Effects of Mn and S on the Grain Growth and Texture in Cold Rolled 0.5 % Si Steel

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The effects of manganese and sulphur on the grain growth and texture development during isochronal annealing have been investigated for cold rolled 0.5 % Si steel. Although both Mn and S affect the grain growth, its dependency on Mn content is influenced by the S level. In steels containing 0.004 to 0.017 % S, an increase in Mn content promotes the grain growth through decreasing the amount of fine manganese sulphide particles. In ultra-low S steels containing less than 0.001 % S, however, the grain growth is inhibited with Mn addition by the precipitation of manganese silicon nitride (MnSiN_2). On the other hand, the changes in recrystallization texture being accompanied by grain growth depend only on Mn content, a higher Mn content results in an increase in {222} component. This fact is considered to be related to the change in solute N content being counterbalanced with MnSiN_2 precipitation.

KEY WORDS: grain growth; texture; silicon steel; recrystallization; precipitation; cold rolled product.

1. Introduction

Fine second-phase particles play an important role in the recrystallization of cold rolled sheet steels. In Al-killed steels, the fine precipitation of AlN has been utilized effectively for controlling the texture favorable for deep-drawing.¹⁾ To the contrary, any precipitate inhibiting grain growth is generally avoided for non-oriented electrical steels, in which Al free steels are occasionally applied.²⁾ The core loss of non-oriented electrical steels is affected by ferrite grain size, precipitates and crystalline texture.³⁾ Usually no sharp texture is formed in commercial process of non-oriented electrical steels, therefore ferrite grain size and precipitates would be main factors affecting the core loss. Especially precipitates are important factor because they have harmful effect on the core loss as a result of not only inhibiting grain growth but also obstructing domain wall motion.

In the case of steels containing a trace amount of Al, MnS particles would become one of the important factors affecting recrystallization. The effect of MnS on the recrystallization and grain growth behavior of rimmed steels had been investigated,⁴⁻⁶⁾ but there are less studies on rimmed steels after the introduction of continuous casting. On the other hand, the influence of manganese silicon nitride (MnSiN_2) on the creep properties⁷⁾ and strain aging⁸⁾ in Si steels are also reported. It is expected that the recrystallization and grain growth behavior of steels containing Si but a trace amount of Al, such as some kinds of non-oriented electrical steels, may be influenced by MnS and/or MnSiN_2 . However, there has been no information on this subject.

In the present study, the authors have investigated the effects of MnS and MnSiN_2 on the recrystalliza-

tion and grain growth behavior in Al free 0.5 % Si steels containing various amounts of Mn and S.

2. Experimental Procedure

Ingots of test steels, the chemical composition being given in Table 1, were prepared by melting in a 50 kg vacuum induction furnace. The base material was an ultra-low carbon steel containing 0.5 % Si but a trace amount of Al, and the oxygen was reduced as low as possible. The composition of the steels covers 3 levels of sulphur {0.0003 % (steels A-1 to A-4), 0.004 % (steels B-1 to B-4), 0.017 % (steels C-1 to C-4)} and various amounts of Mn from 0.05 to 0.97 %. Phosphorus was added to control the hardness of the steels. The ingots were hot-forged to 30 mm in thickness.

The processing after the hot-forging is schematically shown in Fig. 1. The slabs were heated to 1 250°C and kept for 1 h, then hot rolled to 3 mm in thickness by 4 passes with the finishing temperature of 850°C.

Table 1. Chemical composition of test materials. (mass%)

Steel	C	Si	Mn	P	S	sol. Al	N	O
A-1	0.0025	0.50	0.05	0.063	0.0003	<0.001	0.0032	0.004
A-2	0.0013	0.50	0.10	0.065	0.0003	0.001	0.0033	0.004
A-3	0.0015	0.50	0.30	0.066	0.0003	0.001	0.0037	0.003
A-4	0.0014	0.50	0.94	0.068	0.0005	0.001	0.0039	0.003
B-1	0.0045	0.52	0.07	0.073	0.0044	0.001	0.0026	0.003
B-2	0.0043	0.49	0.11	0.059	0.0044	0.001	0.0025	0.003
B-3	0.0010	0.50	0.29	0.064	0.0044	<0.001	0.0041	0.005
B-4	0.0044	0.50	0.86	0.068	0.0047	0.001	0.0029	0.003
C-1	0.0046	0.51	0.07	0.066	0.016	0.001	0.0028	0.003
C-2	0.0048	0.51	0.11	0.065	0.017	0.001	0.0027	0.003
C-3	0.0022	0.51	0.30	0.066	0.017	0.001	0.0027	0.004
C-4	0.0020	0.50	0.97	0.066	0.017	<0.001	0.0030	0.004

Fig. 1. Processing for test materials.

