Development of Carbonitriding Processes Combining Vacuum Carburizing and Atmospheric Pressure Nitriding

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Regarding surface hardening for the steel for structural use, carbonitriding is carried out to improve wear resistance and rolling fatigue. For the carbonitriding treatment, there have scarcely been any reports on vacuum carburizing-based carbonitriding treatment. The reason inferred for this scarcity is the difficulty of nitrogen intrusion under reduced pressure. Thus in this study, after vacuum carburizing, nitriding under atmospheric pressure was performed in a separate room. In addition, the residual ammonia concentration inside the furnace was controlled in an attempt to achieve a treating method under which the required nitrogen concentration distribution is ensured in a stable manner. This resulted in the following conclusion.

1) By increasing the nitriding pressure, the nitrogen concentration in the steel rises even at the same ammonia flow rate. 2) By changing the control for the residual ammonia concentration, any optional value can be attained for the nitrogen concentration in the steel. 3) In this process, the variations for the nitrogen concentration in the furnace and the nitrogen concentration among different batches remained within ±0.05%, meaning that stable nitrogen concentration values can be attained. 4) Based on the above, a carbonitriding treatment process enabling mass production processing was developed. What characterizes this heat treatment process is that in comparison to nitriding under reduced pressure, higher surface nitrogen concentration can be achieved, and that stable quality levels can be attained.

Keywords: *vacuum carburizing, carbonitriding, nitriding*

1. Introduction

Regarding surface hardening for the steel for structural use, when aiming for a higher wear resistance and rolling fatigue than carburizing treatment, carbonitriding treatment is carried out. For the carbonitriding treatment, after carburizing, nitriding is performed by using ammonia gas, with the process based mostly on gas carburizing. At the same time, because vacuum carburizing limits the occurrence of grain oxidation, which enables an increase in the material strength [1)] and thus a reduction in carbon dioxide emissions, there has been an expanded use of vacuum carburizing. If it is possible to conduct carbonitriding in a vacuum carburizing furnace, this means that in addition to the benefits of vacuum carburizing, achieving the result of an increase in wear resistance due to nitrogen intrusion can also be expected. However, there are few reports on vacuum carburizing-based carbonitriding treatment. As the reason inferred for this scarcity, the difficulty of nitrogen intrusion under reduced pressure could be a factor. [2)]

Another issue to address is that if only a constant ammonia flow rate is simply maintained when conducting carbonitriding, the nitrogen concentration may easily vary among different processing batches. [3)] In order to achieve the required nitrogen concentration for the steel at the carbonitriding, there have been attempts in recent years to control the residual ammonia concentration inside the furnace and to control the nitriding potential (Kn) as a part of the carbonitriding process. [4)] The reason is that, while thermal decomposition inside the furnace takes place for the ammonia that was introduced at the nitriding, (eq.1) the residual ammonia that did not decompose becomes the supply source for nitriding reaction, and the nitrogen intrusion into the steel material occurs according to (eq.2).

$$2NH_3 \rightarrow N_2+3H_2 \qquad \text{(eq.1)}$$

$$NH_3 \rightarrow [N]+3/2H_2 \qquad \text{(eq.2)}$$

It is therefore believed that the nitriding reaction is heavily dependent on the partial pressure of the gas inside the furnace, and that for precisely controlling the nitrogen concentration in the steel material, a control method for the nitriding process would be essential.

Even for the gas carbonitriding treatment, there is concern that variations in the nitrogen concentration can easily occur according to the placement inside the furnace. The reason inferred for such variations is that the temperatures and the partial pressure of ammonia could vary according to the zone in the continuous furnace.

In this study, therefore, in order to resolve the various issues, separate rooms were used for carburizing and nitriding, so that changing the carburizing and nitriding pressures would be possible. Also, feedback control was performed for the residual ammonia concentration at the nitriding, in an attempt to establish the treatment method enabling stable achievement of the required nitrogen concentration distribution.

