Effect of Carbon and Nitrogen on $Md_{30}$ in Metastable Austenitic Stainless Steel

Takuro MASUMURA,1,2*, Kohei FUJINO,3) Toshihiro TSUCHIYAMA,1,2,4) Setsuo TAKAKI1) and Ken KIMURA5)

1) Research Center for Steel, Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka, 819-0395 Japan.
2) International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, 744, Moto-oka, Nishi-ku, Fukuoka, 819-0395 Japan.
3) Graduate School of Engineering, Kyushu University, 744, Moto-oka, Nishi-ku, Fukuoka, 819-0395 Japan.
4) Department of Materials Science and Engineering, Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka, 819-0395 Japan.
5) Titanium & Stainless Steel Research Lab., Steel Research Laboratories, NIPPON STEEL CORPORATION, 20-1, Shintomi, Futtsu, Chiba, 293-8511 Japan.

* Corresponding author: E-mail: masumura@zaiko.kyushu-u.ac.jp

© 2021 The Iron and Steel Institute of Japan. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs license (https://creativecommons.org/licenses/by-nc-nd/4.0/).

Effect of Carbon and Nitrogen on $Md_{30}$ in Metastable Austenitic Stainless Steel

Md$_{30}$ is defined as the temperature at which 50 vol.% of $\alpha'$-martensite is formed at a true tensile strain of 0.3 in metastable austenitic steels. The effect of C concentration on Md$_{30}$ is known to be identical to that of N, as shown by Nohara's equation. However, we found that Md$_{30}$ of C-added steel is lower than that of N-added steel, which indicates that the effect of C concentration on the mechanical stability of austenite is more significant than that of N. In addition, the relationship between Md$_{30}$ and C and N concentration is not linear. The effect of C and N concentration on Md$_{30}$ is higher at lower C and N concentration (<0.1%). As this effect was not considered in the previous study, the austenite-stabilizing effects of these elements were underestimated. Therefore, in this study, new equations were proposed to accurately estimate Md$_{30}$ of an Fe–Cr–Ni alloy system. The modified Md$_{30}$ equation is shown below:

$$Md_{30}(K) = 800 - 333 \sqrt{C_{eq}} - 10.3Si - 12.5Mn - 10.5Cr - 24.0Ni - 5.6Mo$$

$C_{eq}$ (C equivalent) is a function of C and N concentrations and temperature.

$$C_{eq} = C +aN$$

$$a = 0.931 - 0.000281 \exp(0.0219T)$$

These equations show that the difference in austenite-stabilizing effects of C and N increases with increasing temperature due to the difference in stacking fault energy between C- and N-added steels.

KEY WORDS: mechanical stability; metastable austenitic steel; Md$_{30}$; deformation-induced $\alpha'$-martensite; stainless steel; carbon; nitrogen.

1. Introduction

Metastable austenitic stainless steels, represented by Fe-18%Cr-8%Ni alloys, undergo phase transformation from austenite to $\alpha'$-martensite during cold processing (deformation-induced $\alpha'$-martensitic transformation). Deformation-induced $\alpha'$-martensite helps strengthen austenitic steels, and also helps enhance elongation and formability owing to the transformation-induced plasticity (TRIP) effect.1,2) However, it can cause negative effects such as hydrogen embrittlement and disturbance of magnetic fields. Therefore, controlling the deformation-induced $\alpha'$-martensitic transformation behavior is essential for the production and application of metastable austenitic steels. Chemical composition is the most important factor affecting the stability of the austenite phase. C and N, which are interstitial elements, are known to exhibit remarkable stabilizing and strengthening effects in austenite.3–9)

The quantitative relationship between the stability of austenite against deformation (mechanical stability) and chemical composition is often evaluated using Md$_{30}$. The relationship between Md$_{30}$ and the alloying elements was first proposed by Angel,13) as shown below:

$$Md_{30}(K) = 686 - 462(C+N) - 9.25Si - 8.1Mn - 13.7Cr - 9.5Ni - 18.5Mo$$

... (1)
In this study, each atomic symbol represents the mass% of the corresponding element unless otherwise indicated. \( Md_{90} \) is defined as the temperature at which 50 vol.% of \( \alpha' \)-martensite is formed at a true tensile strain of 0.3 in metastable austenitic steels. Nohara et al.\(^{10} \) further modified the Eq. (1). They revised the coefficient of Ni and added the terms of Cu and Nb as shown below:

\[
Md_{90} (K) = 824 - 462(C + N) - 9.2Si - 8.1Mn - 13.7Cr - 29.0(Ni + Cu) - 18.5Mo - 68.0Nb
\] ... (2)

These equations show that C and N have much larger effects on the mechanical stabilization than those of other substitutional elements. The austenite stabilization effect of C is estimated to be identical to that of N. On the other hand, that of Angel could not distinguish the effects of C and N separately.\(^{10} \) It was found that the effect of C on the mechanical stability at ambient temperature is higher than that of N in Fe-18%Cr-8%Ni supplemented with 0.1% of C and N separately.\(^{10} \) These equations show that C and N have much larger effects on the mechanical stabilization than those of other substitutional elements. The austenite stabilization effect of C is estimated to be identical to that of N. On the other hand, that of Angel could not distinguish the effects of C and N separately.\(^{10} \)

In this study, we measured \( Md_{90} \) in the metastable austenitic 18%Cr-8%Ni steels supplemented with up to 0.2% C and N separately in order to assess the individual effects of C and N on \( Md_{90} \). Thereafter, we proposed a modified \( Md_{90} \) equation to accurately predict \( Md_{90} \) in metastable austenitic stainless steels.

