Effect of Nb Contents on Size of Ferrite Grains in Ultra-Low Carbon Steel for Cans[†]

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Abstract:

Soft-tempered and fine-grained steel is preferred for film-laminated steel sheets for drawn cans in view of surface deterioration resistance and high formability. Although Nb-added ultra-low carbon steel is used for forming application of cans, the problem of surface deterioration resistance still remains after drawing and ironing. In this study, the further grain refinement of conventional Nb-added ultra-low carbon steel has been attempted. As a result, carbon and niobium contents having an excellent balance of grain size and steel plate strength has been found.

1. Introduction

The need to reduce environmental loads in recent years has led in heightened calls to reduce generation of greenhouse gases (GHG) and discharges of volatile organic compounds (VOC), including the field of surface treatment of steel sheet can materials. In response to these trends, laminated steel sheets coated with an organic resin such as polypropylene or polyethylene terephthalate (PET) have attracted strong interest because the paint baking process and cleaning process can be omitted.

As a substitute for the conventional drawing and ironing (DI) process, the stretch draw and ironing process is suitable for these laminated steel sheets. Beverage cans produced by this process have already been deployed in the market[1], and various knowledge specific to composite materials consisting of steel sheets and films has also been obtained. According to Imazu, rough surface of the steel sheet accompanying forming should be minimized from the viewpoint of avoiding film damage, and it is desirable to apply fine-grained steel corresponding to the balance of the crystal grain size before forming and the degree of forming[2]. On the other hand, soft-tempered steel, which can reduce forming contact pressure, is effective for improving formability and preventing film hair[3]. However, as properties of steel, a mutually contradictory relationship exists between the properties which are desirable in the laminated steel sheets described here, namely, a fine-grained structure and soft-tempered property. The strength of steel sheets for cans is classified by the index called "temper grade," which is specified by Rockwell hardness HR30T, and sheets with various temper grades are used appropriately corresponding to the application[4, 5]. When using steel sheets as the substrate for laminated steel sheets, the above-mentioned problems are avoided by selecting a suitable combination of film thickness, forming die and forming conditions, etc., using low carbon steel of temper grade T3 to DR8 with a proper balance of crystal grain size and strength.

In this research, we studied the possibility of simultaneously realizing both grain refinement and a soft-tempered property, which had been difficult as properties of general steels, in a steel sheet substrate for laminated steel sheets. As steel sheets with an excellent deep drawing property, past research showed that a fine-grained structure and satisfactory r-value can be obtained with IF (Interstitial Free) steel with addition of Nb or compound addition of Nb and Ti to ultra-low carbon steel, in comparison with ultra-low carbon steel without addition of alloying elements[6, 7], but this

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did not lead to a fine-grained steel that can withstand use as the substrate for laminated steel sheets, as described above. Because grain refinement of ferrite by the solute drag effect and pinning effect can be expected by use of Nb, this report describes the results of an investigation of the effect of the Nb content on the size of ferrite grains and strength of the steel sheet with various composition ratios of C and Nb. Concretely, ultra-low carbon steel sheets with C contents of 16 ppm to 66 ppm were used as the base material, as a soft-tempered property can be expected with these materials, grain refinement was attempted by controlling the contents of C, Mn and Nb, and the effect of the contents of these elements on the size of the ferrite grains and the hardness of the steel sheets was investigated.

2. Experimental Method

Table 1 shows the chemical compositions of the steels used in this experiment. Slabs with a thickness of 22 mm were forged from vacuum-melted steel ingots of the specified steel composition, using ultra-low carbon steels with C contents of 0.0016–0.0066% as the base material. Hot rolling was performed after heating at 1 250°C for 1 h, followed by finish rolling at 900°C and water quenching to the coiling equivalent temperature of 580°C. The specimens were inserted directly into an

Table 1 Chemical compositions of steel used in experiment (mass%)