2. Test method

2.1 The material under test

Regarding the chemical composition of the material under test used in this study, the material (0.20C-0.28Si-0.82Mn-1.1Cr) equivalent to SCr420H of JIS G 4053 was used. After heating the rolled steel of φ30 to 1173K and the temperature was retained, furnace cooling and then the shape was machined to φ25mm×5mm.

2.2 Carbonitriding conditions

Fig.1. shows the carbonitriding conditions. For the furnace for carbonitriding, ModulTherm, a vacuum carburizing furnace made by Daido Steel Co., Ltd., was used. After performing vacuum carburizing in a carburizing module at 1203K, nitriding was performed in a nitriding module at 1093K or 1123K. The pressure of the nitriding module was changed to 1.5kPa and 101.3kPa, and the

effects of the pressure were confirmed. As the gases introduced during the vacuum carburizing process, acetylene and nitrogen were used, and as the gases introduced during the nitriding process, ammonia and nitrogen were used. After the treatments, oil quenching was performed. During the nitriding process, a measurement was conducted by an infrared sensor for the residual ammonia concentration inside the furnace, and the ammonia flow rate was controlled so that a constant value would be kept for the residual ammonia concentration. For observing changes in the nitrogen concentration for the material to be treated, the residual ammonia concentration was changed between 0.05% and 0.50%. Furthermore, a dummy angle of 50mm×50mm×150mm equivalent to JIS G 3101 SS300 (0.12C-0.16Si-0.51Mn-0.35Cr) was used, and by changing the loading capacity for the dummy angle, an examination was also conducted for changes in the nitrogen concentration distribution due to changes in the surface area.

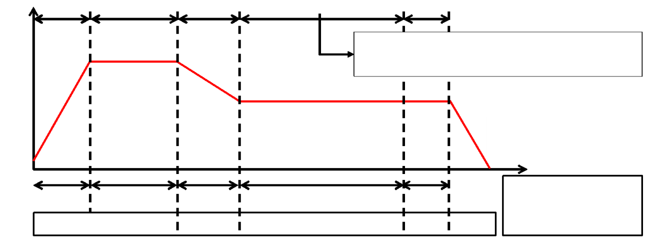

Fig.1. Carbonitriding conditions

2.3 Measurements of the carbon concentration distribution and nitrogen concentration distribution

For the material under test, 1 piece was placed in the center inside the furnace, and 1 piece was placed in each of the 4 corners of the outer circumference. The 5 test pieces per batch were then heat-treated. Measurements were conducted for the carbon concentration and nitrogen concentration for each of the surfaces through method for spark discharge atomic emission spectrometric analysis (SPK-AES), thus checking the variations in surface concentration according to the placement inside the furnace. By repeating this process a number of times, a check was also conducted for the variations among different processing batches. Based on the central samples after the carbonitriding treatment, analysis was conducted for the carbon concentration distribution and the nitrogen concentration distribution for the cross section of the material under test, by using an electron probe micro analyzer (EPMA). It had been confirmed beforehand that the measurement deviation for the surface concentration of identical test pieces was within ±0.05% for SPK-AES and EPMA.

3. Test results and consideration

3.1 Effects of the nitriding pressure

Fig.2. shows the changes in the surface nitrogen concentration when changing the pressure in the furnace at the nitriding treatment. It was confirmed that, with an increase in total pressure, there was a tendency for an increase in the surface nitrogen concentration of the steel material, even if the equivalent ammonia flow rate is maintained. It is supposed that by setting the pressure in the furnace at 101.3kPa, the partial pressure of the ammonia inside the furnace rises even if the flow rate is the same, increasing the reaction rate as in (eq.2), thus leading to the result above.