2. Experimental Procedure

A metastable austenitic stainless steel (Fe-18%Cr-8%Ni) was used as the base steel in this study. To the base steel, 0.021%, 0.051%, 0.100%, and 0.199% C and 0.015%, 0.030%, 0.063%, 0.100%, and 0.196% N were added separately. The chemical compositions (mass%) of the steels are listed in Table 1. This table also presents the atomic fractions of C and N. The atomic fraction of C is approximately 1.16 times higher than that of N while the mass fraction of C and N is the same. With the abovementioned chemical compositions, ingots of 17 kg were produced by vacuum melting. The ingots were hot-rolled to a 4.5 mm thicknesses at 1,423 K. The resultant steel plates were cold-rolled to achieve a 60% reduction in thickness and were solution-treated at 1,273–1,473 K for 1.8 × 10\(^3\) s. Then, the samples were water-cooled to obtain the initial austenitic structure with an average grain size of approximately 40 \( \mu \)m.

Subsequently, tensile testing was conducted at 213–373 K at a strain rate of 5.6 × 10\(^{-3}\) s\(^{-1}\) for the plate specimens with a gauge dimension of 18 × 3 × 1.5 mm\(^3\) (length × width × thickness). In some samples, tensile testing was interrupted at several strains. The saturation magnetization of specimens (\( Is \)) and that of a reference with the full \( \alpha' \)-martensitic structure (\( Is^* \)) were measured and the volume fractions of \( \alpha' \)-martensite (\( V_{\alpha'} \)) in deformed specimens were evaluated as \( Is/Is^* \). A base steel, 85% cold-rolled at 77 K, where the microstructure was confirmed by neutron diffraction analysis to be a 99.5% \( \alpha' \)-martensitic structure, was used as the reference for obtaining \( Is^* \). The microstructures of the specimens were examined by the electron backscatter diffraction (EBSD) analysis using a field emission scanning electron microscope (FE-SEM; SIGMA 500, Zeiss). The data obtained by EBSD were analyzed using software for automatic crystal orientation mapping (OIM analysis, TSL). Crystallographic orientation mapping was taken at step sizes of 200 nm, and the data obtained with a confidence index (CI) value over 0.1 were used for a detailed crystallographic analysis.

The stacking fault energy (SFE) was estimated by thermodynamic calculation, using Eq. (3), as proposed by Olson and Cohen.\(^{11} \)

\[
SFE (\text{mJ/m}^2) = 2 \rho_s (\Delta G_{\text{FCC}\rightarrow\text{HCP}} + E_{\text{strain}}) + 2\sigma \] ... (3)

where \( \rho_s \), \( \Delta G_{\text{FCC}\rightarrow\text{HCP}} \), \( E_{\text{strain}} \), and \( \sigma \) denote the density of atoms on the \{111\} plane (mol/m\(^3\)), chemical free energy change from FCC to HCP (J/mol), strain energy generated by the formation of an HCP phase in the FCC matrix (J/mol), and interfacial energy of the HCP/FCC interface (J/m\(^2\)); respectively. Herein, \( \rho_s \) and \( \sigma \) were estimated to be 2.5 × 10\(^{-5}\) mol/m\(^3\) and 27 × 10\(^{-3}\) J/m\(^2\), respectively, and \( E_{\text{strain}} \) was assumed to be negligible. The same values were applied to all steels used in this study. Thus, the SFE can be said to strongly depend on \( \Delta G_{\text{FCC}\rightarrow\text{HCP}} \).

The Thermo-Calc. software (database: SSOL2) was used for estimating \( \Delta G_{\text{FCC}\rightarrow\text{HCP}} = (G_{\text{HCP}} - G_{\text{FCC}}) \) together with

