

Effects of the Temperature History Following Nitriding Treatment on the Phase Composition of the Formed Compound Layer

Katsushige Shimizu¹, Soichiro Nogami¹ and Koji Abe¹

¹DOWA Thermotech Co., Ltd, Aichi 467-0854, Japan

In gas nitriding of steel, a compound layer is formed on the surface of the steel, which is composed of ϵ -phase and γ' -phase of iron nitrides. It is known that the mechanical properties improved depend on which of these phases is formed more. The compound layer obtained by gas nitriding of iron can be predicted by the Lehrer diagram, which shows the relationship between temperature, nitriding potential KN, and the stable phase in the Fe-N system. However, in industrial steels, ϵ -phase and γ' -phase may be mixed in a complex phase composition due to the influence of alloying elements such as C and Cr. The result is not always consistent with the phase composition shown in the Lehrer diagram. Therefore, further study is needed on the stability of the phase composition of the compound layer of industrial steels.

In this study, the effect of the temperature history following nitriding treatment on the phase composition of the generated compound layer was investigated for industrial steel SCM. In the experiments, specimens were gas nitrided at KN for a predetermined time, moved to the unheated zone in a nitriding atmosphere, held for a predetermined time, and then quenched to room temperature. The phase composition of the compound layer at each temperature history was analyzed by EBSD. As a result, it was confirmed that the phase composition in the compound layer changed by holding at low temperatures, specifically, the ratio of ϵ -phase decreased and γ' -phase increased. This change in phase composition occurred in a relatively short period of time, from 10 to 30 minutes. In addition, the C and N distribution of the ϵ -phase and γ' -phase in the compound layer before and after low temperature holding was analyzed by EPMA. The C enrichment in the ϵ -phase after low-temperature holding was particularly pronounced compared to that before holding. The phase stability of the ϵ -phase in the Fe-C-N system was estimated by the computational phase diagram. The results show that for the ϵ -phase to be stable at low temperatures, C must be more enriched than when held at high temperatures. This implies that the change in phase composition of the compound layer due to holding at low temperatures is caused by the redistribution of C and N, driven by the change in phase stability of the ϵ -phase and γ' -phase due to the temperature change.

Keywords: nitriding, compound layer, phase composition

1. Introduction

In recent years, controlled nitriding, in which the nitriding atmosphere in the furnace is controlled by continuously measuring the ambient gas, has been used to automate the actual operation and reduce the gas volume¹). Mechanical properties of nitrided parts whose surface compound layer is mainly ϵ -phase or γ' -phase have been reported using controlled nitriding²⁻⁵). In particular, when the compound layer is mainly γ' -phase, which has high toughness, the peel strength²) and rotary bending fatigue strength³) are superior, and depending on the optimization including materials, the strength equivalent to carburizing and quenching can be obtained²). Control of the compound layer is an important technology for increasing the strength of nitrided parts.

On the other hand, it has been reported that the phase composition of the compound layer (phase ratio and distribution of ϵ and γ' -phases) during nitriding is affected not only by nitrogen introduced from the atmosphere but also by the carbon supply⁶) from the base metal and alloying elements (Cr, etc.)⁷). Thus, the phase composition of the compound layer is affected not only by the nitriding atmosphere but also by the base metal, and further study is needed on the stability of the phase composition of the compound layer in industrial steels. By the way, according to the Lehrer diagram⁸), the ϵ -phase can be read as a high-temperature stable phase and the γ' -phase as a low-temperature stable phase. Therefore, it is considered that the temperature history after nitridation affects the phase structure of the compound layer, but no systematic experiment has been conducted.

2. Experimental

2.1 Sample and Equipment

JIS-SCM420 quenched and tempered steel was used as the specimen. The diameter of the specimen is 30 mm and its thickness is approximately 5 mm. The surface was polished and cleaned with ethanol before nitriding. Nitriding was performed in a small nitriding furnace at a temperature of 873 K with a nitriding potential of KN = 0.5.