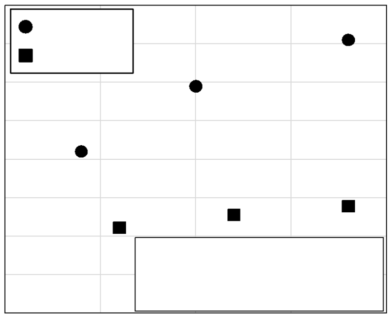

Fig.2. The effects of nitriding pressure on the surface nitrogen concentration

3.2 The effects of the residual ammonia concentration

Fig.3. (a)(b) show the changes in the carbon concentration and nitrogen concentration when the residual ammonia concentration is changed. A tendency was recognized that the higher the residual ammonia concentration is, the higher the surface nitrogen content becomes and the deeper the nitriding depth is. These results are similar to the results of the gas carbonitriding treatment according to Wang et al. [5] It was confirmed that controlling the ammonia concentration can change the nitrogen concentration of the steel, and that the carbon concentration barely changes in the process. Fig.3. (c)(d) show the variations in the surface carbon concentration and the nitrogen concentration according to the placement inside the furnace, under identical conditions. The variations in the surface carbon concentration and the nitrogen concentration remain within ±0.05% of the average values, enabling a stable treatment process.

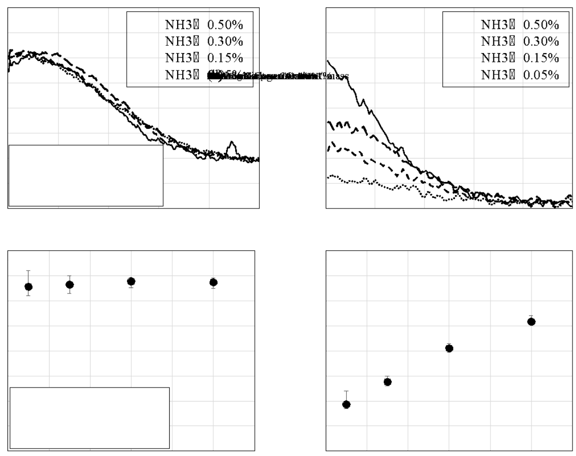

Fig.3. The effects of the residual ammonia concentration (a) The carbon concentration distribution; (b) The nitrogen concentration distribution; (c) The variations in the surface carbon concentration inside the furnace; (d) The variations in the surface nitrogen concentration inside the furnace

(n=5; The center=1, The circumference=4)

3.3 The effects of the surface area (the loading capacity)

It is supposed that when the loading capacity for processing increases, such as in the processing for mass production, the uniformity inside the furnace for the partial pressure of ammonia declines, accounting for more variations in the nitrogen concentration inside the furnace. Thus Fig.4. shows the results of checking as to whether there is any change in the variations in the nitrogen concentration when the surface area is increased from $2m^2$ to $10m^2$, with the purpose of reproducing the gas flows equivalent to mass production. It was confirmed that even when the surface area is considerably increased from $2m^2$ to $10m^2$, there is barely any change in the nitrogen concentration distribution, meaning that stable results can be achieved. The variations in the nitrogen concentration do increase when the surface area is $10m^2$ compared to when it is $2m^2$, but still the difference was within ±0.05%. It is believed that the reason is that sufficient gas flows are maintained even with a surface area of $10m^2$, accounting for uniform partial pressures of ammonia inside the furnace and thus enabling a stable treatment.

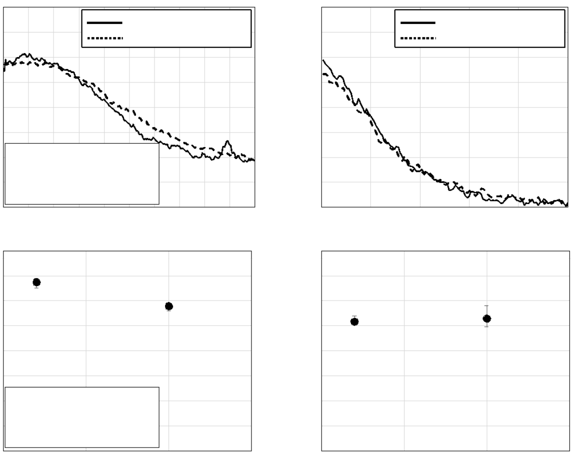

Fig.4. The effects of the surface area for treatment: (a) The carbon concentration distribution; (b) The nitrogen concentration distribution; (c) The variations in the surface carbon concentration inside the furnace; (d) The variations in the surface nitrogen concentration inside the furnace (n=5; The center=1, The circumference=4)

