

Mechanism of Abnormal Surface Carbon Content Reduction in Nb-bearing Case Hardening Steel Gas Carburized after Machining

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In our previous paper, we reported that the surface carbon concentration (Cs) in carburized Nb-bearing steel decreases substantially with increasing the machining speed before carburizing. In the present study, a systematic study was made to clarify the effects of Cr,Nb addition and machining speed on the Cs. Uniform Cr oxide film was observed on the surface of specimens exhibited a large decrease in Cs. The carbon concentration profile was calculated assuming that carbon absorption was ceased after the complete coverage of specimen surface by Cr oxide film. It is confirmed that the present calculation fits well with the measured carbon concentration profile of low Cs. Moreover, it is shown that the value of Cs becomes smaller as the time span between the start of carburization and the time of Cr oxide film formation becomes shorter. The role of Nb is considered to be the retardation of recovery, recrystallization and grain growth through the pinning effect of Nb(CN) during carburizing. The high density of lattice defects introduced by machining is maintained by Nb(CN) and promotes faster Cr diffusion. In the present study, it has been clarified that in machined specimens of Nb-bearing steel, entire coverage of specimen surface by Cr oxide film during carburizing occurs in steels containing even a small amount of Cr like 1%.

KEY WORDS: Nb-bearing steel; machining; gas carburizing; surface carbon concentration; Cr oxide layer.

1. Introduction

Many of the power transmission parts of vehicle, such as gear parts and axle components, are subjected to a carburizing treatment after being formed via machining to enable additional functionality, such as fatigue strength and wear resistance. Gas carburizing is widely used within the automotive industry as the method of heat treatment for these kinds of parts because of its excellent suitability for mass production and its ease of operation.¹⁾ During normal operations, the surface carbon concentration (Cs) is adjusted to approximately 0.7% to 0.8% in many cases to ensure that the parts have the required fatigue strength and wear resistance.

The gas carburizing process involves an equilibrium reaction between the carbon potential (CP) of a carburizing atmosphere (an atmospheric gas containing both carbon monoxide and carbon dioxide gases) and the surface of the steel. This reaction allows the carbon to penetrate into the steel. In our previous study, it was found that even when the gas carburizing was carried out in a carburizing atmosphere with a CP of approximately 0.8%, there were cases where the Cs of the steel largely decreased down to approximately 0.4%.²⁾ In our preliminary experiment, the effect of Nb addition and machining conditions on the decrease in Cs was studied. The results showed that in the case of Nb free

SCM420 steel the machining conditions before carburizing had only a small effect on the Cs. On the other hand, in the case of SCM420 steel with a small amount of Nb, a large abnormal decrease in the Cs was observed²⁾ when subjected to gas carburizing after high-speed machining. The cause of this abnormal decrease in Cs after machining the Nb-bearing steel has not been clarified. Therefore, in this research, alloys containing different amounts of Cr and Nb were subjected to gas carburizing after machining to clarify the effects of these elements and machining on the abnormal decrease in Cs after gas carburizing.

2. Experimental Procedure

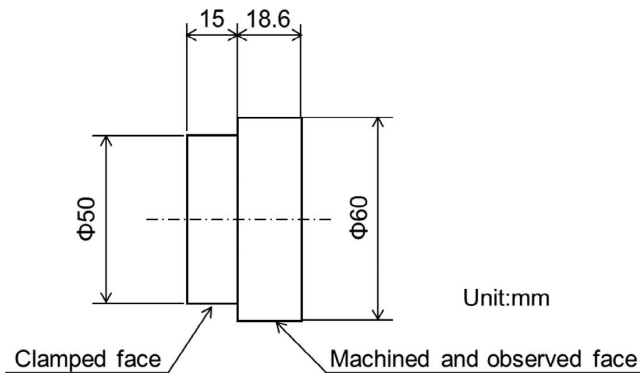
Table 1 shows the chemical compositions of the steel and alloys used in the present study. The case hardened steel of SCM420 (JIS G4053), which is commonly used for vehicle parts, was set as a base material, 12 alloys with different Cr and Nb contents were prepared.

The alloys were cast into 50 kg ingots via vacuum melting, forged to $\phi 65$ mm at 900°C, water cooled after being subjected to a solution treatment at 1300°C for 10.8 ks, which is followed by the normalizing treatment at 900°C for 3.6 ks. Specimens with shape and size shown in **Fig. 1** were machined from these bars. After machined with various cutting depths, cutting speeds, and feed rates, specimens were subjected to the gas carburizing using a continuous gas car-

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Table 1. Chemical composition of materials (mass%).

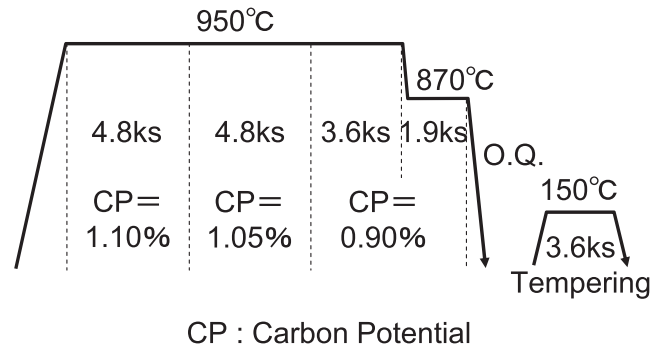
	C	Si	Mn	P	S	Cr	Mo	Nb
Steel A (0Cr0Nb)	0.20	0.25	0.80	0.023	0.020	<0.01	0.15	<0.005
Steel B (0Cr0.05Nb)	0.20	0.25	0.80	0.023	0.022	<0.01	0.15	0.050
Steel C (0Cr0.1Nb)	0.20	0.24	0.80	0.020	0.020	<0.01	0.15	0.100
Steel D (0.5Cr0Nb)	0.20	0.25	0.79	0.020	0.019	0.50	0.14	<0.005
Steel E (0.5Cr0.05Nb)	0.20	0.26	0.79	0.020	0.019	0.50	0.16	0.050
Steel F (0.5Cr0.1Nb)	0.20	0.26	0.79	0.021	0.019	0.50	0.14	0.100
Steel G (1.0Cr0Nb)	0.20	0.25	0.79	0.020	0.019	1.00	0.15	<0.005
Steel H (1.0Cr0.05Nb)	0.20	0.26	0.79	0.019	0.018	1.00	0.14	0.050
Steel I (1.0Cr0.1Nb)	0.20	0.25	0.79	0.020	0.020	1.00	0.14	0.100
Steel J (2.0Cr0Nb)	0.20	0.26	0.80	0.019	0.020	2.00	0.14	<0.005
Steel K (2.0Cr0.05Nb)	0.20	0.26	0.80	0.020	0.020	2.00	0.15	0.050
Steel L (2.0Cr0.1Nb)	0.20	0.26	0.79	0.020	0.020	2.00	0.15	0.100