| Table 1. Chemical compositions and \( Md_{90}^{exp} \) of specimens used in this study (mass%). |
|--------------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Base steel                          | 0.002 | 0.48 | 0.98 | 0.035 | 0.002 | 18.07 | 8.21 | 0.001 | bal. | 383 |
| 0.02C steel                         | 0.021 (0.096 at%) | 0.47 | 1.02 | 0.034 | 0.002 | 18.21 | 8.20 | 0.002 | bal. | 333 |
| 0.05C steel                         | 0.051 (0.233 at%) | 0.48 | 1.02 | 0.033 | 0.002 | 18.24 | 8.13 | 0.002 | bal. | 310 |
| 0.1C steel                          | 0.100 (0.457 at%) | 0.49 | 0.98 | 0.034 | 0.002 | 18.26 | 8.19 | 0.006 | bal. | 278 |
| 0.2C steel                          | 0.199 (0.905 at%) | 0.47 | 0.98 | 0.034 | 0.002 | 18.27 | 8.18 | 0.006 | bal. | 230 |
| 0.015N steel                        | 0.001 | 0.49 | 1.00 | 0.030 | 0.002 | 18.21 | 8.23 | 0.015 (0.059 at%) | bal. | 358 |
| 0.03N steel                         | 0.001 | 0.49 | 1.01 | 0.031 | 0.002 | 18.28 | 8.22 | 0.030 (0.118 at%) | bal. | 343 |
| 0.06N steel                         | 0.001 | 0.47 | 1.00 | 0.029 | 0.002 | 18.30 | 8.15 | 0.063 (0.247 at%) | bal. | 313 |
| 0.1N steel                          | 0.003 | 0.48 | 0.99 | 0.035 | 0.002 | 18.05 | 8.23 | 0.100 (0.392 at%) | bal. | 292 |
| 0.2N steel                          | 0.003 | 0.48 | 0.99 | 0.035 | 0.002 | 18.18 | 8.22 | 0.196 (0.766 at%) | bal. | 247 |
the chemical driving force for FCC→BCC transformation, $\Delta G^{FCC\rightarrow BCC} = G^{BCC} - G^{FCC}$. SSOL2 was used as the database as Saenjarjhan et al.\textsuperscript{14} reported that the SFE value evaluated by XRD was similar to the value calculated using SSOL than TCFE.

3. Results and Discussion

3.1. Effects of Carbon and Nitrogen on Mechanical Property at Various Temperature

Figure 1 shows nominal stress-strain curves of Base, 0.1C, and 0.1N steels that were tensile-tested at 253 K (a), 293 K (b), and 333 K (c). Adding C and N increases the yield stress at any temperature, and the effect of N is larger than that of C, as shown in previous studies.\textsuperscript{15–17} As for work hardening behavior in Base steel, the work hardening rate varies considerably during deformation at any temperature, which is a characteristic of TRIP steels.\textsuperscript{1} Since deformation-induced $\alpha'$-martensitic transformation was enhanced with decreasing temperature, the strain at which the considerable work hardening begins reduced and the tensile strength increased. Additions of C and N suppressed the increase of work hardening, which indicates that deformation-induced $\alpha'$-martensitic transformation was suppressed. In 0.1C and 0.1N steels, the strength-ductility balance improved significantly. Their uniform elongation increased nearly twice as that of the Base steel as the TRIP effect continued until the last stage of deformation due to the improvement in austenitic stability. In addition, the tensile strength of the 0.1C steel is higher than that of the 0.1N steel at any temperature. Tensile strength of metastable austenitic steels depends on the phase fraction, strength of $\alpha'$-martensite, and work hardening of the retained austenite. Since the volume fraction of $\alpha'$-martensite in 0.1N steel was higher than that in 0.1C steel, the high tensile strength in 0.1C steel could be due to either or both of the two remaining factors. Yoshitake et al.\textsuperscript{15} conducted tensile testing on Fe-18%Cr-12%Ni stable austenitic steels with 0.1%C or N and reported that the work hardening rate of C-added steel is slightly higher than that of N-added steel because the formation of the deformation twin is enhanced in C-added steel. However, the difference in the work hardening rate was not significant. Hence, the tensile strength of both austenitic steels is similar, indicating that the main cause of a higher tensile strength in 0.1C steel could be the higher strength of $\alpha'$-martensite formed in 0.1C steel. Studies that compared the effects of C and N on the hardness of $\alpha'$-martensite reported that C has an appropriately 2.5 times hardening effect as compared to that of N.\textsuperscript{18,19} Therefore, the difference in work hardening rate and tensile strength between 0.1C and 0.1N steels increased at a lower temperature where deformation-induced $\alpha'$-martensitic transformation is stimulated.

3.2. Effects of Carbon and Nitrogen on $Md_{30}$ in Metastable 18%Cr-8%Ni Austenitic Steels

Figure 2 shows the changes in the volume fraction of $\alpha'$-martensite induced by a tensile true strain at 0.3 as a function of testing temperature in C-added (a) and N-added (b) steels. Volume fraction of $\alpha'$-martensite increased with decreasing testing temperature in all the specimens. Addition of C and N shifted the curves to a lower temperature region, indicating that the mechanical stability of austenite...
is improved by adding C and N. Temperatures where volume fraction of α'-martensite corresponds to 50 vol.% in each approximate curve are the experimental value of \( M_{d30} ^{30} \) (\( M_{d30} ^{30} \)). The changes in \( M_{d30} ^{30} \) as a function of C and N concentration are represented in Fig. 3. The relationships between \( M_{d30} ^{30} \) and C and N concentration are non-linear, where the decreasing tendency varied between low (below 0.1%) and high (above 0.1%) concentration regions, which is inconsistent with the results of Eq. (2). Since almost all specimens studied by Angel\(^{3}\) and Nohara \textit{et al.}\(^{4}\) contained above 0.1%(C+N), the decreasing tendency at high C and N region in this study and the coefficient of (C+N) in Eq. (2) (\(-462 \text{ K/(C+N)}\): dotted line in Fig. 3) were similar. However, Angel\(^{3}\) and Nohara \textit{et al.}\(^{4}\) could not account for the large concentration dependence in the low C and N region, leading to an underestimation of the effects of C and N. The cause of the large concentration dependence at low C and N region is not clear, but we suspect that the segregation of small amount of C and N to the grain boundary, dislocation, and stacking fault, which are the nucleation sites of α'-martensite, would influence the elementary process of deformation-induced α'-martensitic transformation. Comparison between C and N revealed that the effect of C on decreasing \( M_{d30} \) was higher than that of N. The difference in \( M_{d30} \) between both elements was constant at approximately 20 K in the concentration region above 0.03%. When the results were arranged by atomic fraction of C and N, the difference in \( M_{d30} \) between C and N decreased. This difference was rarely observed at the high concentration region.

