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Atom probe analysis on interaction between Cr and N in bake-hardening steels with anti-aging properties at RT

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ABSTRACT

One-dimensional atom probe (1DAP) analysis was performed on chromium and nitrogen added bake hardening steel sheets that have both high bake-hardenability and anti-aging properties at room temperature (RT). The atomic data of more than 2 million atoms were collected for sample steels with and without low-temperature aging after recrystallization annealing and quenching. The correlation in atomic position between chromium and nitrogen atoms in a solid solution was investigated by a statistical analysis using the binomial distribution function. In the samples with low-temperature aging, the probability that a chromium atom was observed near a nitrogen atom was significantly higher than that estimated from the null hypothesis that there was no attractive atomic interaction. This suggests that there is an attractive interaction between a nitrogen atom and a chromium atom in bcc iron, which led to the anti-aging properties at RT. In contrast, such correlation was not observed definitely in the samples without low-temperature aging, which implied that the atomic pair formation is a thermal activation process.

1. Introduction

Paint bake-hardening (BH) steel sheets have been widely used for the automotive outer panels because of their deep drawability and certain dent resistance. In addition to high bake-hardenability, the anti-aging property at room temperature (RT) is required for suppressing stretcher-strain during forming in the steel sheets. However, it is not easy to realize these two conflicting properties simultaneously [1–4]. With increasing solute content of carbon and nitrogen, both RT aging and BH hardening are enhanced. In contrast, with decreasing solute content, the RT aging as well as the BH hardening decrease [2–4].

Recently, BH steel sheets with high bake-hardenability and anti-aging property have been developed with the addition of chromium (Cr) and nitrogen (N) [5]. In the steel, N was used as strengthening interstitial element instead of carbon (C). Maruyama et al. proposed a hypothesis that the RT aging is suppressed by the reduction of the diffusion of N atoms in ferrite because of an attractive interaction between N and Cr atoms [5]. This hypothesis suggests that atomic pairs of Cr and N form in the matrix at the viewpoint of snapshot. Observation of the atomic pairs in the steel confirms the hypothesis.

Atomic pairs consisting of an interstitial atom and a substitutional atom in steel are considered to play an important role for recovery, recrystallization, phase transformation, and creek properties [6–8]. However, they are difficult to observe in steels because analytic techniques with atomic sensitivity and resolution are necessary. It is expected that atomic scale analysis using atom probe is suitable for the direct observation of the atomic pairs. Using field ion microscopy and one-dimensional atom probe, Murayama et al. actually detected Mo–N atomic pairs in the austenitic stainless steel, which was attributed to the improvement in the fatigue properties. The Mo–N pairs were identified as bright spots on the FIM image and Mo–N molecular ions were detected in the atom probe mass spectrum of nitrogen doped samples only [9].

Interaction energy between an interstitial atom and a substitutional atom in bcc Fe has been systematically investigated by the internal friction method and combustion analysis method [10–13]. The interaction energy between Cr and N in bcc Fe was estimated to be −0.18 eV from the analysis of the Snoek peak by the internal friction method [13]. First-principles calculations were also applied to the issue [14,15]. Table 1 shows the interaction energy between an interstitial atom and a substitutional atom in bcc Fe. The experimentally determined values of interaction energy are

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Table 1
Interaction energy between an interstitial and a substitutional atom in bcc Fe, examined by internal friction, combustion analysis [10–13] and first-principles calculation [14,15].

	Internal friction (eV)	Combustion analysis (eV)	First principles calculation (eV)
Cr–N	−0.18	–	0.12
Mo–N	−0.18	−0.18	0.55
Mn–N	−0.09	−0.19	–
V–N	−0.21	–	0.06
Cr–C	–	–	0.17*
Mo–C	−0.16	−0.18	–
Mn–C	−0.14	–	0.21*

* Average values of the 1st to 5th nearest sites (0 °C).

not consistent with the values estimated by *ab initio* calculations. Most of the elements have attractive interactions based on internal friction measurements, and contrarily, a repulsive interaction by first-principles calculations. The interaction energy between a C atom and a dislocation was reported to be 0.50–0.75 eV [4], which was significantly larger than those between interstitial and substitutional atoms.

In this study, the existence of Cr–N atomic pairs in the Cr and N added BH steels is investigated by using one-dimensional atom probe (1DAP) analysis to clarify the mechanism of anti-aging properties at RT. The correlation in atomic position between Cr and N is analyzed by a statistical analysis technique using the binomial distribution function. We discuss the existence of Cr–N atomic pairs and the cause of anti-aging properties.