Fig. 1. Schematic illustration of specimen shape.

burizing furnace. The $\phi 50$ mm portions of the specimens shown in Fig. 1 were clamped and the $\phi 60$ mm outer diameters portions were subjected to turning operations during the machining process. Machining was performed using NL-2500 (manufactured by MORI SEIKI Co., Ltd.) with cemented carbide tips (Sandvik CNMG120408-MM 2025) in wetting condition. Two machining conditions with high and low-speed were selected. The high-speed machining condition was with cutting depth of 2.0 mm, cutting speed of 5.8 m/s, and feeding rate of 0.5 mm/rev. The low-speed machining condition was with cutting depth of 0.1 mm, a cutting speed of 0.8 m/s, and feeding rate of 0.1 mm/rev. In addition, electro-polishing was used to obtain specimen surface with an ideal un-machined state.

Figure 2 shows gas carburizing condition applied. The CP in the figure denotes carbon potential. The gas carburizing was performed using the roller-hearth type continuous gas carburizing furnace (manufactured by DOWA Thermotech Co., Ltd.) for a total of 13.2 ks at 950°C. After carburizing, the specimens were quenched into oil kept at 150°C. Propane gas was used as the carburizing gas.

After the specimens were subjected to the gas carburizing process, the carbon concentration distribution was measured using an electron probe micro-analyzer (EPMA) and the microstructure was observed with a field emission scanning electron microscope (FE-SEM). An elemental analysis and composition analysis were performed on the surfaces of the



CP : Carbon Potential

Fig. 2. Gas-carburizing process.

specimens using X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDS). For the observation of microstructure 5% nital was used as an etching solution.

3. Experimental Results and Discussion

3.1. Effects of Cr and Nb Addition on the Abnormal Decrease in Cs

The 12 alloys containing different amounts of Cr and Nb were subjected to gas carburizing after being machined using one of three machining conditions: electropolishing, low-speed machining, or high-speed machining. After gas carburizing, the Cs was measured using the EPMA. **Figure 3** shows the change in the Cs as a function of Cr content. Figure 3(a) shows the change in the Cs for the specimens gas carburized after electropolishing (shorten ECS: electropolished and carburized specimens). In the specimens without Nb, the Cs stayed at an almost constant value, regardless of the amount of Cr. On the other hand, in the specimens with 0.05% and 0.1% Nb, the Cs decreased with increasing the amount of Cr. The amount of decrease in Cs was very slight and even when the Cr content was 2.0%, the decrease in Cs was only about 0.1%C. Figure 3(b) shows the change in the Cs as a function of Cr content for the specimens gas carburized after low-speed machining (shorten LMCS: low-speed machined and carburized specimens). In the LMCS, the Cs remained almost constant at 0.9%C in the Nb-free steel regardless of the Cr content. However, in the 0.05 Nb specimen and the 0.1 Nb specimen, the Cs decreased with the increase in Cr content. When the Cr content was 2.0%, the Cs of the 0.05 Nb specimen was 0.6%C and the Cs of the 0.1 Nb specimen was 0.55%C. In the LMCS, the Cs of the 0.1 Nb specimens was about 0.05%C lower than the Cs of the 0.05 Nb specimens at all Cr contents. Figure 3(c) shows the change in the Cs as a function of Cr content for the specimens gas carburized after high-speed machining (shorten HMCS: high-speed machined and carburized specimens). In these HMCS, the Cs of the Nb-free specimens remained constant, regardless of the amount of added Cr, the same as the LMCS. However, in the 0.05 Nb and 0.1 Nb specimens, there was a large decrease in Cs with the increase in the amount of Cr. When the amount of Cr was 1.0%, the Cs of the 0.05 Nb specimen was 0.58% and the Cs of the 0.1 Nb specimen was 0.5%. Even when the amount of Cr was increased to 2.0% the Cs remained at approximately the same levels obtained when

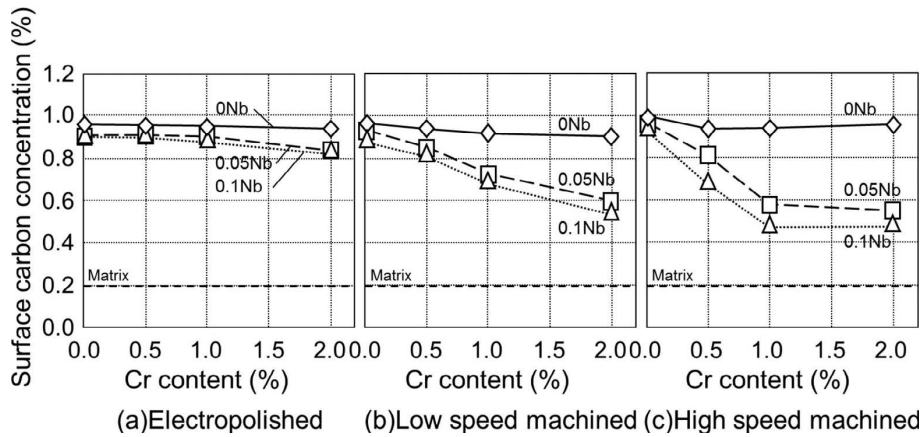


Fig. 3. Surface carbon concentration as a function of Cr and Nb content. (a) electropolished, (b) low speed machined and (c) high speed machined.