The atmosphere was measured using a non-dispersive infrared ammoniometer and a hydrogen gas analyzer with thermal conductivity measurement, and the flow rates of ammonia, nitrogen, and hydrogen gas in the furnace were varied to maintain the target KN. A schematic diagram of the nitriding furnace used in the experiments is shown in figure 1.

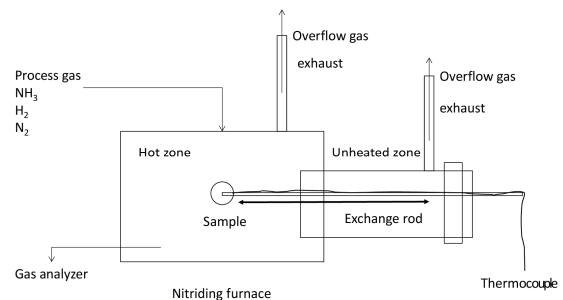


Figure 1 Schematic diagram of the nitriding furnace.

2.2 Experimental Procedure

The samples were placed in a nitriding furnace; after 7.2ks of nitriding, they were transferred to an unheated zone at 773K with a constant nitriding gas overflow, with the same atmosphere as the KN heated zone. The holding time conditions were as follows: (i) 0ks, (ii) 0.3ks, (iii) 0.6ks, and (iv) 1.8ks. After each holding time, the samples were cooled to room temperature and removed. Temperature changes were recorded with thermocouples. Figure 3(b) shows the details of the post-nitridation process. In (i), (ii), and (iii) are samples cooled from 873 K, 823 K, and 773 K, respectively. In (iv), the sample cooled to 773 K in 0.6 ks and remained there for 1.2 ks.

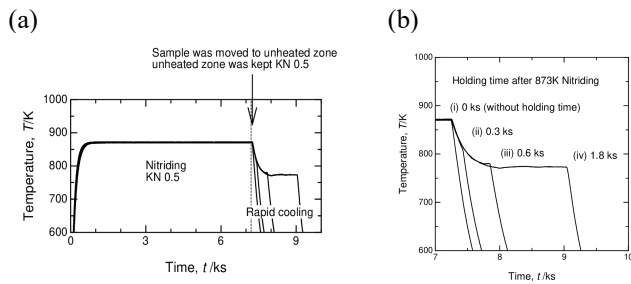


Figure 2 (a) Temperature history of the samples during the nitriding treatment. (b) Temperature transition diagram of cooling and isothermal holding process after nitriding (Enlarged view of (a))

3. Results and Discussion

Figure 3 presents the EBSD phase maps corresponding to conditions (i) through (iv), overlaid with a gray Image Quality Map for clarity. The degree of darkness differentiates the α -phase, γ' phase, and ε -phase. The upper section of each map shows the sample surface, while the lower part indicates the base metal. Black areas are unanalyzable. In (i), the γ' phase is about 2 μ m from the surface and is polygonal polygonal grain morphology, while the ε -phase, dominant on the base metal side, has a columnar grain morphology. (ii) exhibited a phase composition similar to (i) without much variation. By (iii), there's an increase in the γ' phase area and changes in the compound layer. In (iv), the γ' phase area further expands, reversing the γ' to ε -phase fraction.

Figure 4 shows the results of EPMA analysis under each condition. The left column is a contour plot of C-K α intensity, the middle column is a contour plot of N-K α intensity, and the right column is a scatter plot showing the correlation between C-K α intensity and N-K α intensity (CN correlation diagram), expanded to the range of intensity corresponding to the compound layer. The brightness of the contour plot reflects the intensity of C-K α or N-K α , and higher C-K α or N-K α intensity indicates a higher concentration of carbon or nitrogen. Contour lines in the scatter plots indicate kernel density estimates (KDE), which represent the density of the plots. The upper panel shows the results for condition (i) and the lower panel shows the results for condition (iv).