3.3. Temperature Dependence of Mechanical Stabilization Effects by Carbon and Nitrogen in Metastable 18%Cr-8%Ni Austenitic Steels

Figure 4 shows the changes in the volume fraction of α'-martensite as a function of true strain in each specimen that was tensile-tested at 253 K (a) and (d), 293 K (b) and (e), and 333 K (c) and (f). The tendency of the volume fraction of α'-martensite to increase with deformation is strongly correlated to C and N concentrations. Thus, deformation-induced α'-martensite is markedly suppressed by the additions of C and N. In order to clarify the difference between the effects of C and N, the volume fraction of α'-martensite at various true strains was replotted against C or N concentration, as represented in Figs. 5(a)–5(c). The difference in α'-martensite fraction between C-added and N-added steels for the same strain at temperatures of 253 K (a), 293 K (b), and 333 K (c) is highlighted with the gray bands. Addition of C and N improved the mechanical
stability of austenite at all temperatures, and C was found to be more effective in stabilizing austenite as compared to N, as reported in a previous study. In addition, the difference between carbon and nitrogen was found to vary with temperature. For example, in the low-C or low-N region with less than 0.05% C or N (the regions with dotted texture in Figs. 5(a)–5(c)), the difference between the \(\alpha'\)-martensite fractions between C- and N-added steels was negligible when tested at 253 K. At 293 K, however, the difference slightly increased; the \(\alpha'\)-martensite fraction of C-added steels was lower than that of N-added steels by approximately 10 vol.% at a true strain of 0.2. Furthermore, the difference increased at 333 K; the \(\alpha'\)-martensite fraction in C-added steels was lower than that in N-added steels by as much as 30 vol.% or more at a true strain of 0.4.

To unify the austenite-stabilizing effects of C and N, \(C_{eq}\) (C equivalent) was defined for each temperature as follows:

\[
C_{eq} = C + aN
\]

where parameter \(a\) corresponds to the relative mechanical austenite-stabilizing effects of N based on that of C. In this study, using the Eq. (4), the parameter \(a\) was decided for different temperatures to minimize the difference in the \(\alpha'\)-martensite fraction between C-added and N-added steels when the horizontal axis was set as \(C_{eq}\) as shown in Figs. 5(d)–5(f). The parameter \(a\) was calculated such that the average correlation coefficients could be maximized when the data of both C-added and N-added steels were fitted to the sigmoidal curve \(V_{\alpha'} = b/[1 + \exp(-k(C_{eq} - x_c))]\), \(b\), \(k\) and \(x_c\): fitting parameters). As a result, the value of \(a\) at 253, 293, and 333 K were 0.86, 0.76, and 0.52, respectively. The relationship between the parameter \(a\) and temperature is represented in Fig. 6. The value of \(a\) decreased with increasing temperature, which means that the difference between the austenite-stabilizing effects of C and N gradually increases with increasing temperature. At 333 K, the mechanical austenite-stabilizing effect of C was approximately twice as high as that of N, while this difference was only 1.15 times at 253 K. When arranged in atomic fractions of C and N, the effects of both elements was similar at 253 K, while there was a significant difference at 333 K. These results indicate that the effect of temperature on the result of Fig. 3 is significant. One of the reasons for the fact that the difference in \(M_{d30}\) between C-added and N-added steels does not increase in the high concentration region could be the reduction in difference in the mechanical stabilization effects of both elements at lower temperature.

### 3.4. Relationship between Mechanical Stabilization Effects by Carbon and Nitrogen and Deformation Microstructure

In this section, difference in the temperature dependence of the austenite-stabilizing effects of C and N has been discussed from the viewpoints of thermodynamics. Figure
7(a) shows the relation between the temperature and chemical free energy change from FCC to BCC ($\Delta G^{\text{FCC->BCC}}$) in Base, 0.1C, and 0.1N steels. Chemical driving force for FCC→BCC transformation increased with the increase in the absolute value of $\Delta G^{\text{FCC->BCC}}$. This indicates that both C and N additions lowered the chemical driving force for $\alpha'$-martensitic transformation, while the effect of N was larger than that of C at all temperatures. Moreover, there was negligible difference between the slope of the lines corresponding to the temperature dependence of $\Delta G^{\text{FCC->BCC}}$ in each specimen. Therefore, the thermodynamic driving force explained neither the higher mechanical stability of austenite in C-added steels nor the increased difference between the C- and N-added steels in the austenite-stabilizing effects at higher temperatures. On the other hand, we investigated the thermal stability of the same specimens in a previous study, and found that the thermal stabilization effect of N was larger than that of C, corresponding to the thermodynamic calculations.