Steel	Chemistry (mass%)					Nb/C
	C	Mn	Al	N	Nb	
Steel A-1	0.0019	0.13	0.054	0.0029	0.018	1.2
Steel A-2	0.0020	0.13	0.053	0.0027	0.039	2.5
Steel A-3	0.0016	0.14	0.048	0.0029	0.097	7.8
Steel B-1	0.0064	0.13	0.061	0.0022	0.020	0.4
Steel B-2	0.0065	0.13	0.051	0.0023	0.057	1.1
Steel B-3	0.0062	0.13	0.053	0.0021	0.097	2.0
Steel C-1	0.0066	0.60	0.050	0.0023	0.020	0.4
Steel C-2	0.0063	0.60	0.050	0.0029	0.058	1.2
Steel C-3	0.0063	0.61	0.051	0.0025	0.102	2.1

electric furnace which had been set in advance to the coiling equivalent temperature, held for 1 h, and then cooled to room temperature in the furnace. After cooling, the specimens were removed from the furnace and the surface scale was removed by grinding. The specimens were cold rolled from 2.8 mm to 0.24 mm and annealed at 750°C for 45 s by the electrical heating method, which was followed by 1.5% temper rolling. Hardness was measured from the tempered rolled sheets based on the Rockwell superficial hardness test (HR30T).

As the optical microstructure, the ferrite microstructures of the cross section in the rolling direction
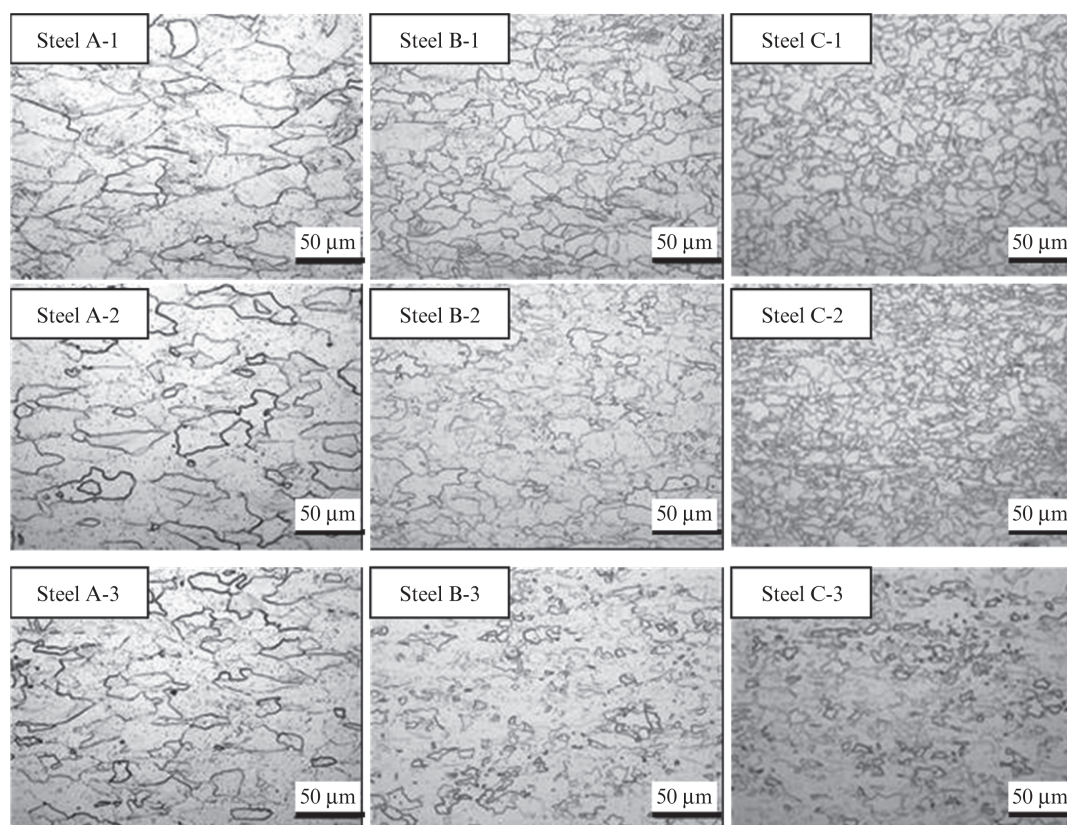
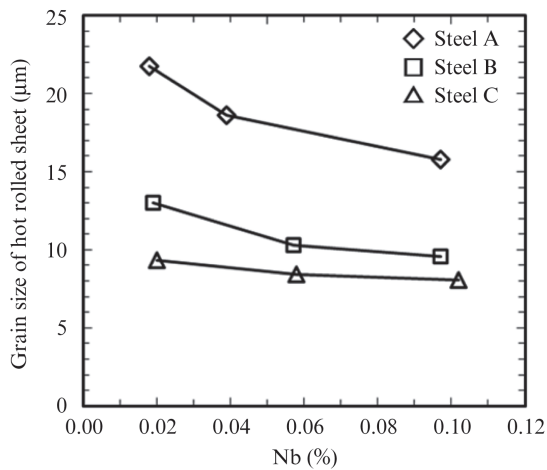Photo 1 Cross-section microstructures of hot rolled sheets

