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The difference in thermal and mechanical stabilities of austenite between carbon- and nitrogen-added metastable austenitic stainless steels

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Abstract—In order to evaluate the effects of carbon and nitrogen addition on the stability of austenite, athermal and deformation-induced α' -martensitic transformation behaviors were investigated using type 304-metastable austenitic stainless steels containing 0.1 mass% carbon or nitrogen. The difference in the development of the deformation microstructure in particular is discussed in terms of the stacking-fault energy (SFE). Since carbon-added steel has a lower SFE than that of nitrogen-added steel, deformation twins and ϵ -martensite were preferentially formed in the carbon-added steel, whereas a dislocation cell structure developed in the nitrogen-added steel. Crystallographic analysis using the electron backscatter diffraction method revealed that the difference in the deformation microstructure has a significant influence on the growth behavior of deformation-induced α' -martensite, that is, the interface of the deformation twins and ϵ -martensite suppresses the growth of α' -martensite, whereas dislocation cell boundaries are not effective. As a result, the mechanical stability of carbon-added steel is slightly higher than that of nitrogen-added steel, although the thermal stabilization effect of carbon is much lower than that of nitrogen. © 2014 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Austenite stability; Stainless steel; Carbon; Nitrogen; Stacking-fault energy

1. Introduction

Metastable austenitic stainless steels, e.g., type 304, exhibit large strain hardenability attributed to the formation of deformation-induced body-centered cubic (bcc) martensite (α' -martensite). For optimization of the mechanical properties of this kind of steel, it is therefore very important to control the strength and volume fraction of deformation-induced α' -martensite formed by cold deformation [1,2]. Since the addition of interstitial alloying elements strengthens α' -martensite markedly [3,4], it is generally accepted that the addition of carbon and nitrogen is an effective method of increasing the strength of metastable austenitic stainless steels. On the other hand, carbon and nitrogen suppress the formation of deformation-induced α' -martensite through the thermodynamical stabilization of the austenite phase [5,6]. From this point of view, it is industrially

important to understand how much of the austenite phase is stabilized by the carbon and nitrogen additions.

The austenite stability is usually discussed in terms of two different standards, the so-called thermal and mechanical stabilities. These standards refer to the austenite stability against athermal α' -martensitic transformation and deformation-induced α' -martensitic transformation, and they are evaluated with Ms and Md_{30} , respectively, where Ms is the athermal α' -martensitic transformation start temperature upon cooling and Md_{30} is the temperature at which 50% of α' -martensite is formed at 30% true tensile strain. Many researchers have investigated and formulated Ms in various kinds of steels. In the formulation proposed by Eichelman [7], which describes *Ms* in Fe–Cr–Ni alloy systems, the austenite stabilization effect of carbon is estimated to be identical to that of nitrogen. As for Md_{30} , a similar tendency is reported in Nohara et al.'s formulation [6], which is a modification of the Md_{30} formulation proposed by Angel [5]. However, in both cases, the specimens for the investigation contained carbon and nitrogen simultaneously. In addition, the composition ranges of the

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carbon and nitrogen used for the formulation were narrow. Although the carbon content was varied up to 0.14%, the nitrogen content added was at most only 0.04% in the specimens (hereinafter all percentages refer to mass%). These facts suggest that the previous Ms and Md_{30} formulations might be inadequate for predicting the individual effects of carbon and nitrogen, particularly when their contents are not very low. Therefore, it is necessary to investigate the effect of both elements on the austenite stability in more detail by using specimens in which carbon and nitrogen are independently added.

In our previous study, we reported that the fraction of deformation-induced α' -martensite was different between cold-rolled and cold-drawn type 316L steels at the same equivalent strain, leading to the conclusion that the difference in deformation-induced α' -martensitic transformation behavior is caused by the difference in the development of the deformation microstructure [8]. Since the deformation microstructure of austenitic stainless steel varies depending on stacking-fault energy (SFE), the change in chemical composition results in considerable variation of the deformation microstructure, i.e., the formation of hexagonal close packed (hcp) martensite (ɛ-martensite), deformation twins and planar dislocation arrays [9]. Considering that the effect of carbon addition on the deformation microstructure is obviously different from that of nitrogen in a stable austenitic stainless steel (Fe–18%Cr–12%Ni) [10], there should be some differences in the mechanical stability of austenite between carbon- and nitrogen-added metastable austenitic stainless steels.

In this study, the differences between the effects of carbon and nitrogen addition on the thermal and mechanical stabilities of austenite were investigated in a metastable austenitic stainless steel (Fe–18%Cr–8%Ni). Especially, the difference in the deformation-induced α' -martensitic transformation behavior between carbon- and nitrogenadded steels is discussed in terms of the development of the deformation microstructure related to SFE.