In another previous study, we reported that the mechanical stability of metastable austenite at ambient temperature depends on the SFE in 18%Cr-8%Ni-C and N steels. We found that the mechanical stability of austenite in 0.1C steel was higher than that in 0.1N steel, despite its higher chemical driving force for the FCC→BCC transformation. This is because the frequently formed high-angle grain boundaries (derived from $\varepsilon$-martensitic transformation and deformation twinning due to the lower SFE in 0.1C steel) hinder the growth of deformation-induced $\alpha'$-martensite. Although several researchers have looked at the relationship between SFE and chemical composition, the effects of C and N on SFE have not yet been unified. Also, there are very few studies on the temperature dependence of SFE. Hence, we calculated the dependence of C and N concentration on SFE using Eq. (3), and confirmed that the calculated values were consistent with the deformation microstructure. Therefore, the same calculation was done for several temperature values in this study. Figure 7(b) shows the temperature dependence of the SFE of Base, 0.1C, and 0.1N steels. This figure also shows Remy’s classification, showing the relationship between SFE and the types of deformation structures formed in high-manganese austenitic steels. It is generally known that an increase in SFE results in the transition of the deformation structure from $\varepsilon$-martensite and deformation twin to the dislocation cell. Addition of C and N increased the SFE, and the effect of N was larger than that of C. The SFE increased with increasing temperature for all the specimens, and the temperature dependence of SFE is almost the same among all the specimens. Figure 8 shows Phase+IQ (Image Quality) maps of 0.1C steel (a)–(c) and 0.1N steel (d)–(f) tensile-tested at 253 K (a) and (d), 293 K (b) and (e), and 333 K (c) and (f). In the Phase maps, austenite, $\varepsilon$-martensite, and $\alpha'$-martensite are gray, blue, and (red + pink), respectively. The band-like microstructure colored dark gray in the IQ maps might correspond to fine $\varepsilon$-martensite and deformation twin that cannot be detected in the Phase maps. The $\alpha'$-martensites have been colored based on their morphologies: red indicates a fine band-like or granular $\alpha'$-martensite which is contiguous to deformation twin and $\varepsilon$-martensite, while pink indicates a blocky and coarse $\alpha'$-martensite. In 0.1C steel (Figs. 8(a)–8(c)) with a lower SFE, the band-like fine $\alpha'$-martensitic structure developed at all temperatures. Figure 9(A) shows the Phase map (A-1) and the crystallographic orientation map (A-2) (only the bcc phase) corresponding to the square region (A) in Fig. 8(b). In Figs. 8(a) and 8(b), $\alpha'$-martensite looks like an elongated band-like or granular morphology. However, ultrafine $\alpha'$-martensite with different variant exists within $\varepsilon$-martensite with an HCP structure in Fig. 9(A). Such a structure is an evidence for the two step transformation: band-like fine $\varepsilon$-martensite and deformation twin are formed first, followed by deformation-induced $\alpha'$-martensitic transformation within the band-like microstructures which are the nucleation sites of $\alpha'$-martensite. In contrast, in the 0.1N steel (Figs. 8(d)–8(f)) with a higher SFE, not only the band-like fine $\alpha'$-martensite (red), but also the blocky $\alpha'$-martensite (pink) was formed in the deformation structure. The Phase map and the crystallographic orientation map, focused on the blocky $\alpha'$-martensite (square region (B) in Fig. 8(d)), are represented in Fig. 9(B). The fine $\alpha'$-martensite (Fig. 9(A)) consists of several variants, while the blocky $\alpha'$-martensite was formed via a single-variant transformation, and there was no $\varepsilon$-martensite and deformation twin near the blocky $\alpha'$-martensite. Therefore, the grain boundary and dislocation cell wall would also become nucleation sites for deformation-induced $\alpha'$-martensite in the 0.1N steel with a higher SFE as the $\varepsilon$-martensite and deformation twin, which are the preferred nucleation sites of $\alpha'$-martensite, are insufficiently distributed as compared to the 0.1C steel. Such $\alpha'$-martensite can only grow coarsely owing to the less high-angle grain boundaries in the vicinity and leads to a reduction in the mechanical stability of austenite.
Fig. 8. Phase + IQ (Image Quality) maps of 0.1C steel (a)–(c) and 0.1N steel (d)–(f) tensile tested at each strain at 253 K (a) and (d), 293 K (b) and (e), and 333 K (c) and (f). Gray, blue, and (red + pink) represent austenite (FCC), \(\varepsilon\)-martensite (HCP), and \(\alpha'\)-martensite (BCC), respectively. (Online version in color.)