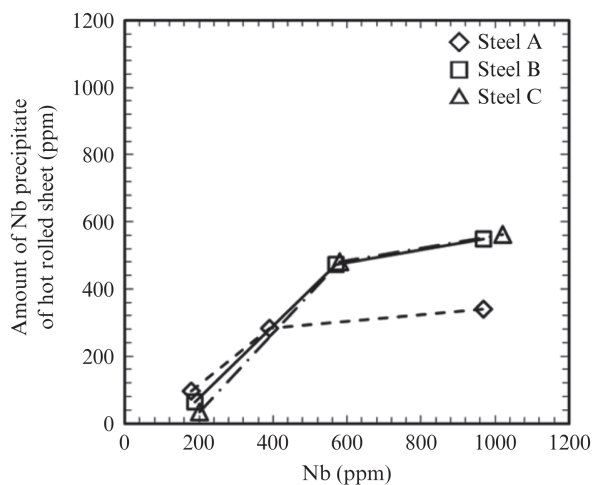Fig. 1 Relationship between Nb addition and grain size of hot rolled sheet

Fig. 2 Relationship between Nb addition and amount of Nb precipitate of hot rolled sheet

Fig. 3 Relationship between Nb addition and grain size and HR30T of annealed sheet

were observed in the hot rolled sheets and temper rolled sheets, and the average crystal grain size was obtained by the intercept method. The content of Nb precipitate in the steel was determined by inductively coupled plasma-atomic emission spectrophotometry (ICP-AES) analysis of the extracted residue obtained by constant current electrolysis (20 mA/cm^2) in a 10% acetyl acetone-1% tetramethyl ammonium chloride-methanol solution. As the precipitate morphology, after sampling the precipitates by the extraction replica method, the size of the precipitates was measured by observation using a transmission electron microscope (TEM), and the precipitates were identified by energy dispersive X-ray spectroscopy (EDX).

