was no change in the hardness distribution in the diffusion layer of the test pieces. The hardness in the diffusion layer is dependent on the concentration of the nitrogen diffused in the layer, and the diffusion speed of nitrogen is dependent on the concentration gradient of active nitrogen if the material and temperature are the same.

Fig. 17 shows a schematic of the phase generation and the change in nitrogen concentration when nitriding takes place in the ϵ region.

I. At the initial stage of the process, nitrogen dissociated from ammonia dissolves and increases its concentration in the α phase.

II. The γ' phase is produced when the nitrogen concentration in the α phase reaches the saturation point at the process temperature,

III. Similarly, the ϵ phase is produced when the γ' phase reaches the saturation point. The nitrogen concentration on the steel surface becomes equilibrium with the potential K_N of the atmosphere.

When γ' compound is produced along the way of the process, the α phase is supplied with nitrogen through the γ' phase. Therefore, it is considered that the nitrogen diffusion in the α phase is dependent on the concentration difference between the γ' and α phases, and is not affected by the potential K_N of the atmosphere after γ' is generated.

Fig. 18 is a schematic of the nitrogen concentration when the K_N decreases, which shows that the reduction of the K_N affects the nitrogen concentration in the ϵ phase only without causing changes in the concentration difference between the γ' and α phases. This is considered to be the reason why there is no difference in the nitrogen concentration distribution and a similar hardness distribution is obtained in Fig. 14.

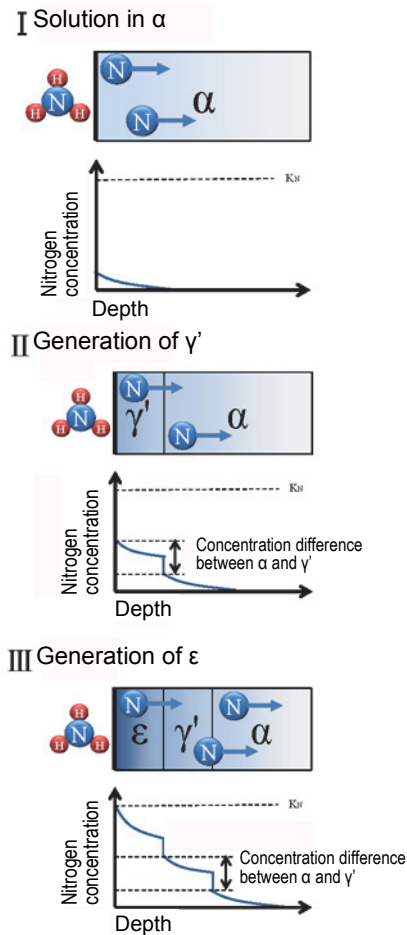


Fig. 17 Schematic of phase formation and nitrogen concentration in nitriding process

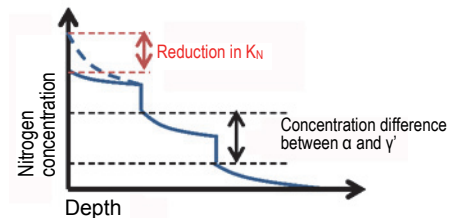


Fig. 18 Schematic of nitrogen concentration when K_N reduces

8. Application to Mass Production Processes

An example of applying nitriding potential control to a mass production process is shown below. We conducted the optimization of the K_N while maintaining the current hardness distribution and phase formation in the nitriding process of transmission gears.

As a result, the NH_3 gas flow rate decreased during the process, and we succeeded to reduce the gas consumption per charge including the necessary displacement of in-furnace atmosphere by 46% (Fig. 19).

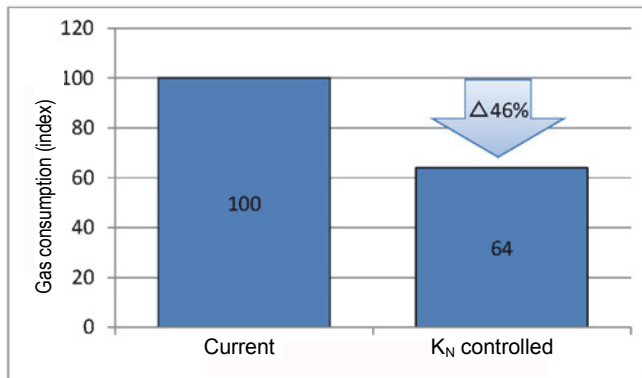


Fig. 19 Comparison of gas consumption

9. Conclusion

We introduced nitriding potential control that combines atmosphere control techniques and a condition setting method using the Lehrer phase diagram in the nitriding process for manufacturing transmission gears for construction equipment. This has allowed us to predict the compound layer produced on the workpiece surface and to determine the optimum nitriding conditions for achieving the target quality. As a result, we have succeeded in controlling the compound layer while maintaining the current hardness distribution, thus reducing NH₃ gas consumption.

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Introduction of the writers



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Joined Komatsu Ltd. in 2009.
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[A few words from writers]

Our effort has contributed to the cost reduction of main components. Based on this technology, we would like to further develop heat treatment technologies including component layer control for quality improvement and composite heat treatment that combines nitriding and other heat treatment processes for better functionality, thus contributing to the competitiveness of Komatsu, which manufactures components in-house.