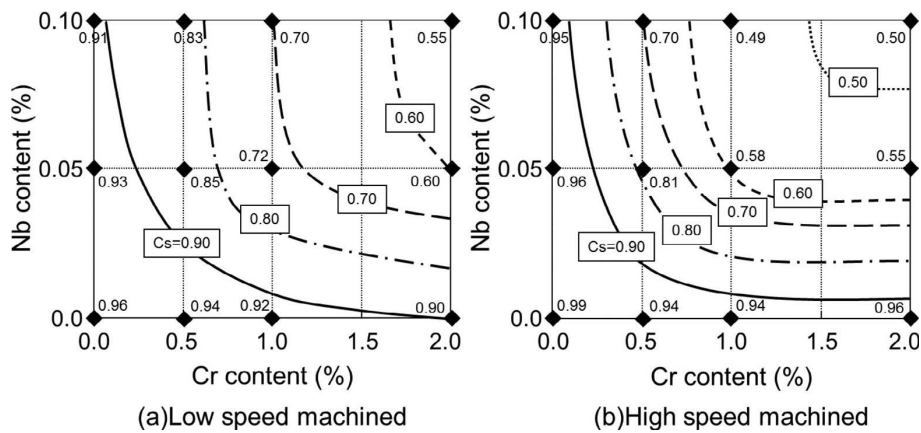


Fig. 4. Contour of surface carbon concentration as a function of Cr and Nb content in carburized specimens after (a) low speed machining and (b) high speed machining.

the amount of Cr was 1.0%. In both the HMCS and LMCS, the specimens with the same Cr content showed a similar trend of a decrease in Cs with the increase in Nb content. The results described above indicated that the abnormal decrease in Cs became pronounced with the addition of the Cr and Nb. In addition, it was also found that the higher the speed in machining, the abnormal decrease in Cs appeared more clearly.

Figure 4 shows the relationship between the contents of Cr and Nb and the Cs when the specimens were subjected to gas carburizing after being machined under low-speed and high-speed machining conditions. Figures 4(a) and 4(b) show the results from the low-speed and high-speed machining, respectively. The numbers near the data points indicate the Cs values. The curves in the figures indicate the boundaries where $C_s = 0.9\%$, 0.8% , 0.7% , 0.6% , and 0.5% . These results in Fig. 4 indicate that the Cs tends to decrease with the increase in the Cr and Nb contents for both low-speed and high-speed machining. It was found that the higher the speed in the machining conditions, the larger the decrease in Cs, even when the amounts of added Cr and Nb were small. However, when Cr or Nb was added separately, a large decrease in Cs did not occur, regardless of the machining conditions. Therefore, it was found that the simultaneous addition of both Cr and Nb is essential for this large decrease in Cs to occur. In summary, the above results

clearly reveal that specimens containing both Cr and Nb, which are then subjected to machining, exhibit a decrease in Cs. Furthermore, this decrease becomes larger with the increase in the amounts of Cr and Nb and the speed of the machining.

3.2. Microstructure Observations of Surfaces of Specimens with Abnormal Decreases in Cs after Gas Carburizing

Figure 5 shows top surface (a) and cross section (b) SEM micrographs of a high-speed machined 2.0 Cr 0.05 Nb specimen which showed a large decrease in Cs. Figure 5(a) indicates that the surface of the specimen is covered with a dense product fine particles formed during carburizing. Figure 5(b) indicates that the surface is covered with a film thickness of approximately 600 nm.

Underneath the film, a pearlite structure that was produced as a result of slack quenching is observed. It is considered that below the film is the metal substrate. **Figure 6** shows the results of EPMA analysis taken from a cross section of the specimen to study the distributions of Cr and oxygen (O). The EPMA analysis reveals that Cr and O are concentrated on the surface of the specimen. There is a strong possibility that the film that formed on the surface of the specimen after gas carburizing is Cr oxide. The chemical state of Cr on the surface of the specimen was then analyzed

using XPS. **Figure 7** shows the analysis results of the binding energy peak of XPS associated with Cr after sputtered the surface to a depth of approximately 20 nm. In the case of the metal Cr, the spectrum peaks for $\text{Cr}2p_{3/2}$ and $\text{Cr}2p_{1/2}$ are at approximately 574.4 eV and 584.2 eV, respectively. In the case of Cr oxide, the peaks for $\text{Cr}2p_{3/2}$ and $\text{Cr}2p_{1/2}$ are at approximately 576.5 to 579.5 eV and 586.3 to 589.3 eV respectively.³⁾ The peaks of the 2.0 Cr 0.05 Nb specimen, which exhibited a large decrease in Cs, were observed near

to 577 eV and 586.5 eV. This clearly confirmed that the film that formed on the surface of the specimen was Cr oxide. In our present and previous study, Cr oxide has not been observed on specimens after machining and before carburizing.⁴⁾ Therefore, it can be concluded that the Cr oxide observed in the present study was produced during the gas carburizing process.

3.3. Effects of Elements Addition and Machining on the Formation of Cr Oxide Film

The effects of Cr and Nb addition, as well as the machining conditions on the surface structure were observed. The effect of Cr content in 0.05% Nb-bearing specimens subjected to gas carburizing after high-speed machining was studied first. **Figure 8** shows SEM micrographs of the top surface of specimens with various Cr content. Cr free specimen (Figs. 8(a) and 8(e)) showed disk-shaped product as large as micrometer size and small holes mostly along grain boundaries. The small holes appeared as black were considered to be the traces of small oxides that peeled off during preparing the specimens. **Figure 9** shows the results of a composition analysis performed on the surface of a 0 Cr 0.05 Nb specimen using EDS. A strong correlation of the locations with high concentrations of silicon (Si), manganese (Mn), and

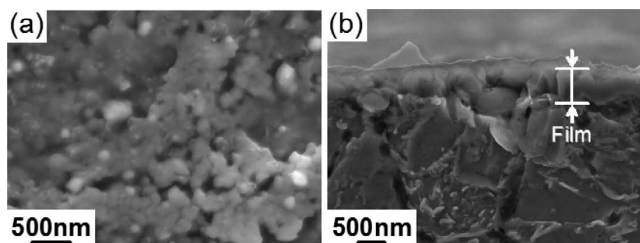


Fig. 5. SEM images of carburized 2.0%Cr0.05%Nb specimen after high speed machining. (a) surface and (b) cross section.

