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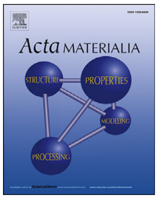

Full length article

Direct observation of niobium segregation to dislocations in steel

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ABSTRACT

It is well known that niobium in solute solution retards the recovery of dislocations in steel. Segregation of niobium atoms to dislocations was observed for the first time by atom probe tomography in niobium added ferritic stainless steels for high temperature use. The observation results suggest that solute niobium atoms solely have strong attractive interaction with dislocations. We name it niobium-Cottrell atmosphere, and discuss the trapping site and interaction energy through a comparison with segregation to the grain boundary in the same steel.

1. Introduction

Niobium is important alloying element in steels, because it is used for grain refinement by the retardation of recrystallization in the hot-rolling process [1–3]. The solute drag effect by solute niobium atoms and the pinning effect by niobium carbonitride precipitates have been proposed for the mechanism of recrystallization retardation [4,5]. Based on calculations, the former is reported to be more effective in ferrite, while in austenite phase, depending on the exact recrystallization temperature, either the former or the latter may be more effective [6].

Niobium in solid solution also significantly retards the recovery of dislocations in steel [3,7]. Recently, Shrestha et al. reported by in situ heating transmission electron microscopy (TEM) that niobium addition impeded the dislocation movement during aging at 575 °C [8]. However, it is unclear why solute niobium impeded the dislocation movement and retarded recovery strongly. Niobium atoms have been reported to attractively interact with vacancies in steel, and thus impede the dislocation movement (climbing) by decreasing the self-diffusion of iron through decrease in the density of mobile vacancies [7]. Furthermore, niobium atoms are also reported to make dipole or clusters with solute carbon and nitrogen atoms, and consequently suppress the dislocation migration because carbon and nitrogen atoms have strong attractive interactions with dislocations [8,9]. In contrast, the direct interaction between dislocations and lattice distortion by solute niobium atoms was proposed [3]. Dang and Wang reported the strong interaction between the dislocation core and niobium atoms by the calculation based on the first-principles discrete variational method [10]. Kirchheim reported that solute segregation to dislocations reduces the line energy of the dislocations, and consequently, reduces the driving force for recrystallization [11,12]. To elucidate the mechanism, direct observation of the attractive interaction between niobium atoms and dislocations is required.

Atom probe tomography (APT) is widely used for the atomic-scale observation of alloying elements in steel. Wilde et al. reported that the Cottrell atmosphere of carbon atoms around dislocations was observed in low-carbon martensite steels, wherein the dislocation was identified by spiral steps on field ion microscopic (FIM) images [13,14]. Furthermore, some simulations of the Cottrell atmosphere of carbon have been reported, wherein the difference in carbon distribution between edge and screw dislocations was predicted by the static energy calculation [15,16].

Recently, the analysis region of the atom probe was enlarged using new technologies, namely, wide-angle reflectron and short flight length [17]. Many studies have reported on solute segregation and precipitation to the dislocation were reported [18–20]. However, most of the reports were conducted in neutron-irradiated

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materials because the high density of point defects introduced by neutron radiation increased bulk diffusion and produced radiation-induced segregation. There have been few reports on the segregation of substitutional atoms to dislocations in commercial steels, even though the phenomena are very important to directly discuss the interaction between solute atoms and dislocations.

This paper investigated the state of solute niobium atoms in niobium added ferritic steels by APT. The segregations of niobium atoms to single dislocations and the dislocation wall were observed in the steel. From the quantitative estimation of segregating atoms, their trapping sites and interaction energies were discussed.

2. Experimental

2.1. Materials

Niobium added ferritic stainless steel was used in this study. The steel is actually applied for exhaust manifold in the automotive industry because of its high performance against thermal fatigue, where the proof strength is sufficiently maintained under repeated heating cycles. The improvement of proof strength at the high temperature was considered attributable to solid solution strengthening including the effect of niobium in solid solution on the retardation of recovery and recrystallization [21]. The chemical composition of the steel is shown in Table 1. Sufficient amounts of niobium and titanium were added to scavenge solute carbon and nitrogen for the improvement of ductility, high temperature strength, high thermal fatigue and corrosion resistance. A small amount of molybdenum and copper was added for further improvement of the heat-resistance property [22]. Moreover, a very small amount of boron was added for the suppression of secondary work cracking by grain boundary segregation [23]. This stainless steel did not undergo austenite transformation, and hot-rolling was conducted in the ferrite phase. The slab was homogenized at 1250 °C for 3.6 ks and then hot-rolled to a thickness of 4 mm. The final temperature of hot-rolling was about 860 °C, and the hot-rolled sheet was immediately cooled by water spray and coiled at about 520 °C. The yield stress and tensile stress of the hot-rolled sheet were 515 MPa and 571 MPa at room temperature.