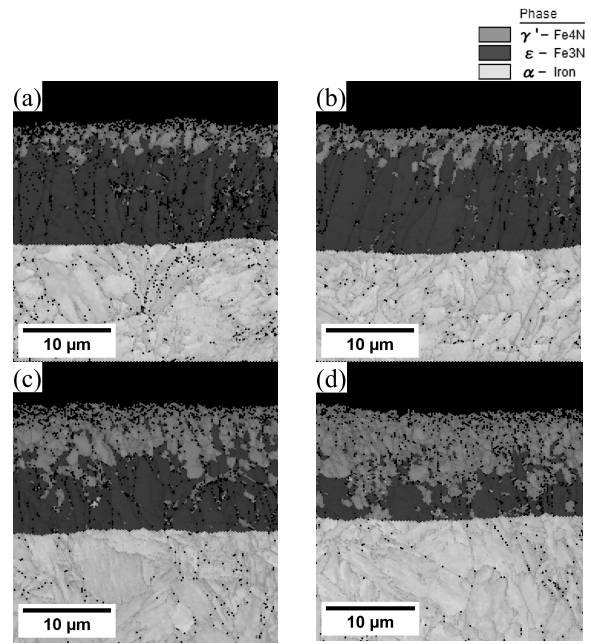


Figure 3 Phase map by EBSD (a) no holding time [condition(i)], (b) 0.3 ks holding [condition(ii)], (c) 0.6 ks holding, [condition(iii)], (d) 1.8 ks holding [condition(iv)].

(a) In the precipitation zone of γ' -phase on the surface side, the carbon concentration is low and the nitrogen concentration is high; the EBSD results show that all but the surface area is in ε -phase, but the nitrogen concentration is high on the surface and decreases toward the interior, while the carbon concentration is high on the interior and decreases toward the surface. This result is also confirmed by the rightward declining CN correlation diagram.

(d) The region of low carbon concentration is greatly extended; the CN correlation diagram shows that the population is divided into two groups, one with high nitrogen concentration and low carbon concentration and the other with low nitrogen concentration and high carbon concentration.

Figure 3 shows that the γ' -phase increased and the ε -phase decreased with continued low-temperature holding after nitriding. Figure 4 shows that the phase compositions of the γ' -phase and ε -phase were varied with changes in the ratio of the phase fraction in compound layer. Especially carbon concentration of the ε -phase was increased.

Therefore, the carbon and nitrogen concentrations of each phase in the γ' and ε co-existence region in the Fe-N-C ternary system at KN = 0.5 873 K and 773 K were determined by thermodynamic calculations. Thermo-Calc was used for the thermodynamic calculations, and SSOL5 and SSUB6 were used as databases. The calculation results are shown in Table 1.

Table 1 Thermodynamic calculations of the composition of the compound layer in the γ' and ε -phase co-existence region of the Fe-N-C system at KN = 0.5 at 873 K and 773 K.

	Carbon Content (mass%)		Nitrogen Content (mass%)	
	γ'	ε	γ'	ε
873 K	0.014	0.550	5.82	6.80
773 K	0.107	1.192	5.73	6.92