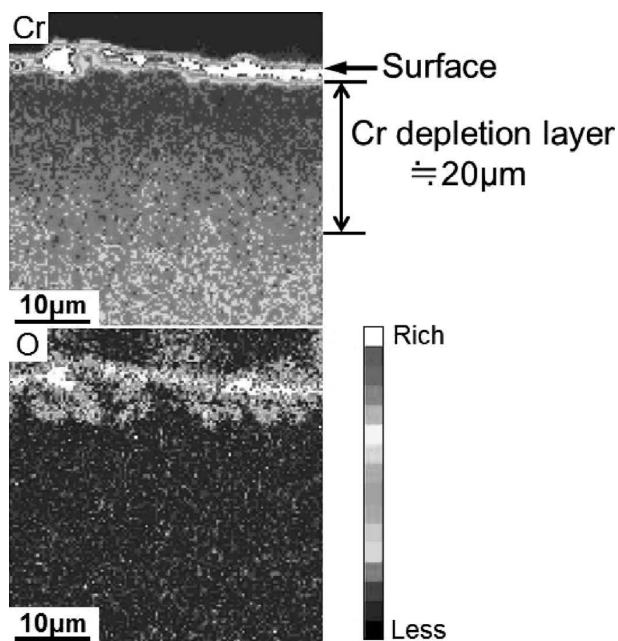


Fig. 6. Cross sectional EPMA analysis of 2.0%Cr0.05%Nb specimen carburized after high speed machining.

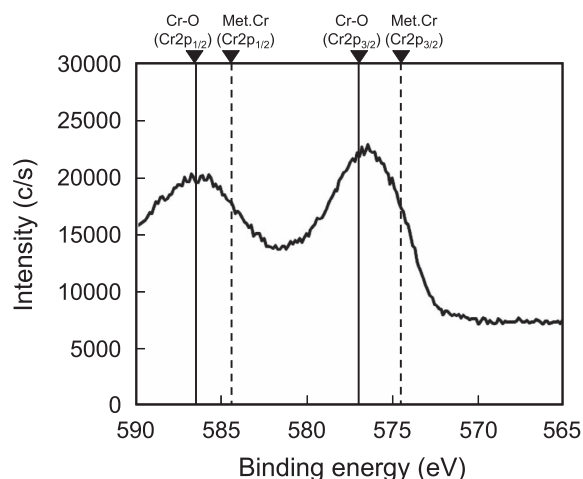


Fig. 7. XPS spectrum around Cr after 1 min sputtering (2.0%Cr0.05%Nb specimen carburized after high speed machining).

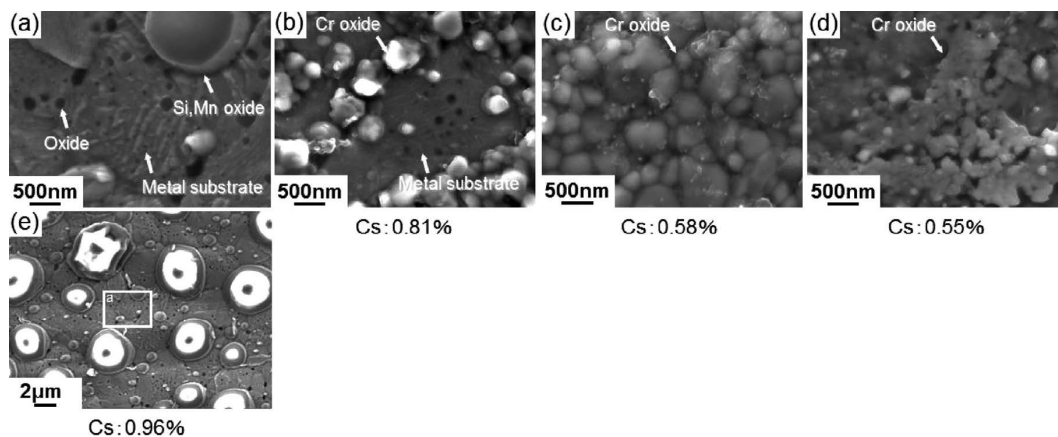


Fig. 8. Surface SEM images of specimens carburized after high speed machining. (a)(e) 0%Cr, (b) 0.5%Cr, (c) 1.0%Cr and (d) 2.0%Cr in 0.05% Nb bearing steel.

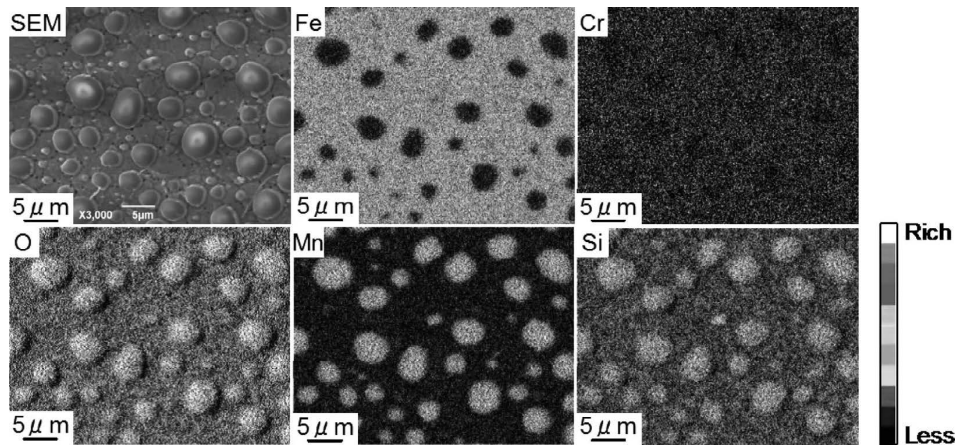


Fig. 9. Surface EDS images of 0%Cr0.05%Nb specimen carburized after high speed machining.

oxygen indicating the formation of Si and Mn oxides on the surface during carburizing.