Fig. 9. Phase maps (A-1), (B-1) and crystallographic orientation maps (A-2), (B-2) corresponding to the square area in Figs. 8(b) and 8(d). (Online version in color.)
ratio between the amount of the blocky $\alpha'$-martensite and the total amount of $\alpha'$-martensite increased with increasing temperature in the 0.1N steel. At the lowest test temperature of 253 K, $\varepsilon$-martensite and the deformation twin were found to be well developed even in 0.1N steel because of its relatively low SFE and limited dislocation motion due to low temperature. This resulted into similar morphologies of deformation-induced $\alpha'$-martensites in both 0.1C and 0.1N steels. In this case, the ratio of blocky $\alpha'$-martensite in the 0.1N steel was small. The value of $\alpha$ at this temperature was close to 1.0, which is not because C and N are essentially similar elements at this temperature but because the higher chemical stabilization effect of N (Fig. 7(a)) and the deformation-induced $\alpha'$-martensitic transformation promoting effect due to formation of blocky $\alpha'$-martensite in N-added steels balanced each other at 253 K. In contrast, at 293 and 333 K, since the SFE of 0.1N steel increased sufficiently for developing the dislocation cell structure, the ratio of the blocky $\alpha'$-martensite doubled and the difference in the volume fractions of austenite between 0.1C and 0.1N steels increased significantly.

3.5. Proposal of Modified Equation to Predict $Md_{30}$

Based on the above results, we attempted to modify the equation of $Md_{30}$ to reflect the difference between C and N. First, we considered if the effects of C and N can be simply added. Angel et al. used the specimen of Fe-18.2%Cr-8.6%Ni-0.42%Si-0.42%Mn-0.09%C-0.053%N alloy whose compositions, except C and N concentration, are similar with the Base steel. As shown in Fig. 3, the variations in $Md_{30}$ by the addition of 0.09% C and 0.053%N were estimated to be $-105$ K and $-60$ K, respectively. When the additional value ($-165$ K) was added to $Md_{30}$ of the Base steel (383 K), the $Md_{30}$ of Angel's alloy was found to be 218 K. However, the $Md_{30}$ of this alloy was mentioned as 272 K, which is about 50 K higher than the calculated value. This is because the decreasing tendency of $Md_{30}$ weakened in the high C and N region (see Fig. 3). Hence, it can be concluded that simple addition of the effects of C and N resulted in overestimation.

To avoid this overestimation, $Md_{30}$ was rearranged by the $C_{eq}$ introduced in section 3.3, as shown in Fig. 10. The temperature dependence of the $a$ value in $C_{eq}$ was formulated, based on Fig. 6, in order to calculate $C_{eq}$ at the $Md_{30}$ of each specimen. In Eqs. (5) and (6), the simple functions as much as possible which provided the best fits for the experimental results were selected.

$$a = 0.931 - 0.000281 \exp\left(0.0219Md_{30}\right) \ldots \ldots \ldots (5)$$

The influence of C and N on $Md_{30}$ can be uniformly evaluated by using $C_{eq}$ and the decrease in $Md_{30}$ by addition of both elements, $\Delta Md_{30}^{CN} (>0)$, was formulated as a function of $C_{eq}$ as follows:

$$\Delta Md_{30}^{CN} (K) = 333 \sqrt{C_{eq}} \ldots \ldots \ldots \ldots (6)$$

$\Delta Md_{30}^{CN}$ of the alloy that Angel used (0.09%C, 0.053%N) was calculated as 124 K by Eqs. (4)–(6), which was similar to the experimental value ($\Delta Md_{30}^{CN} = 383 - 272 = 111$ K).

Based on the above concept, we improved the equation of $Md_{30}$ using Eqs. (4)–(6), as shown in Fig. 11. In Figs. 11(a) and 11(b), the horizontal axis shows the experimental values of $Md_{90}^{CN}$ obtained by Angel (○), Nohara et al. (△), and this study (■), and the vertical axis shows the calculated values from Eqs. (1) (a) and (2) (b), respectively. The plots are close to a solid line in the figure means that the experimental values were similar to the calculated values, and the degree of data variation was evaluated by the coefficient of determination ($R^2$). Angel’s and our results were similar to the calculated values obtained by using Angel’s equation (a), while the experimental values, of the specimen with various Ni concentration, from Nohara et al. were significantly different from the calculated values. Accordingly, Nohara et al. tried to modify the coefficient of Ni, but the experimental data, other than their results, were significantly different from the $Md_{90}$ values calculated by Eq. (2) (see Fig. 11(b)). In both the cases, $R^2$ values were as low as approximately 0.5. The deviation in the $Md_{90}$ values calculated by both the equations could be due to the underestimation of the effects of C and N and that the resulting error was assigned to other elements. Therefore, in this study, a more accurate equation was reconstructed by the following procedure. First, the decrease in $Md_{30}$ due to C and N (−$\Delta Md_{30}^{CN}$) was subtracted from $Md_{90}$, i.e., $Md_{90}^{CN}(=Md_{90}^{CN} + \Delta Md_{90}^{CN})$, which is $Md_{30}$ without the effects of C and N. Assuming that $Md_{90}^{CN}^{withoutCN}$ is a function of Si, Mn, Cr, Ni, and Mo concentrations, a multiple regression analysis was performed, and −$\Delta Md_{30}^{CN}$ was added to the equation of $Md_{90}^{CN}^{withoutCN}$, as follows:

$$Md_{30} (K) = 800 - 333\sqrt{(C + aN) - 10.3Si - 12.5Mn} \ldots \ldots (7)
-10.5Cr - 24.0Ni - 5.6Mo$$