3. Experimental Results

3.1 Ferrite Microstructure of Hot-Rolled Sheets

The cross-sectional microstructures after hot rolling are shown in **Photo 1**. The coarsest hot-rolled sheet
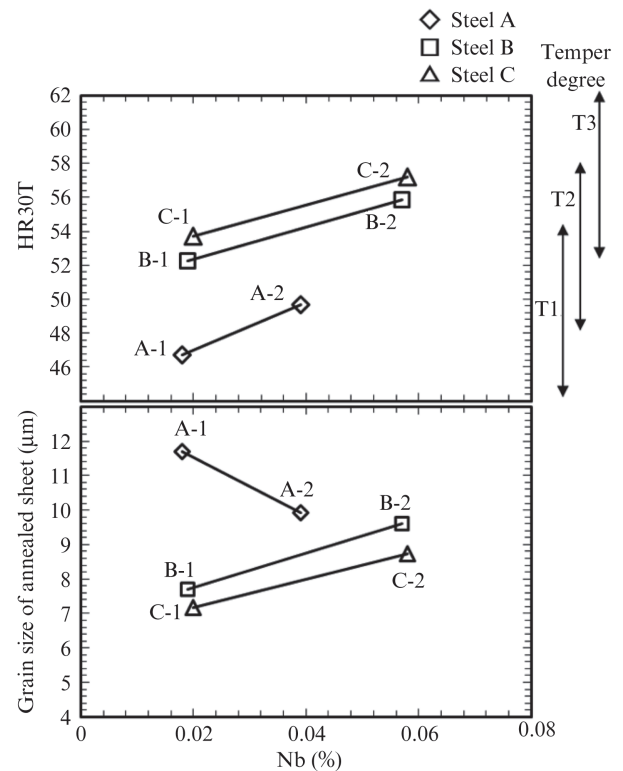
grain size was observed in Steel A, and the grain size was finer in Steel B and Steel C in that order. Furthermore, as shown in **Fig. 1**, the hot-rolled sheet grain size became finer as Nb addition increased in all of the Steels A, B and C. The relationship between the amount of addition and the amount of Nb precipitate is shown in **Fig. 2**. The increment of the amount of Nb precipitate decreased in the region where Nb/C>1.

3.2 Ferrite Microstructure of Annealed Steel Sheet

The cross-sectional microstructure after annealing is shown in **Photo 2**. In Steel A-3, Steel B-3 and Steel C-3, recrystallization was not completed, as an unre-crystallized microstructure remained after annealing. The relationship between Nb addition and the grain size and HR30T is shown in **Fig. 3**. As Nb addition increased, the grain size of the annealed sheets became finer in Steel A, but coarsening of the grain size of the annealed sheets occurred in Steels B and C. The grain sizes of Steel B-1 and Steel C-1 are finer than that of Steel A-1, which is a conventional Nb-added ultra-low carbon steel, and the former two steels also show hardness of around the median value, i. e., temper grade T2, which is softer than the temper grade T3 steel used in DI forming applications. Thus, Steel B and Steel C have characteristics which are close to suitable for film laminated steel sheets for DI forming. **Figure 4** shows the relationship between Nb addition and the amount
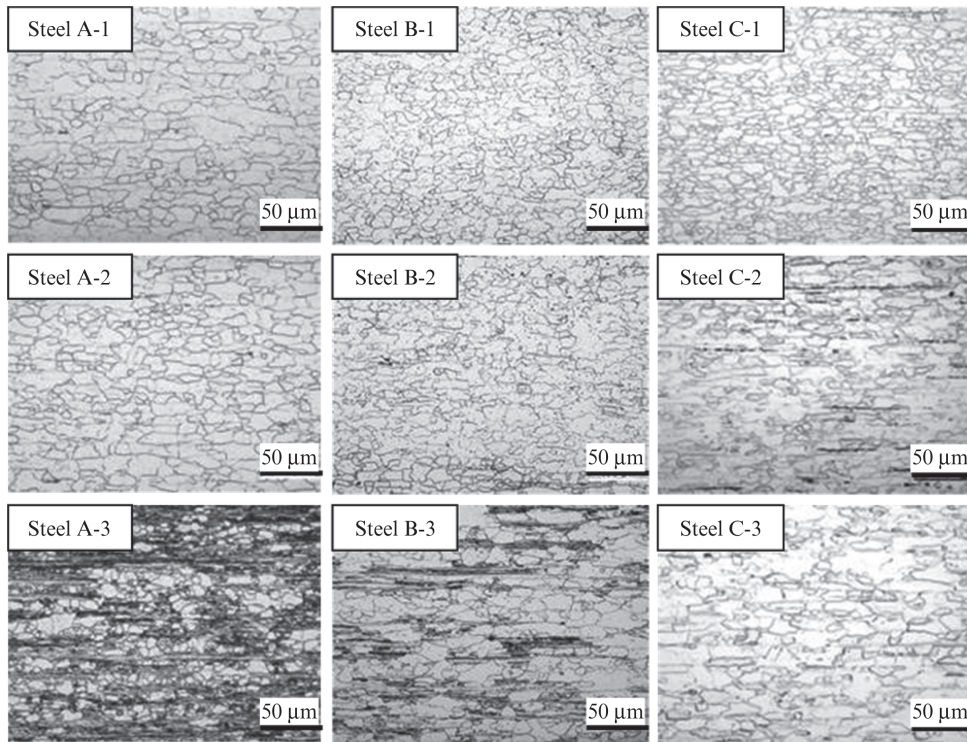
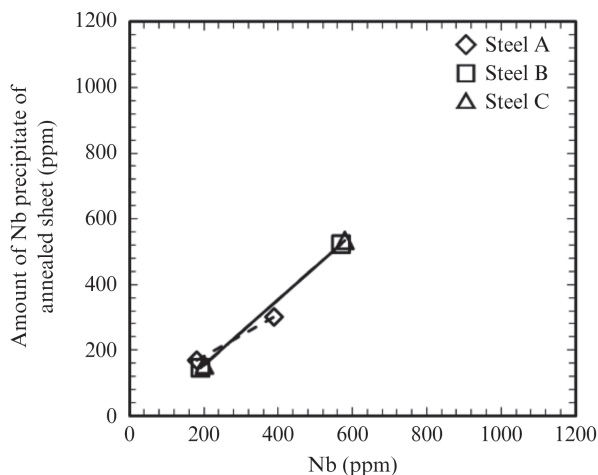Photo 2　Cross-section microstructures of annealed sheets