The SEM photographs of Figs. 8(a), 8(e) and 9 indicate that the outside of oxides are pearlite that was produced as a result of lowered hardenability. Outside of oxides iron (Fe) was also detected in the composition analysis using EDS, so it was concluded that this was the metal substrate. In contrast to the Cr free specimen, 0.5 Cr specimen showed no trace of disk-shaped Si and Mn oxides (Fig. 8(b)). Instead, the formation of new particles with a diameter of approximately $0.3 \mu\text{m}$ was observed. Rest of the surface was considered to be the metal substrate from the pearlite structure. The number and the area fraction of new particles increase with the increase in Cr content. Particles cover the entire surface of both the 1.0 Cr specimen (Fig. 8(c)) and the 2.0 Cr specimen (Fig. 8(d)). XPS was used to analyze the chemical state of the Cr in 0.5 Cr and 1.0 Cr specimens and the results are shown in Fig. 10. From the positions of the XPS spectrum peaks, it was concluded that the product material on the surfaces of both the 0.5 Cr specimen and 1.0 Cr specimen is Cr oxide same with the case of 2.0 Cr as shown in Fig. 7. It was noticed that the grain size of Cr oxide is smaller in 2.0 Cr specimen than that of 1.0 Cr specimen. In summary, the present study revealed that in machined 0.05% Nb-bearing specimens the amount of Cr oxide during gas carburizing increases with increasing Cr content and Cr oxide covers almost entire surface when the content exceeds more than 1.0%.

The effect of Nb addition on the surface structure was investigated. 1.0% Cr-bearing specimens with different amounts of Nb were subjected to gas carburizing after high-speed machining. Figure 11 shows SEM micrographs of top surface of specimens with various amount of Nb. It is seen that the surface is partially covered with Cr oxide in Nb-free specimen and covered completely in 0.05 and 0.10 Nb bearing specimens. Compared 0.05 and 0.10 Nb bearing specimens, the grain size of Cr oxide is almost same.

The effect of machining on the surface microstructure was investigated. Specimens of 1.0% Cr and 0.05% Nb were subjected to gas carburizing either after electropolishing (ECS) or high-speed machining (HMCS). SEM micrographs shown in Fig. 12 compares surfaces of these two types of conditions. It is seen that the formation of Cr oxide is less pronounced in ECS than HMCS. In the ECS, the formation

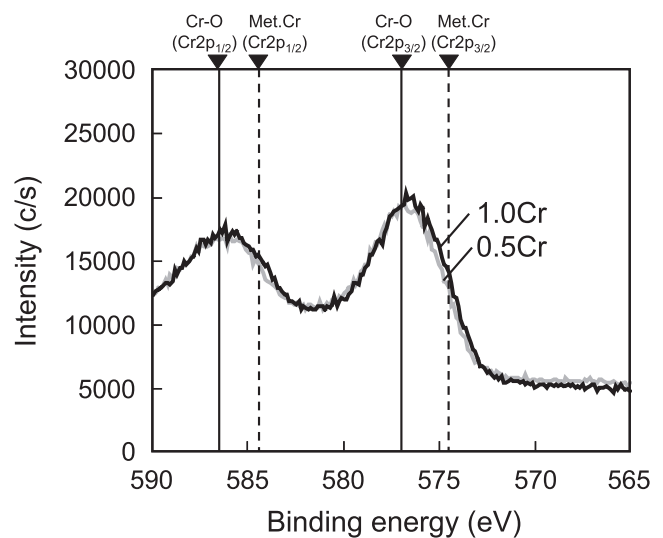


Fig. 10. XPS spectra around Cr after 1 min sputtering (0.5%Cr and 1.0%Cr specimens carburized after high speed machining in 0.05%Nb bearing steel).

of Cr oxide is observed only along the grain boundaries. On the other hand, in the HMCS, a Cr oxide film that covers almost entire surface was observed. These observations indicate that even in specimens with the same chemical composition, the formation of Cr oxide is promoted by machining. It is thought that the pronounced formation of Cr oxide is due to the enhanced diffusion of Cr to specimen surface by the lattice defects that are introduced during machining.

SEM micrographs shown in Fig. 13 compares the cross sectional area of 0.05% Nb-bearing specimens with various Cr content machined in high-speed before subjected carburizing. It is seen that Cr oxide on the surface increases with increase in Cr content. Cr oxide completely covers the surface in specimens containing more than 1.0%Cr and the thickness of Cr oxide layer increases with increasing Cr content. From the picture the thickness of the Cr oxide layer was measure as approximately 350 nm in 1.0%Cr and 600 nm in 2.0%Cr. It was noted that the Cr oxide layer produced in the 2.0 Cr specimen have more uniform thickness compared to the one in the 1.0 Cr specimen.

Using the same specimens subjected to SEM observation, XPS analysis was performed to determine how deep Cr and

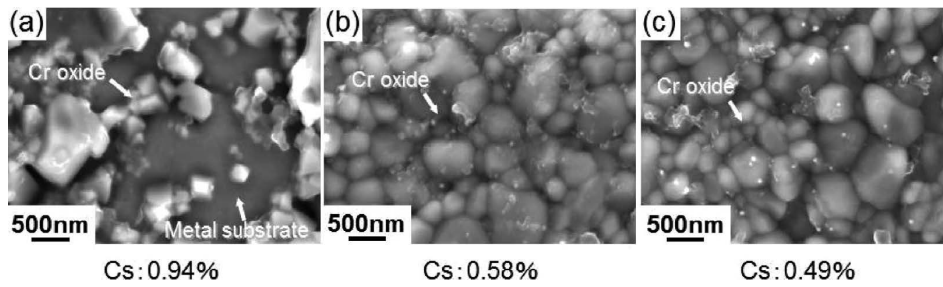


Fig. 11. Surface SEM images of specimens carburized after high speed machining. (a) 0%Nb, (b) 0.05%Nb and (c) 0.1%Nb in 1.0% Cr bearing steel.