($C<0.24\%$, $N<0.196\%$, $0.15\%<Si<0.88\%$, $0.33\%<Mn<9.1\%$, $15.3\%<Cr<19.35\%$, $4.2\%<Ni<9.2\%$, $Mo<0.77\%$)

The $Md_{90}$ in the above compositions ranges can be predicted using Eqs. (5) and (7). Figure 11(c) shows a comparison between the calculated values and $Md_{90}^{CN}$. It was found that the accuracy of Eq. (7) is high since the correlation ($R^2 = 0.927$) is higher than that of Figs. 11(a) and 11(b). In addition, since Eq. (7) can be applied from 240 K to 400 K, the results can be applied not only for the Fe-18%Cr-
8%Ni alloy but also for other austenitic stainless steels. However, Saenarjhan et al. reported that the mechanical stabilization effect of N is higher than that of C in the Fe-15%Cr-15%Mn-4%Ni alloy, which means that we need to be careful while using Eq. (7) if the alloy systems differ significantly. Matsuoka et al. studied the effect of grain size on mechanical stability, and reported that there is no grain size dependence in the Fe-16%Cr-10%Ni alloy with austenitic grain size of 1 μm to 100 μm. Hence, Eq. (7) does not include the effect of grain size.

Since the mechanical stabilization effects of C and N cannot be compared with other elements in Eqs. (7), (8), which is the linear approximation for chemical composition, was obtained by multiple regression analysis for the coefficients of C and N by keeping the coefficients of Si, Mn, Cr, Ni, and Mo in Eq. (7) fixed. The calculated $M_{sd}$ is shown in Fig. 11(d).

$$M_{sd} (K) = 756 - 555C - 528N - 10.3Si - 12.5Mn - 10.5Cr - 24.0Ni - 5.6Mo$$

The correlation ($R^2 = 0.854$) is lower than that in Fig. 11(c), but higher than that of Figs. 11(a) and 11(b) due to revising the coefficients of all elements. In addition, the absolute values of the coefficients of C and N were larger than previously reported value (462), with significant differences between C and N. The deviation was found to be particularly large in ultra-low C and N steels with high $M_{sd}$. However, the Eq. (8) can be applied to industrial stainless steels containing C and N. However, the reliability of the coefficient of Si and Mo is poor because the composition ranges of these elements is very narrow, and the temperature and concentration dependence other than C and N have not been considered in this study. Furthermore, the validity of the linear approximation needs to be assessed. In order to predict $M_{sd}$ from chemical composition, the process of machine learning, which has been developed in recent years, seems to be extremely effective. At present, experimental data is insufficient for machine learning, and a theoretical approach based on thermodynamics and morphology of microstructure is also important. In future, it will be necessary to accumulate data, and develop the technology for predicting the microstructure and its properties.

### 4. Conclusion

The effects of C and N on the mechanical stability of metastable austenitic stainless steel were investigated at a temperature range from 233 K to 393 K. The results are summarized as follows:

1. The mechanical stabilization effect of C was found to be higher than that of N at all temperatures. However, there was a temperature dependence of the difference in the effects of both the elements. The difference becomes remarkable at a higher temperature, which can be quantitatively explained by the C equivalent $C_{eq}$ as follows:

$$C_{eq} = C + aN$$

   $a = 0.931 - 0.000281 \exp(0.0219T)$

2. At a lower temperature where SFE of austenite is low, there was little difference in the deformation-induced transformation behavior of C- and N-added steels as $\varepsilon$-martensite and deformation twin act as nucleation sites of deformation-induced $\alpha'$-martensite in all the specimens. On the other hand, at a higher temperature, the difference
between the mechanical stabilization effects of C and N increased. This is because a temperature rise leads to the suppression of \(\varepsilon\)-martensite and deformation twin, which hinder the growth of \(\alpha'\)-martensite, in N-added steels with high SFE, resulting in the stimulation of the deformation-induced \(\alpha'\)-martensitic transformation in N-added steels at higher temperatures.

(3) As opposed to the previous study,\(^3,4\) the effect of C on \(M_d\) was higher than that of N. In addition, both C and N decreased \(M_d\) by a higher margin than previously reported. This is because the large stabilization effect in the low C and N concentration region of below 0.1% has not been considered so far.

(4) The conventional empirical equation for \(M_d\) had a large error as it underestimated the effects of C and N. In this study, the modified \(M_d\) equation was proposed, as follows:

\[
M_d(K) = 800 - 333\sqrt{(C + aN)} - 10.3Si
- 12.5Mn - 10.5Cr - 24.0Ni - 5.6Mo
a = 0.931 - 0.000281\exp(0.0219M_d)
\]

In addition, the following linear approximate equation with respect to chemical composition was obtained by multiple regression analysis.

\[
M_d(K) = 756 - 555C - 528N - 10.3Si - 12.5Mn
- 10.5Cr - 24.0Ni - 5.6Mo
\]

Acknowledgement

This work was supported by JSPS KAKENHI Grant Number JP18K14016.