Fig. 4　Relationship between Nb addition and amount of Nb precipitate of annealed sheet

Photo 3　TEM image of Nb precipitates of annealed sheet

of Nb precipitate of the annealed sheets. At all levels, the amount of Nb precipitation increased with the amount of Nb addition.

3.3 Condition of Precipitate Dispersion

As shown in the previous section, in Steels B and C, coarsening of the grain size of the annealed sheets occurred irrespective of increases in the amount of Nb addition in the annealed sheets. TEM observation of the precipitates of the annealed sheets was performed to determine the cause of this behavior in detail. Although the Mn contents of Steel B and Steel C are different, from Fig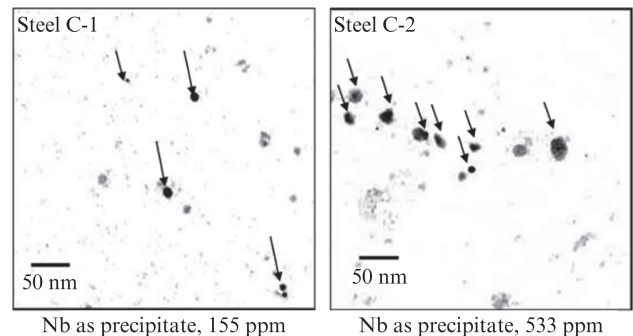. 4, the behavior of the change in the amount of Nb precipitation accompanying Nb addition can be regarded as substantially the same in both steels. Therefore, this section will describe Steel C, in which finer grains were obtained.