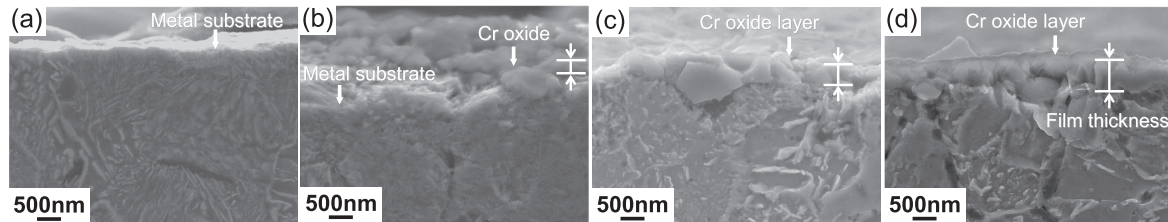


Fig. 13. Cross sectional SEM images of specimens carburized after high speed machining. (a) 0%Cr, (b) 0.5%Cr, (c) 1.0%Cr and (d) 2.0%Cr in 0.05%Nb bearing steel.

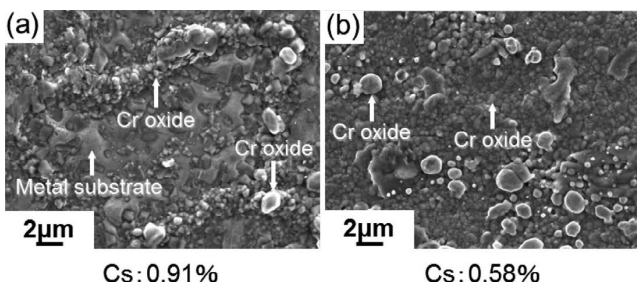


Fig. 12. Surface SEM images of carburized 1.0%Cr0.05%Nb specimens. (a) electropolished and (b) high speed machined.

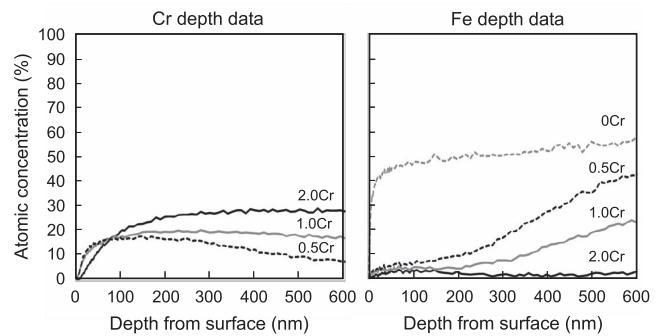


Fig. 14. XPS depth profiles of 0.05%Nb specimens carburized after high speed machining.

Fe could be detected from the surface. In this analysis, the sputter rate in the depth direction from the surface was 20 nm/min.

Figure 14 shows the results of XPS analysis. It is seen that Cr concentration peaks becomes deeper as the Cr content increased. In the 0.5 Cr specimen and 1.0 Cr specimen the Cr concentration peak was found at depths of approximately 150 nm and 300 nm, respectively. In the 2.0 Cr specimen the Cr maintained a high atomic concentration of about 30% even down to 600 nm in depth. Fe distribution is shown in the right hand side of Fig. 14. Although Fe was detected from the surface of the 0 Cr specimen it detected at deeper depth as the Cr content increases. In the 2.0 Cr specimen, almost no Fe is detected, even at a depth of 600 nm. As described above, a homogeneous Cr oxide layer was produced on the surfaces of both the 1.0 Cr and 2.0 Cr specimens. The Cr peak concentration depth and the depth at which Fe concentration starts to increase in these specimens are practically the same as the thickness of the Cr oxide film shown in Fig. 13. Since the Fe was not detected in the surface layer, it is concluded that the Cr oxide film observed on the surface of the specimen is Cr_2O_3 not containing Fe. In the 0.5 Cr specimen, the estimated thickness of the Cr oxide layer is about 100 nm by XPS measurement

and about 250 nm measured by SEM observation. This difference is considered to occur from the incomplete coverage by Cr oxide layer in 0.5 Cr specimen.

Summarizing the above mentioned results obtained using SEM, EDS, and XPS the following points were clarified about the formation of the Cr oxide film during gas carburizing. 1) The Cr oxide layer that is produced on the surfaces of the specimens increased in conjunction with the increase in the Cr and Nb content. In specimens containing Cr, a dense Cr oxide layer forms only when Nb is added at the same time as Cr. 2) The complete coverage of specimen surface by Cr oxide layer was observed in the specimens containing more than 1.0% Cr and more than 0.05% Nb subjected to high-speed machining. 3) In the specimens not subjected to machining, Cr oxide layer forms only partially even the Cr and Nb are added at the same time. Thus addition of both Cr and Nb and machining is necessary to obtain the complete coverage of specimen surface by Cr oxide layer.

The present study confirmed for the first time that the formation of the Cr_2O_3 layer which is responsible for the large decrease in Cs is produced by the addition of Nb and performing machining even when the amount of Cr addition is as low as 1%.

3.4. Calculation of Carbon Concentration Distribution when Oxide Layer Forms during Gas Carburizing

The present study confirmed a strong correlation between the Cs and the Cr oxide layer. Since the Cr oxide layer was not detected before carburizing, it is considered that the oxide layer grew during the carburizing process. It is expected that the Cs is related to the formation time of the Cr oxide layer during carburizing process. Since the solubility of carbon in Cr oxide is undetectable small amount and the carbon cannot diffuse within the Cr oxide,⁵⁾ the carbon absorption during carburizing occurs until the surface of the steel specimen covered by the Cr oxide film. After the oxide layer has coated the steel surface, the carbon that had already penetrated into the steel prior to the formation of the oxide layer can diffuse within the specimen. The diffusion of carbon after the oxide layer coating might be the cause of the decrease in Cs.