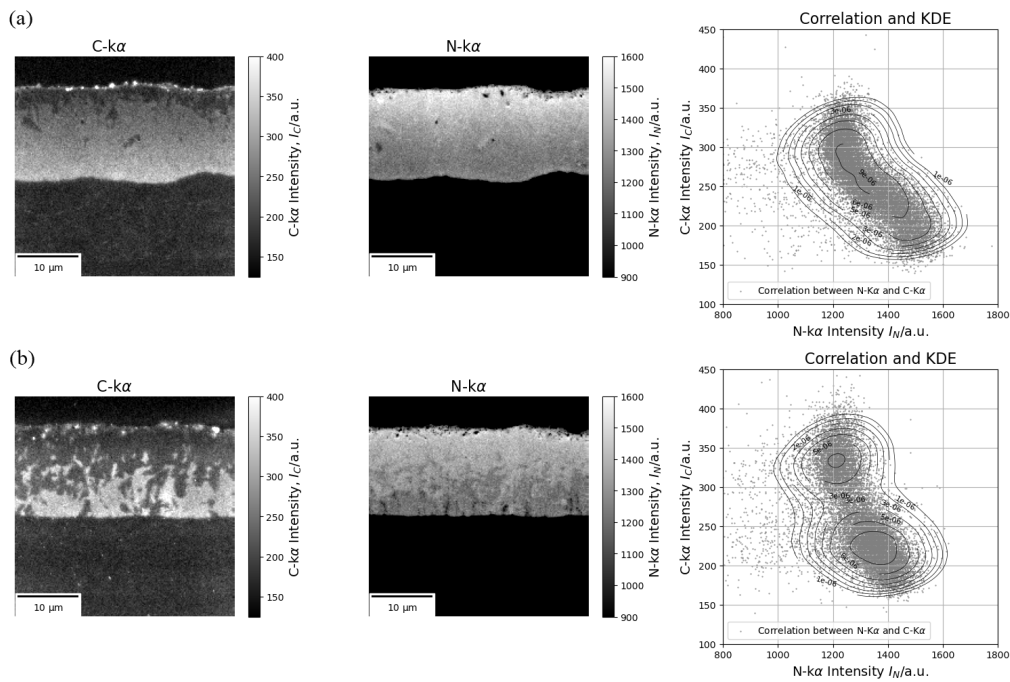


Figure 4 EPMA analysis results: (a) represents the results for condition (i), and (b) for condition (iv). The left column shows the C- α intensity, the middle column shows the N- α intensity, and the right column is a scatter plot showing the correlation between the C- α and N- α intensities. The contour lines represent kernel density estimates (KDE) on the scatterplot.

Table 1 implies that the carbon concentration in the ϵ -phase increases, if the temperature changes from 873 K to 773 K. Therefore, an Fe-C pseudo binary phase diagram for the Fe-N-C ternary system under the constraint condition of $KN = 0.5$ was calculated. The outcome is displayed in Figure 5. The arrows in the figure 5 indicate the temperature history: for the epsilon phase to exist at 773 K, the carbon concentration must be higher than at 873 K. The carbon concentration in the ϵ -phase is higher than at 873 K. This suggests that the low-carbon ϵ -phase, formed at elevated temperatures, might experience a phase separation from ϵ -phase (with a low carbon concentration) to ϵ -phase (with a high carbon concentration) + γ' -phase when maintained at cooler temperatures.

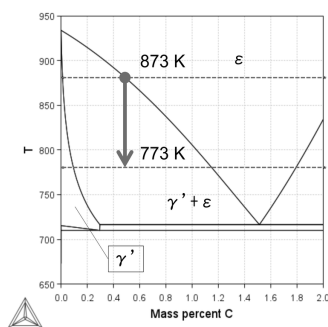


Figure 5 Fe-C pseudo binary calculated phase diagram obtained with the constraint $KN = 0.5$ in the Fe-N-C ternary system.

4. Conclusion

In this study, the effect of the temperature history following nitriding treatment on the phase composition of the compound layer was investigated. It was confirmed that the proportion of ϵ -phase in the compound layer decreased and the proportion of γ' -phase increased by holding at low temperature after nitriding treatment. The results of thermodynamic calculations imply that this change in phase composition of the compound layer is caused by the redistribution of C and N due to temperature change.

References

- 1) T. Umeda and K. Miyabe: KOMATSU TECHNICAL REPORT, **60-167**(2015) 17-23.
- 2) A. Kobayashi, S. Maeda, H. Imataka, Y. Gyotoku, M. Yuya, Y. Shimizu, M. Kanayama: Transactions of Society of Automotive Engineers of Japan **45**(2014) 1153-1158
- 3) Y. Hiraoka, A. Ishida, O. Umezawa: NETSUSHORI **57**(2017) 64-72.
- 4) S. Takagi, Y. Tonozuka, N. Nakamura, T. Itou: Tetsu-to-Hagane **104**(2018) 594-601.
- 5) Y. Yamada, K. Takahashi, H. Eto: NETSUSHORI **60**(2020) 193-198.
- 6) T. Umehara, M. Yuya: NETSUSHORI **59**(2019) 61-66.
- 7) K. Asada, S. Kumagai, Y. Watanabe: NETSUSHORI **58**(2018) 43-44.
- 8) E. Lehrer: Zeitschrift für Elektrochemie und angewandte physikalische Chemie **36**(1930) 383-392.