Photo 3 shows the results of TEM observation of the precipitates of Steel C-1 and Steel C-2. An analysis of the precipitates shown by the arrows in Photo 3 revealed that these precipitates were Nb carbonitrides (Nb (C, N)). **Figure 5** shows the condition of distribution of the individual Nb precipitates and the grain size measured from the area of the precipitates in the observation photographs for all of the precipitates analyzed in other measured views. The number of fine Nb precipitates that formed in Steel C-1 was larger than that in Steel C-2. The average grain sizes of the Nb precipitates in Steel C-1 and Steel C-2 were 6.9 nm and 9.3 nm, respectively.
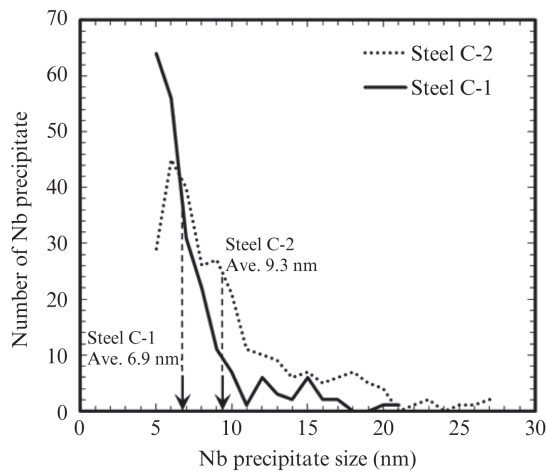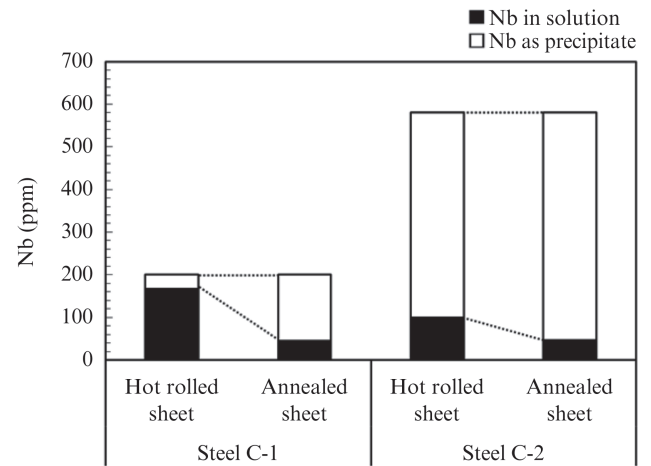
Fig. 5   Distribution of Nb precipitates size

Fig. 6   Comparison of Nb amount between hot rolled and annealed sheets of Steel C

4. Discussion

As an approach to refinement of the ferrite grain size, the effect of Nb addition on grain size was investigated using steels with different contents of C and Nb. The following results were obtained.

1) In the hot-rolled steel sheets, the ferrite grains were more refined in Steel B and Steel C, which had C contents of 62–66 ppm in comparison with Steel A, which a C content of 16–20 ppm.

2) In the annealed sheets, the ferrite grain size was refined with increasing Nb addition in Steel A, but coarsened with increasing Nb addition in Steels B and C.

In result 1), because Nb addition suppresses recrystallization of austenite during hot rolling, it is thought that the ferrite grains are refined accompanying the refinement of austenite by that effect. The amount of C addition in Steels B and C is larger than that in Steel A, and Steel C also contains a large amount of added Mn. Since carbides and other precipitates such as MnS form in greater number, the increase number of nucleation sites originating from those precipitates and suppression of ferrite grain growth after the ferrite transformation due to lowering of Ar_3 transformation temperature are considered to be factors in grain refinement.

In result 2), the cause of coarsening of ferrite grains by increased addition of Nb will be discussed. **Table 2** and **Fig. 6** show the results of a calculation of the amount of solute Nb in the hot-rolled sheet and annealed sheet based on the amount of Nb precipitates in those respective conditions. Solute Nb in the hot-rolled sheet of Steel A increases with increasing Nb addition, whereas solute Nb decreases with increasing Nb addition in Steel B and Steel C. It is known that solute Nb delays the progress of recrystallization by the solute drag effect, which suppresses grain boundary migration[8]. Since Steels B-2 and C-2 had small contents of solute Nb before annealing in spite of their large contents of added Nb, it is thought that grain coarsening was greater in those steels than in Steels B-1 and C-1, in which recrystallization was suppressed by the solute drag effect.