REFERENCES

1) N. Tsuchida, Y. Morimoto, T. Tonan, Y. Shibata, K. Fukaura and R. Usji: ISIJ Int., 51 (2011), 124. https://doi.org/10.2355/isijinternational.51.124
2) J. P. Bressanelli and A. Moskowitz: Trans. Am. Soc. Met., 59 (1966), 223.
3) T. Angel: J. Iron Steel Inst., 177 (1954), 165.
4) K. Nohara, Y. Ono and N. Ohashi: Tetsu-to-Hagané, 63 (1977), 772 (in Japanese). https://doi.org/10.2355/tetsutohagane1955.63.5_772
5) T. Hirayama and M. Oginuma: J. Jpn. Inst. Met., 34 (1970), 507 (in Japanese). https://doi.org/10.2320/jinstmet1952.34.5_507
6) M. Sanga, N. Yukawa and T. Ishikawa: J. Jpn. Soc. Technol. Plast., 41 (2000), 64 (in Japanese).
7) T. Oshima, Y. Habura and K. Kuroda: Tetsu-to-Hagané, 93 (2007), 544 (in Japanese). https://doi.org/10.2355/tetsutohagane.93.544
8) J. H. Kang, H. S. Noi, K. M. Kim, S. C. Lee and S. J. Kim: J. Alloy. Compd., 696 (2017), 869. https://doi.org/10.1016/j.jallcom.2016.12.061
9) T. Takemoto, Y. Murata and T. Tanaka: Tetsu-to-Hagané, 76 (1990), 894 (in Japanese). https://doi.org/10.2355/tetsutohagane1955.76.6_894
10) T. Masumura, N. Nakada, T. Tsuchiya, S. Takaki, T. Koyano and K. Adachi: Acta Mater., 84 (2015), 330. https://doi.org/10.1016/j.actamat.2014.10.041
11) G. B. Olson and M. Cohen: Metall. Trans. A, 7 (1976), 1897. https://doi.org/10.1007/BF02659822
12) S. Allain, J. P. Chateau, O. Bouaziz, S. Migot and N. Guetton: Mater. Sci. Eng., 387-389 (2004), 158. https://doi.org/10.1016/j.msea.2004.01.059
13) P. U. Volosevich, V. N. Gridnev and Y. U. Petrov: Phys. Met. Metallogr., 42 (1976), 126.
14) N. Saenarjhan, J. H. Kang and S. J. Kim: Mater. Sci. Eng., A 742 (2019), 608. https://doi.org/10.1016/j.msea.2018.11.048
15) M. Yoshitake, T. Tsuchiya and S. Takaki: Tetsu-to-Hagané, 98 (2012), 223 (in Japanese). https://doi.org/10.2355/tetsutohagane.98.223
16) N. Ohkubo, K. Miyakasu, Y. Uematsu and H. Kimura: ISIJ Int., 34 (1994), 764. https://doi.org/10.2355/isijinternational.34.764
17) K. J. Irvine, D. T. Lewellyn and F. B. Pickering: J. Iron Steel Inst., 199 (1961), 153.
18) H. K. L. Ngo, K. Nakashima, T. Tsuchiya and S. Takaki: Tetsu-to-Hagané, 98 (2012), 25 (in Japanese). https://doi.org/10.2355/tetsutohagane.98.25
19) K. Takano, M. Sakakibara, T. Matsui and S. Takaki: Tetsu-to-Hagané, 86 (2000), 123 (in Japanese). https://doi.org/10.2355/tetsutohagane1955.86.2_123
20) T. Masumura, T. Tsuchiya, S. Takaki, T. Koyano and K. Adachi: Scr. Mater., 154 (2018), 8. https://doi.org/10.1016/j.scriptamat.2018.05.019
21) T. H. Lee, H. Y. Ha, B. Hwang, S. J. Kim and E. Shin: Metall. Mater. Trans. A, 43 (2012), 4455. https://doi.org/10.1007/s11661-012-1423-y
22) T. H. Lee, E. Shin, C. S. Oh, H. Y. Ha and S. J. Kim: Acta Mater., 58 (2010), 3173. https://doi.org/10.1016/j.actamat.2010.01.056
23) R. E. Schramm and R. P. Reed: Metall. Trans. A, 6 (1975), 1345. https://doi.org/10.1007/BF02641927
24) L. Remy and A. Pineau: Mater. Sci. Eng., 28 (1977), 99. https://doi.org/10.1016/0025-5416(77)90093-3
25) N. Nakada, H. Ito, Y. Matsuoka, T. Tsuchiya and S. Takaki: Acta Mater., 58 (2010), 895. https://doi.org/10.1016/j.actamat.2009.10.004
26) Y. Tian, O. I. Gorbatov, A. Borgenstam, A. V. Ruban and P. Hedström: Metall. Mater. Trans. A, 48 (2017), 1. https://doi.org/10.1007/s11661-016-3839-2
27) Y. Matsuoka, T. Iwasaki, N. Nakada, T. Tsuchiya and S. Takaki: ISIJ Int., 53 (2013), 1224. https://doi.org/10.2355/isijinternational.53.1224
28) Z. L. Wang and Y. Adachi: Mater. Sci. Eng. A, 744 (2019), 661. https://doi.org/10.1016/j.msea.2018.12.049
29) Y. Adachi, Y. Matsuoka, I. Kanamura and I. Inoue: Syst. Control Inf., 61 (2017), 188 (in Japanese). https://doi.org/10.11509/isciesci.61.5_188