2. Thermodynamic calculation of atomic pair formation

In this section, we discuss the ratio of atomic pair formation using thermodynamic calculation. N trapping ratio, namely, ratio of the Cr–N atomic pair formation was calculated on the basis of the thermodynamic model assuming that Cr and N have a small attractive interaction. The following three assumptions were adopted in the calculation.

(i) Cr atoms homogeneously distribute substitutionally in bcc Fe.
(ii) N atoms can be trapped on one of six first nearest interstitial sites of a Cr atom as the Cr–N atomic pair.
(iii) N atoms can occupy at most one of the six nearest interstitial sites of Cr.

The total number of arrangements in the system is given by

$$W = \frac{(aN_s)!}{(nx)!(aN_s-nx)!}\cdot\frac{(3N-aN_s)!}{\{n(1-x)\}!\{3N-aNs-n(1-x)\}!}\cdot 6^{nx} \quad (1)$$

where N_s, n, a, and N are the numbers of Cr atoms, N atoms, trap sites for a Cr atom, and the total atoms including matrix Fe, respectively. Here, the total number of interstitial sites is $3N$ in the bcc lattice structure. On the right-hand side of the equation, the first and second terms correspond to the number of arrangements for Cr and N sites, respectively. The third term corresponds to the number of arrangements for the nearest interstitial sites of N around Cr atoms. According to the assumptions, a is set to be 1 in Eq. (1). Thus, the free energy is given by

$$F(x,T) = \Delta Enx - kT\ln W \quad (2)$$

where x and ΔE are the trapping ratio and the interaction energy between Cr and N, respectively. Using the condition of minimizing the free energy, the trapping ratio is obtained by

$$x = \frac{B-\sqrt{B^2+4(n/N)(N_s/N)(A-1)}}{2(1-A)(n/N)} \quad (3)$$

where

$$A = \frac{\exp(\Delta E/kT)}{6} \quad (4)$$

and

$$B = A(3-N_s/N-n/N)+N_s/N+n/N \quad (5)$$

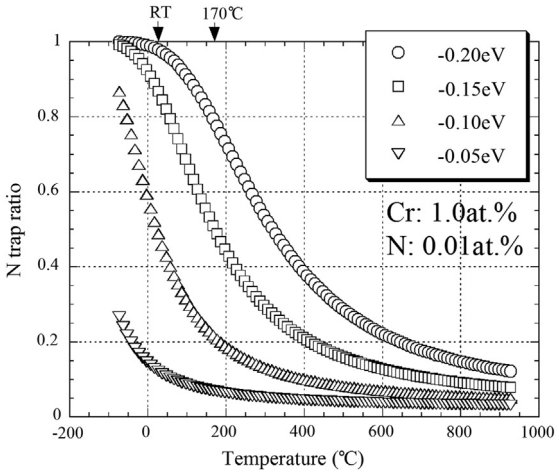

Fig. 1. Temperature dependence of N trapping ratio because of Cr–N atomic pair formation for various interaction energies, obtained by thermodynamic free energy calculation.

Fig. 1 shows N trapping ratios as a function of temperature with various interaction energies, obtained by the calculation, where Cr and N atomic concentrations are 1.0 and 0.01 at% respectively, which approximately corresponds to concentrations in our sample steels (Table 2). In the interaction energy of −0.15 eV, the trapping ratio is about 0.8 at RT and less than 0.5 at 170 °C. It is expected that the formation of Cr–N atomic pairs suppresses the diffusion of N atoms in the steel at RT, while N atoms dissolved from the atomic pairs contribute to bake hardenability at 170 °C. If the interaction energy is in the range of −0.10 to −0.20 eV, high BH property is expected while the diffusion of N is suppressed at RT. It should be noted that N atoms are not trapped to Cr atoms around 800 °C, which corresponds to the annealing temperature for recrystallization. This reveals that the formation of Cr–N atomic pairs is thermally equilibrium at low temperatures. Therefore, to observe the atomic pairs using atom probe, the samples with aging at low temperatures must be investigated.

3. Cr and N added BH steels

3.1. Sample steels

We prepared three sample steels containing different contents of Cr and N. The chemical compositions (at%) of the steels are shown in Table 2. 0Cr is the reference sample steel containing N without Cr addition, and 0.5Cr and 1Cr are sample steels containing N and Cr of the different contents, where the contents of N and Cr in 1Cr sample is about twice as much as those in 0.5Cr sample. The amount of C was suppressed as little as possible since C significantly influences the aging properties. Further, the amount of Si was also suppressed since a peak of $^{28}Si^{2+}$ overlaps with that of $^{14}N^{+}$ in the mass-to-charge spectrum. Each cast slab was hot-rolled in works, and then cold-rolled by 80% reduction to 0.8 mm