Scripta Materialia 154 (2018) 8–11

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Regular article

# Difference between carbon and nitrogen in thermal stability of metastable 18%Cr-8%Ni austenite

Takuro Masumura [a,b,*], Toshihiro Tsuchiyama [a,b,c], Setsuo Takaki [a], Tamotsu Koyano [d], Kazuhiko Adachi [e]

[a] Research Center for Steel, Kyushu University, 744, Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan
[b] International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, 744, Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan
[c] Department of Materials Science and Engineering, Kyushu University, 744, Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan
[d] Cryogenics Division, Research Facility Center, University of Tsukuba, 1-1-1, Tennodai, Tsukuba, Ibaraki 305-8577, Japan
[e] Titanium & Specialty Stainless Steel Research Lab, Steel Research Lab, Nippon Steel & Sumitomo Metal Corporation, 20-1, Shintomi, Futtsu, Chiba 293-8511, Japan [1]

## ARTICLE INFO

*Article history:*
Received 14 April 2018
Received in revised form 15 May 2018
Accepted 16 May 2018
Available online xxxx

*Keywords:*
Austenitic steels
Stainless steels
Martensitic phase transformation
Thermodynamics
Thermal stability

## ABSTRACT

The effects of carbon and nitrogen addition on the athermal α′-martensitic transformation in metastable 18%Cr-8%Ni austenite are investigated. The thermal stability of austenite in nitrogen-added steel is higher than that in carbon-added steel, and the difference between the effects of carbon and nitrogen addition becomes remarkable as the amount of both elements increases. As the two-step transformation (γ → ε → α′) always occurs in metastable 18%Cr-8%Ni austenite, the suppression of ε-martensite results in the thermal stabilization of austenite. Nitrogen is more effective than carbon for increasing the stacking fault energy, leading to a higher thermal stability of the nitrogen-bearing 18%Cr-8%Ni steels.

Austenitic stainless steels are used as cryogenic structural materials in superconducting facilities and fusion devices. To suppress the formation of athermal α′-martensite, which causes a disturbance in magnetic fields, the thermal stability of the austenite phase must be increased. As the addition of interstitial elements markedly increases the stability [1] and strength [2–4] of austenite, carbon and nitrogen addition should improve the cryogenic characteristics of austenitic stainless steels. In general, the effect of carbon and nitrogen addition on the thermal stability of austenite is regarded to be similar. For example, Eichelman et al. [1] investigated the *Ms* temperature (athermal α′-martensitic transformation starting temperature upon cooling) in Fe-Cr-Ni alloy systems and reported that the effect of carbon on the *Ms*. temperature is identical to that of nitrogen in the $C < 0.14\%$ and $N < 0.04\%$ composition ranges. On the other hand, the authors [5] studied the thermal stability of austenite in Fe-18%Cr-8%Ni alloys containing either 0.1% carbon or 0.1% nitrogen, and found that the austenite stabilization effect by nitrogen is higher than that by carbon. This result is different from that of the previous study because the specimens used by Eichelman contained both carbon and nitrogen and the composition range of nitrogen was too narrow. Therefore, to design new alloys with higher amounts of carbon and nitrogen, the individual effects of both elements on the athermal α′-martensitic transformation behavior must be understood in wide composition ranges.

Herein, the thermal stability of austenite was investigated in a Fe-18%Cr-8%Ni alloy in which different amounts of carbon or nitrogen were independently added. The athermal α′-martensitic transformation behavior of the carbon- and nitrogen-added steels was then compared in terms of microstructure and thermodynamic phase stability. For the metastable austenitic stainless steels with low stacking fault energies (SFE) used in this study, the martensitic transformation undergoes not only a γ → α′ (bcc) transformation but also a γ → ε (hcp) transformation upon cooling. When the two-step (γ → ε → α′) transformation occurs, the α′-martensitic transformation is stimulated by ε-martensite [6,7]. Therefore, the thermal stability of metastable austenite was discussed by taking the transformation process of each specimen into consideration.

A metastable austenitic stainless steel (Fe-18.3%Cr-8.2%Ni-1.0%Mn-0.5%Si-0.002%C-0.001%N alloy) was used as the Base steel in this study. To the Base steel, 0.021, 0.051, 0.100, and 0.199% carbon and 0.015, 0.030, 0.063, 0.100, and 0.196% nitrogen were separately added. Ingots of 17 kg having the above chemical compositions were produced by vacuum melting and hot-rolled to thicknesses of 10 mm at 1423 K. The steel plates were cold-rolled for a 50% reduction in thickness and then solution-treated at 1273 K to 1473 K for $1.8 \times 10^3$ s, followed by water-cooling to obtain the initial austenitic structure with an average grain size of approximately 40 μm. The athermal α′-martensitic

---

[*] Corresponding author at: Research Center for Steel, Kyushu University, 744, Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan.