To verify this idea, the relationship between the time that carbon ceases penetration from surface and Cs was calculated. The distribution of the carbon concentration was calculated by solving Fick's second law, which is shown in Eq. (1) below, via the finite difference method.

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} \right) \dots \dots \dots (1)$$

where, C is the carbon concentration (mass%), D is the diffusion coefficient, and x is the distance from the surface. For diffusion coefficient, the experimental value obtained by Zhang *et al.*⁶⁾ that are shown in Eq. (2) below were used.

$$D = 7.7 \times 10^{-7} \exp(-107400/RT) \dots \dots \dots (2)$$

where, D is the carbon diffusion coefficient ($\text{m}^2 \cdot \text{sec}^{-1}$), R is the gas constant ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$), and T is the absolute temperature (K). In the simulation Eqs. (1) and (2) were used under the following two assumptions. 1) The three levels of CP during gas carburizing shown in Fig. 2 were applied: CP = 1.10%, 1.05%, and 0.90%. Since Cs depends on the alloying elements in specimens, Cs was calculated over the range of Cr 0 to 2.0% and Nb 0 to 0.1% using the reported equations.²⁾ To compare the calculated Cs among various composition of alloys, the average values of Cs in each of the 3 carburizing stages was set as Cs = 1.19%, 1.13%, and 0.97%. 2) It is assumed that during gas carburization the coverage of surface by Cr oxide layer occurs in a short time. Once surface is completely covered by Cr oxide layer, the carbon penetration (or decarburization) no longer occurs and only the carbon diffusion within the steel takes place. The relationship between the time it takes for the carbon to stop penetrating into the specimens from the surface (*i.e.*, the time Cr oxide film forms) and the Cs was calculated based on the two assumptions described above. **Figure 15** shows the calculated Cs as a function of the formation time of Cr oxide layer. It is seen that the shorter the time it takes for the carbon to stop penetrating into the specimen from the surface, the lower the Cs. Cs value of 0.5%C can occur when Cr oxide layer forms after 2.5 ks from the start of the gas carburizing. This value is almost the same as the lowest Cs value that was actually measured (0.49%) in the 2.0 Cr 0.1 Nb specimen. In Fig. 15, the data of the specimens containing Cr 1.0% and 2.0% and Nb 0.05% and 0.10% subjected to high-speed machining were plotted. The time it

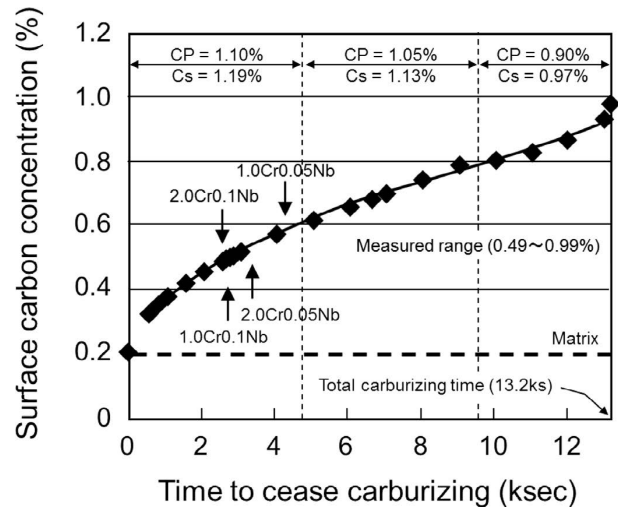


Fig. 15. Surface carbon concentration as a function of time carburizing is ceased.

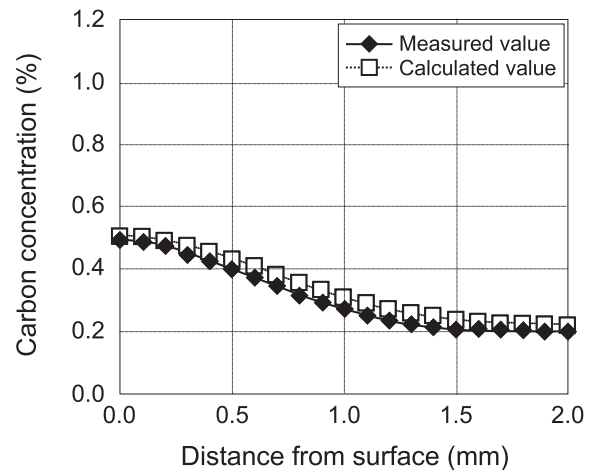


Fig. 16. Comparison of measured and calculated carbon concentration profiles of 2.0%Cr0.1Nb specimens carburized after high speed machining. Carburizing was ceased after 2.5 ks.

took for the Cr oxide film to form on these specimens was estimated from the Cs and shown in Fig. 15 by the arrows. It is seen that as the Cr and Nb content increases, the time it takes for the Cr oxide film to form becomes shorter. **Figure 16** shows the calculated carbon concentration distribution assumed that the carbon penetration into the specimen stopped 2.5 ks after the start of carburization. In the figure measured carbon concentration distribution in the 2.0 Cr 0.1 Nb specimen was shown for comparison. A good correlation between the calculated and measured values is seen. The simulation described above showed that the origin of the substantial decrease in Cs is the formation of a Cr oxide layer on the surface of the specimen during the carburizing process, which inhibited the penetration of the carbon into the specimen. Furthermore, after this layer forms, the carbon that already penetrated into the specimen prior to the formation of oxide layer diffuse in the specimen. The Cr oxide layer is probably thin when it becomes effective to stop the penetration of the carbon, but it continues to grow during 'carburizing process' and becomes several hundred nm in thickness, such as those shown in Fig. 13, by the time that the gas carburizing is finished.