2.2. Analysis methods

A transmission electron microscope (H8000, Hitachi) operated at 200 kV was used to investigate the distribution and number density of dislocations in the steel sheet. Thin film with a thickness of about 50 μm was fabricated from the steel sheet by mechanical and chemical polishing. Thin foil specimens for TEM observation were thinned by electropolishing in an electrolyte containing 10% perchloric acid in acetic acid held at 286 K with an applied potential of DC 30 V.

An energy-compensated three-dimensional atom probe (3DAP, Oxford NanoScience Ltd.) with a large-angle reflectron was used to investigate the distribution of alloying elements in the steel. The two-stage electropolishing method was applied for the needle tip fabrication, since gallium radiation of focused ion beam (FIB) milling may influence solute segregation to dislocation through the formation of point defects [24]. Small square rods (0.3 mm × 0.3 mm × 10 mm) cut from the steel sheet were directly electropolished using the standard electrolytes of 25% perchloric acid in acetic acid for the first stage and 2% perchloric acid in 1-butoxyethanol for the second stage [25].

APT measurements of five million atoms were performed at a specimen temperature of 40–60 K, total probe voltage of 8–15 kV, pulse fraction of 20%, and pulse frequency of 20 kHz. FIM images were observed at 90 K using neon as the imaging gas. The crystallographic direction of dislocations and grain boundaries in three-dimensional (3D) elemental maps was determined by the FIM pole-fitting method [26]. Atomic data sets were analyzed using IVAS software (version 3.6.4). Peaks of 27, 28, 28.5 and 29 Da were assigned to Fe^{2+}, a peak of 27.5 Da to Mn^{2+}, peaks of 31 and 46.5 Da to Nb^{3+} and Nb^{2+}, respectively, peaks of 5 and 5.5 Da to B^{2+}, peaks of 10 and 11 Da to B^{+}, peaks of 25, 26 and 26.5 Da to Cr^{2+}, peaks of 10.3 and 15.5 to P^{3+} and P^{2+}, peaks of 31.5 and 32.5 Da to Cu^{2+}, Peaks of 63 and 65 to Cu^{+}, peaks of 14, 14.5 and 15 Da to Si^{2+}, peaks of 30.7, 31.3, 31.7, 32, 32.3, 32.7, 33.3 Da to Mo^{3+}, and peaks of 46, 47, 47.5, 48, 48.5, 49, 50 Da to Mo^{2+} in the mass-to-charge spectrum. Carbon is normally assigned as peaks at 6 Da (C^{2+}) and 12 Da (C^{+}), but such peaks were not observed in the steel, indicating that most solute carbon was scavenged by carbide precipitation with niobium and titanium. Nitrogen is assigned as a peak at 14 Da (N^{+}), which overlaps with the main isotopic peak of Si^{2+}. But locally enriched nitrogen can be identified by the peak.

3. Experimental result

Fig. 1 shows TEM bright field images of the niobium added stainless steel. Grain size was in the range of several micrometers, and a slightly high number density of dislocations was observed in each grain. Fine particles locking the dislocations were not observed with TEM although submicron-sized particles of chromium intermetallic compounds were occasionally observed in the grains and at the grain boundaries. The dislocations were almost homogeneously distributed within the grains although the dislocation cell like structures were occasionally observed. The dislocation density in the region with homogeneous distribution of dislocations was estimated to be about 1.8×10^{10} cm^{-2} with TEM. The density means that the analyzed volume of 5 million atoms (168000 nm^{-3}; *e.g.*, ~40 nm × 40 nm × 105 nm) has a dislocation line of about 30 nm on average, where the ion detection efficiency is 0.35 in 3DAP. This suggests that the dislocation included in the analyzed volume may be about 50% in the dataset of 5 million atoms.

Fig. 2a shows 3D elemental maps within a grain in the steel, obtained by APT measurement in a random direction. Niobium atoms were homogeneously in solid solution. The niobium concentration (~0.28 at.%) in the analyzed volume was nearly coincident with the excess niobium estimated by subtracting the content of (Nb,Ti)(C,N) precipitates from the total content (Table 1). Niobium-enriched regions were observed as curved lines, which are indicated by the arrow heads. To visualize the enriched regions clearly, the isoconcentration surface of 1.2 at.% is represented in Fig. 2b. Neither carbon nor nitrogen was observed in the niobium-enriched regions, indicating that the niobium-enriched regions correspond not to precipitation such as carbide and nitride, but to

Table 1
Chemical comparison of the niobium ferritic stainless steel.

	C	Si	Mn	P	Cr	Mo	Cu	Ti	Nb	N	B
mass%	0.008	0.21	1.02	0.025	16.95	0.31	1.25	0.12	0.53	0.013	0.0008
at.%	0.037	0.42	1.04	0.045	18.20	0.18	1.10	0.14	0.32	0.052	0.0041