2. Experimental procedure

A metastable austenitic stainless steel (Fe–18%Cr–8%Ni) was used as the Base steel in this study. In addition, 0.1% carbon and nitrogen were separately added to the base steel (0.1C and 0.1N steels, respectively). The chemical compositions of the steels are listed in Table 1. The compositions of carbon and nitrogen were analyzed by the infrared absorption method after combustion (analytical range: 0.001–5.0%) and the thermal conductimetric method after fusion in a current of inert gas (analytical range: 0.0008–0.5%), respectively. In this table, the atomic fraction of carbon and nitrogen are also represented. The ingots were hot-rolled to thicknesses of 10 mm at 1423 K, and then solution-treated at 1273 K (Base steel) or 1373 K (0.1C and 0.1N steels), followed by water cooling in order to obtain an initial austenitic structure with the same average grain size.

For the investigation of the thermal and mechanical austenite stability, cryogenic cooling to liquid helium temperature (4 K) and cold rolling to achieve a thickness reduction of up to 70% were conducted, respectively. The cold-rolled specimens were water-cooled after each rolling pass to avoid the processing heat. The microstructures of the specimens were observed by optical and transmission electron microscopy (TEM; JEM-2010, JEOL). The crystallographic orientation of each phase was mapped by means of the electron backscatter diffraction (EBSD) method using a field emission scanning electron microscope (FE-SEM; S-4300 and SU6600, Hitachi High Technologies). The data obtained by EBSD were analyzed using software programs for automatic crystal orientation mapping (OIM analysis, TSL). Crystallographic orientation mapping was taken at step sizes of 50, 100 and 200 nm, and then obtained data with a confidence index (CI) value over 0.1 were used for a detailed crystallographic analysis. The volume fraction of α' -martensite was estimated by magnetic measurements. The change in volume fraction of athermal α' -martensite formed 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 in a magnetic field of 1 T, the change in saturation magnetization (I_s) was measured. The volume fraction of α' -martensite (V α') was then calculated as the ratio of I_s to the saturation magnetization of the specimen with a full α' -martensitic structure (I_s^* , at 300 K). I_s^* was evaluated by using a 40% cold-rolled Base steel that had been identified as having a deformation-induced full α' -martensitic structure by X-ray diffraction (XRD) analysis. The effects of carbon and nitrogen on I_s^{\dagger} were ignored. As for deformation-induced α' -martensite, $V_{\alpha'}$ was calculated as the ratio of I_s of the cold-rolled specimen to I_s^{T} at ambient temperature. The volume fraction of ε -martensite was evaluated by the integral intensity ratio of the XRD peaks of *\varepsilon*-martensite to those of austenite and α' -martensite. The diffraction peaks of $(220)_{\gamma}$, $(311)_{\gamma}$, $(200)_{\alpha'}$, $(211)_{\alpha'}$, $(10-11)_{\epsilon}$, and $(10-12)_{\varepsilon}$ were used for this evaluation [11].

The SFE value was estimated by Eq. (1) proposed by Olson and Cohen [12] and is listed in Table 1:

$$SFE(mJ m^{-2}) = 2\rho_A(\Delta G^{fcc \to hcp} + E^{strain}) + 2\sigma$$
(1)

where ρ_A , $\Delta G^{fcc \rightarrow hcp}$, E^{strain} and σ denote the density of atoms on {1 1 1}_{γ} (mol m⁻²), the chemical free energy change from face centered cubic (fcc) to hcp (J mol⁻¹), the strain energy generated by the formation of hcp in the fcc matrix (J mol⁻¹) and the interfacial energy of the hcp/fcc interface (J m⁻²), respectively. In this study, ρ_A and σ were estimated to be 2.5 × 10⁻⁵ mol m⁻² [13] and 27 × 10⁻³ J m⁻² [14], respectively, and E^{strain} was assumed to be negligible. There would be no change in these values among the three steels, and thus SFE strongly depends on $\Delta G^{fcc \rightarrow hcp}$. The $\Delta G^{fcc \rightarrow hcp}$ of the Base, 0.1C and 0.1N steels were calculated to be -870, -760 and -600 J mol⁻¹, respectively, by Thermo-Calc software (database: SSOL2, at 300 K).

Table 1. Chemical compositions (mass%) and SFE of specimens used in this study.

	С	Si	Mn	Р	S	Cr	Ni	Ν	Fe	SFE (mJ/m ²)
Base steel	0.002	0.48	0.98	0.035	0.002	18.07	8.21	0.001	Bal.	10
0.1C steel	0.100 (0.46 at.%)	0.49	0.98	0.034	0.002	18.26	8.19	0.006	Bal.	17
0.1N steel	0.003	0.48	0.99	0.035	0.002	18.05	8.23	0.100 (0.39 at.%)	Bal.	24

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