3.4 The variations in the carbon concentration and the nitrogen concentration among different processing batches

It has traditionally been observed that in controlling the ammonia flow rate, the variations in the nitrogen concentration were extensive among different processing batches, [3] and a check was conducted if a similar tendency emerges also in controlling the ammonia concentration. Fig.5. shows the variations in the carbon concentration and the nitrogen concentration, when identical processing was performed three times under the conditions of the ammonia concentration at 0.50% and a nitriding time of 7.2 ks. The carbon concentration and the nitrogen concentration both remained within ±0.05% of the average values. It is believed that a factor for this was that by adopting a module used exclusively for nitriding, there was no contamination by the carburizing gas, inside the furnace, and achieving stability was easy for the furnace atmosphere. Thus it was confirmed that for different processing batches, achieving stable results is possible.

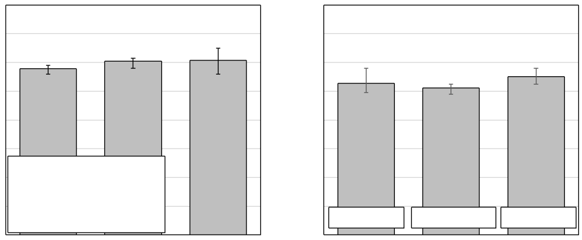

Fig.5. The effects of the variations among different processing batches: (a) The surface carbon concentration; (b) The surface nitrogen concentration (n=5; The center=1, The circumference=4)

4. Conclusion

In this study, the nitriding under atmospheric pressure was performed in a separate room after the vacuum carburizing process, and the residual ammonia concentration inside the furnace was controlled. This was an attempt at a treatment method for stably achieving the required nitrogen concentration distribution. What follow are the results of the study.

(1) It was confirmed that, by increasing the pressure from 1.5kPa to 101.3kPa, the surface nitrogen concentration rises even when the same ammonia flow rate is maintained.

(2) It was confirmed that by changing the residual ammonia concentration from 0.05% to 0.50%, the surface nitrogen concentration in the nitrogen concentration distribution rose by approximately 0.3%.

(3) It was confirmed that, when the surface area was $2m^2$, the variations in the surface nitrogen concentration according to the placement inside the furnace remained within ±0.05%. It was also confirmed that when the treatment was carried out for n=3, identical results were achieved, meaning the attainment of stable results. It was confirmed that, even when examining the conditions with the surface area considerably increased to $10m^2$, stable results were also achieved.

(4) By using the ModulTherm, a carbonitriding treatment process with mass production possible has now been developed. What characterizes this heat treatment process is that in comparison to nitriding under reduced pressure, higher surface nitrogen concentration can be achieved, and that stable quality levels can be attained.

※ModulTherm is a trade mark or registered trademark of ALD Vacuum Technologies GmbH.

References

1) K. Ohbayashi: Daido Steel Technical Report, 79 (2008), 53-60
2) K.Kawata: Netsu Shori 50,6 (2010) 601-607
3) S. Bischoff, H. Klümper-Westkamp, F. Hoffmann, H.-W. Zoch: HTM J. Heat Treat. Mater., 67 (2012), 217-222
4) K. Tsujii, M. Skalecki, M. Steinbacher, H.-W. Zoch: ISIJ international 60, (2020) 2051-2058.
5) Bo Wang, Bin Liu, Jianfeng Gu, Marce A. J. Somers:

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