*E-mail address:* masumura@zaiko.kyushu-u.ac.jp (T. Masumura).

[1] (Currently Nippon Steel & Sumikin Research Institute Corporation, 20-1, Shintomi, Futtsu, Chiba 293-8511, Japan.)

https://doi.org/10.1016/j.scriptamat.2018.05.019
1359-6462/

transformation upon cryogenic cooling was evaluated with a superconducting quantum interference device (SQUID) magnetometer (MPMS-5.5, Quantum Design, Inc.). When the solution-treated specimens were cooled from 300 K to 5 K at a cooling rate of 1 K/min in a magnetic field of 1 T, the change in saturation magnetization (*Is*) was continuously measured. The volume fraction of α′-martensite was then calculated as the ratio of *Is* to the saturation magnetization of the specimen with a full α′-martensitic structure, $Is^*$ (at 300 K). The $Is^*$ was determined using a 40% cold-rolled Base steel whose microstructure was confirmed to be a full α′-martensitic structure by X-ray diffraction analysis. The microstructure of the specimens was observed by transmission electron microscopy (TEM; JEM-2010, JEOL) and electron backscatter diffraction (EBSD) analysis using a field emission scanning electron microscope (FE-SEM; SIGMA 500, Zeiss). The SFE value was estimated by Eq. (1), which was proposed by Olson and Cohen [8].

$$\mathrm{SFE}\ (\mathrm{mJ/m^2}) = 2\rho_A\left(\Delta G^{fcc\rightarrow hcp} + E^{strain}\right) + 2\sigma \qquad (1)$$

where $\rho_A$, $\Delta G^{fcc\rightarrow hcp}$, $E^{strain}$ and $\sigma$ denote the density of atoms on the $\{111\}_\gamma$ plane (mol/m$^2$), the chemical free energy change from fcc to hcp (J/mol), the strain energy generated by the formation of an hcp phase in the fcc matrix (J/mol), and the interfacial energy of the hcp/fcc interface (J/m$^2$), respectively. Herein, $\rho_A$ and $\sigma$ were estimated to be $2.5 \times 10^{-5}$ mol/m$^2$ [9] and $27 \times 10^{-3}$ J/m$^2$ [10], respectively, and $E^{strain}$ was assumed to be negligible. These values are constant for all steels used in this study, and thus, the SFE strongly depends on $\Delta G^{fcc\rightarrow hcp}$. $\Delta G^{fcc\rightarrow hcp}$ was calculated using the Thermo-Calc. software (database: SSOL2, at 300 K).

Fig. 1a shows the changes in the volume fraction of the athermal α′-martensite phase upon cryogenic cooling from 300 K to 5 K. Although a small amount of α′-martensite was detected at 300 K in some specimens, it is thought to be due to the destabilization of austenite at the surface of the specimen. Hence, to avoid the surface effect, the transformation curves were extended from the lower temperature (dashed line in the Base steel). The result for the Base steel reveals that the *Ms*. temperature is 297 K, and the volume fraction of α′-martensite gradually increases with decreasing temperature; however, the α′-martensitic transformation stopped at temperatures below 100 K and proceeded to saturation, around 45 vol%. Such saturation below 100 K is observed in all other specimens. Carbon and nitrogen addition leads to the decrease in *Ms*. temperature and saturated α′-martensite fraction. The *Ms*. temperature decreases to 189 K in 0.1C steel, while it completely disappears and no α′-martensitic transformation takes place in 0.2C steel. The austenite stabilization effect by nitrogen is regarded to be larger than that by carbon since the α′-martensitic transformation never occurs, even in 0.1N steel. Fig. 1b shows the relationship between the carbon or nitrogen content and the *Ms*. temperature. There is an apparent difference between the effects of carbon and nitrogen on the *Ms*. temperature, and the difference in *Ms*. temperature increases as the amount of both elements increases. Compared to the result proposed by Eichelman ($\Delta Ms = -1667$ K / [%(C + N)]) [1], the stabilization effect of carbon in this study ($\Delta Ms = -1141$ K / [%C]) is markedly smaller, and conversely, that of nitrogen ($\Delta Ms = -1823$ K / [%N]) is slightly larger. This result suggests that carbon and nitrogen should be separately evaluated when the thermal stability of austenite is discussed, even for small amounts of both elements.