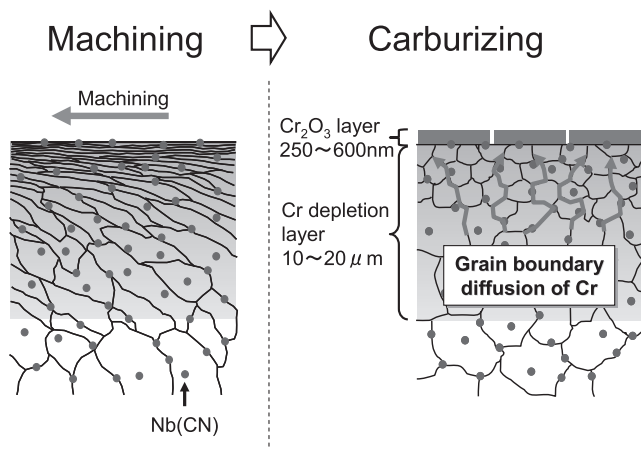


Fig. 17. Schematic illustration of Cr oxide layer formation during carburizing in machined specimen.

3.5. Mechanism Causing Decrease in Cs

Based on the above mentioned results, the mechanism of the Cr oxide layer formation in the specimens of Nb-bearing steel subjected to gas carburizing after machining which results in the large decrease in Cs was considered. **Figure 17** shows a schematic illustration of the Cr oxide film formation. After machining, surface layer contains many lattice defects. Due to the heating during gas carburizing, the density of lattice defects in the deformed layer decrease due to the recovery and recrystallization. In Nb free specimen, the density of lattice defects would rapidly decrease in conjunction with the rise in temperature and the defects would have no effect on the Cs. In contrast, in the specimens containing Nb, the Nb (CN) acts as pinning particles that retard or inhibit the recovery, recrystallization, and grain growth of the machined structure during gas carburizing.⁷⁻⁹⁾ Fast diffusion of Cr occurs along lattice defects and form Cr oxide on the surface instead of inside specimens. It is thought that increasing the speed of machining also increases the density of lattice defects acting as diffusion paths. This then leads to more rapid Cr diffusion to the surface of the specimen, which causes the formation of Cr oxide in shorter time. Consequently, the abnormal decrease in Cs that was observed in this research is considered to be due to the high-density lattice defects that were introduced by the machining and those are maintained by the Nb (CN) during the gas carburizing. The Cr passes through these lattice defects, diffuses to the surface of the specimen, and then a dense Cr oxide film forms on the surface of the steel. Furthermore, the addition of cerium (Ce) to Fe- (10-20) Cr alloy promotes the production of Cr oxide.¹⁰⁾ Therefore, it was considered that the Nb (CN) in this research may also become a nucleation site when the Cr oxide is produced. The possibility of this is supported by the fact that the addition of Nb to the ECS caused only a minor decrease in Cs, as shown in Fig. 3(a). Detailed study on the effect of Nb on the abnormal decrease in Cs is expected.

4. Conclusions

In the present study, the effects of Cr and Nb contents and machining condition on the decrease in surface carbon content (Cs) after gas carburizing were investigated using 12 alloys with composition close to a conventional case hardening steel. The origin of the decrease in Cs was discussed. The main results obtained from this research are as follows.

(1) A large decrease in Cs up to 0.5%C was observed in specimens containing both Cr and Nb and subjected to machining prior to the gas carburizing.

(2) The decrease in Cs becomes larger as the Cr and Nb content are increased and the speed of the machining is increased.

(3) In the electro-polished sample, the decrease in Cs is less than 0.1%C. This decrease is much smaller than that of machined sample.

(4) In the Cr bearing sample, Cr oxide was produced on the surface of the steel after gas carburizing. A uniform and dense Cr oxide layer formed as the Cr and Nb content increased and the speed of the machining increased. It was concluded that the Cr oxide, which does not dissolve carbon into a solid solution, was responsible to prevent the penetration of the carbon into the sample.

(5) The effect of machining on the formation of Cr oxide layer is considered to be the fast diffusion of Cr along grain boundaries and dislocations. Nb (CN) is expected to act as pinning particles that retard the annihilation of the lattice defects at the carburizing temperature.

(6) To estimate the decrease of Cs by Cr oxide layer, a carbon diffusion simulation during carburizing process was carried out. The results indicated that Cs decreases with time after the formation of Cr oxide and the earlier the formation of Cr oxide layer, the larger the decrease in Cs. The calculated value of Cs was in the range measured in the present experiment and supporting that the origin of the decrease in Cs is the formation of Cr oxide which prevents the penetration of carbon into specimen.

REFERENCES

- 1) T. Naito: Practical Carburizing Technology, Nikkan Kogyo Shimbun, LTD., Tokyo, (1979), 3.
- 2) Y. Eto, M. Umamoto, K. Sasaki and M. Yoshida: *Tetsu-to-Hagané*, **99** (2013), 706.
- 3) J. Chastain and R. C. King, Jr.: Handbook of X-ray Photoelectron Spectroscopy, ULVAC-PHI, Chigasaki, (1995).
- 4) Y. Eto, M. Umamoto and M. Yoshida: *Tetsu-to-Hagané*, **99** (2013), 564.
- 5) I. Wolf and H. J. Grabke: *Solid State Comm.*, **54** (1985), 5.
- 6) X. Zhang, R. Takahashi, T. Akiyama and J. Yagi: *Tetsu-to-Hagané*, **83** (1997), 299.
- 7) T. Murakami, H. Hatano and H. Yaguchi: *Tetsu-to-Hagané*, **92** (2006), 448.
- 8) Y. Maehara, T. Kunitake and N. Fujino: *Tetsu-to-Hagané*, **67** (1981), 362.
- 9) M. Kubota and T. Ochi: *Nippon Steel Tech. Rep.*, **378** (2003), 72.
- 10) T. N. Rhys-Jones, H. J. Grabke and H. Kudielka: *Werkstoffe Korrosion*, **38** (1987), 65.