In addition to the drag effect of solute Nb, the pinning effect is also thought to influence grain size. Therefore, the pinning effect will be discussed in the following. In general, the amount of precipitation increases with increasing Nb addition. However, focusing on the Nb precipitation during annealing, the increment of Nb precipitation decreases accompanying larger addition of Nb. From the viewpoint that all of the Nb precipitates in Steel B and Steel C demonstrate

Table 2   Amount of solute Nb and Nb precipitate in hot rolled sheet and annealed sheet (ppm)

Steel	Total C	Total N	Total Nb	Hot rolled sheet		Annealed sheet		Increment of Nb precipitate in annealing
				Nb precipitate	Sol.Nb	Nb precipitate	Sol.Nb	
Steel A-1	19	29	180	95	85	168	12	73
Steel A-2	20	27	390	282	108	301	89	19
Steel B-1	64	22	190	65	125	166	24	101
Steel B-2	65	23	570	474	96	523	47	49
Steel C-1	66	23	200	33	167	155	45	122
Steel C-2	63	29	580	480	100	533	47	53

a pinning effect, the ferrite grains in steel with heavy addition of Nb should be refined, but the experimental result is different. Therefore, the pinning effects of the total amount of Nb precipitate and the increment of Nb precipitate during annealing were compared in Steel C-1 and Steel C-2.

According to a study by Zener[9], pinning force P can be expressed by Eq. (1), where, σ is grain boundary energy, f is the volume fraction of dispersed particles and r is the mean particle radius of the dispersed particles.

$$P = 3\,\sigma \cdot f/r \quad \text{...} \quad (1)$$

Pinning force is affected by the volume fraction of dispersed particles (Nb precipitates) and the grain size of the dispersed particles, and the action that suppresses grain growth is strengthened by dispersing a large amount of fine particles. Assuming that the grain boundary energy is the same, the magnitude relationship of pinning force can be shown by f/r. **Table 3** shows the results of a calculation of the volume fraction f from the mean particle size r of NbC and the amount of Nb precipitate in Steels C-1 and C-2, the density of NbC (7.6 g/cm^3) based on those values, and the density of steel (7.85 g/cm^3) for the case in which all of the NbC precipitate is assumed to be NbC.

Here, the measurement result shown in Fig. 5 was used for the mean particle size of NbC. Calculations were performed using the total Nb precipitate after annealing and the increment of the Nb precipitate by annealing as the amounts of Nb precipitate. When calculated using the increment of Nb precipitate by annealing, the pinning force of Steel C-1 is greater than that of Steel C-2, which is consistent with the fact that the grain size of the annealed sheet displayed coarsening. This suggests the possibility that the Nb precipitates formed during annealing demonstrate the pinning effect more strongly than the Nb precipitates prior to annealing. However, in order to discuss the contribution of the pinning effects of these respective precipitates, a more detailed investigation will be necessary, including an analysis of the morphology of the precipitates in the hot-rolled sheets, etc.

From the above discussion, the factors in the coarsening of the grain size in the annealed sheets of Steel B and Steel C with increased Nb addition are estimated

Table 3   Ratio of NbC volume fraction to size in annealed sheet

	Steel	NbC (ppm)	r (nm)	f	f/r
Total Nb precipitate	Steel C-1	155	6.9	1.60×10^{-4}	2.32×10^{-5}
	Steel C-2	533	9.3	5.51×10^{-4}	5.92×10^{-5}
Increment of Nb precipitate	Steel C-1	122	6.9	1.26×10^{-4}	1.83×10^{-5}
	Steel C-2	53	9.3	5.47×10^{-5}	5.89×10^{-6}

to be the small content of solute Nb prior to annealing and the decrease in Nb precipitation during annealing.

5. Conclusion

As a fundamental study of laminated steel sheets for DI cans having fine-grained structure like that in low carbon steel in combination with a soft-tempered property like that of ultra-low carbon steel, the effect of the C and Nb contents of ultra-low carbon steel on ferrite grain size was investigated. As a result, the following knowledge was obtained.

(1) After hot rolling, refinement of the ferrite grain size with increasing Nb contents of the steel was observed in the 16–66 ppm C steels.

(2) Refinement of ferrite grains with increasing Nb contents was also observed in the 16–20 ppm C steels after annealing, but coarsening of ferrite grains with increasing Nb contents occurred in the 62–66 ppm C steels.

(3) A grain size of 7.1–$7.5\,\mu$m and temper grade equivalent to T2 were achieved in 62–66 ppm C steel with 0.02% Nb addition.

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