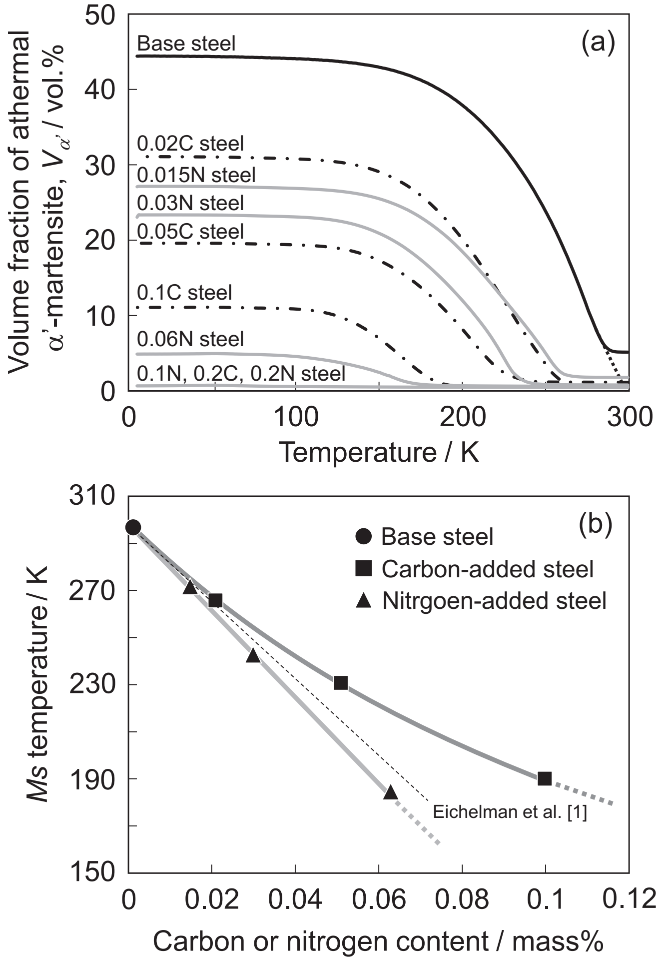

**Fig. 1.** (a) Changes in volume fraction of athermal α′-martensite formed upon cryogenic cooling. (b) Changes in *Ms* temperature as a function of carbon or nitrogen content in Fe-18.3%Cr-8.2%Ni-1.0%Mn-0.5%Si alloys.

To identify the cause for the difference in the thermal stabilization effects of carbon and nitrogen, the microstructure was observed with SEM-EBSD and TEM, and the corresponding images are shown in Fig. 2. Fig. 2a–c show the phase maps of the Base, 0.06N, and 0.05C steels after subzero treatment at 77 K. In these maps, austenite, ε-martensite, and α′-martensite are colored in grey, yellow, and red, respectively. The black lines indicate the austenite grain boundaries. In all specimens, α′-martensite exists as a banded-structure in which ε-martensite is distributed. In austenitic stainless steels with low SFE, ε-martensite acts as an intermediate phase in the two-step γ → ε → α′ transformation [6,7,11,12]. Herein, the arrangement and distribution of the α′-martensite phase suggest that the transformation proceeded through the formation of plate-like ε-martensite along the $\{111\}_\gamma$ planes upon cryogenic cooling, followed by α′-martensitic transformation with ε-martensite consumption. As a result, the ε-martensite phase in the austenite matrix obeys the Shoji-Nishiyama (S-N) relationship $[(111)_\gamma//(0001)_\varepsilon, [-110]_\gamma//[11-20]_\varepsilon]$, and the ε-martensite and α′-martensite phases obey the Burgers relationship $[(0001)_\varepsilon//(101)\alpha', [1-210]_\varepsilon//[-111]\alpha']$. To reveal the microstructure, the α′-martensite phase of the 0.1C steel cooled at 4 K was observed with a higher magnification, as shown in Fig. 2d and e. The crystallographic orientation map (Fig. 2d) obtained by transmission EBSD [13,14] indicates that ultrafine-grained α′-martensite lies on a straight line, while ε-martensite is observed between the α′-martensite grains. Analysis of the variants of α′-martensite reveals the formation of all six kinds of variants which could be generated from one variant of ε-martensite [11,15]. The TEM image corresponding to the square region in Fig. 2d indicates that the α′-martensite substructures include dislocations (see Fig. 2e). Although it is well known that lenticular α′-martensite is often formed upon cryogenic cooling in Fe-Ni alloys [16], in this study, the lattice invariant shear did not take place by twin deformation but by slip deformation. This seems to be because ε-martensite already contains many dislocations [17].

As the athermal α′-martensitic transformation of metastable 18%Cr-8%Ni austenitic stainless steel proceeds in two-steps (γ → ε → α′), detailed investigation of the ε-martensitic transformation is required to