In order to simulate the coiling condition after a tandem-mill, the hot-bands were air-cooled to 500°C, annealed for 1 h in a furnace kept at 500°C, and cooled to room temperature with a rate of 20°C/h. To prepare a uniform and homogeneous microstructure, the hot-bands were machined from both surfaces to 2.3 mm in thickness and annealed at 800°C for 1 h in Ar atmosphere. The equiaxial ferrite grains of average grain size between 50 and 70 μm were obtained after hot-band annealing. The grain size of the hot-band has been known to have an influence on the recrystallization texture,⁹⁾ but the change in the grain size in the present study could be regarded to be within a range which exerts little influence on the texture. The hot-bands were cold rolled to 0.5 mm in thickness with a total reduction of 78 %.

The cold rolled sheets were subjected to an isochronal annealing of 1 min steps at an interval of 50°C from 600°C up to 900°C by immersing in a salt bath followed by air-cooling. This treatment was intended to study the metallurgical changes during continuous annealing process. The salt was a mixture of BaCl_2 , KCl , NaCl . Since A_{c3} transformation point was near 900°C in the high Mn steels, the maximum annealing temperature was confined to 900°C.

Ferrite grain size and inverse pole intensity were measured for each step of the isochronal annealing. The ferrite grain size was measured on the longitudinal section with an optical microscope of 100 magnifications by the comparative method. The inverse pole intensities for {110}, {200}, {211} and {222} planes parallel to the sheet surface were measured at quarter thickness with Mo-K α radiation as multiples of those respective intensities of a random-oriented specimen. Precipitates were observed after the hot-band annealing and at each step of the isochronal annealing with a transmission electron microscope by the blank replica method. The amounts of nitrides before and after hot-band annealing were measured by the extraction method using bromine-ester.

3. Experimental Results

3.1. Effects of Mn and S Contents on Recrystallization and Grain Growth

The changes in the fraction recrystallized during isochronal annealing are shown in Fig. 2 for several steels. Primary recrystallization is completed in every

Fig. 2. Influence of Mn and S contents on recrystallization process during isochronal annealing.

Fig. 3. Change in grain size during isochronal annealing.

steel in a temperature range between 650 and 700°C. The recrystallization is somewhat delayed with increasing Mn content, while it shows little change with increasing S content. Manganese in solution seems to cause a delay of recrystallization.¹⁰⁾ However, the effects of Mn and S contents on the rate of recrystallization are negligible small in the present study.

Fig. 3 shows the change in grain size during isochronal annealing. The grain size immediately after the completion of primary recrystallization at 650–700°C is almost same regardless of the chemical composition of the steel. However, the rate of grain growth at higher temperatures depends remarkably on the Mn and S contents. The grain growth was promoted by a decrease in S content. This phenomenon can be qualitatively explained by Zener's theory^{11,12)} in which the equilibrium grain size is considered to be inversely proportional to the volume fraction of MnS precipitates. The effect of Mn content on the grain growth is rather complicated. In the case of a high S content (0.017 % S), the grain growth is promoted with an increase in Mn content. Such a tendency has already been observed in rimmed steels.¹³⁾ According to the previous study,¹³⁾ the amount of fine MnS particles which precipitate during hot rolling decreases as the Mn content is increased. On the basis of Zener's theory,^{11,12)} the equilibrium grain size becomes larger as the size of MnS particles is increased. In the case of an ultra-low S content (0.0003 % S), however, the grain growth is retarded with an increase in Mn content. This phenomenon cannot be explained by considering only the size of MnS particles.

The grain size after heating up to 850°C is shown

in Fig. 4 as a function of Mn content for 3 levels of S content. The effect of Mn addition on the grain size is inverted at a certain S level. The data given in Fig. 4 are insufficient to tell the critical content of S at which such an inversion occurs, but it must be around 0.001 % S.

3.2. Effects of Mn and S Contents on the Recrystallization Texture

The changes in the pole intensity for several texture components during isochronal annealing are shown in Fig. 5. The changes in the pole intensity by recrystallization are similar to those observed in rimmed steels.¹⁴⁾ The {222} intensity decreases by primary recrystallization, but increases during the process of grain growth on heating at higher temperatures. The {110} intensity increases by primary recrystallization, and remains almost unchanged or has a tendency to decrease during the grain growth. Both {200} and {211} intensities decrease to almost random level by

Fig. 4. Effect of Mn and S contents on the grain size after 850°C annealing.

Fig. 5. Influence of Mn and S contents on texture development during isochronal annealing.

primary recrystallization, and show a tendency to decrease slightly by the grain growth.

The effect of the chemical composition on the changes in texture components is noticeable only at the stage of the grain growth, and inappreciable at the stages of cold rolling and primary recrystallization. Especially the change in the {222} intensity during grain growth should be noted. In general, the {222} intensity during grain growth may be correlated with the grain size. Making a comparison between the {222} intensity data, Fig. 5, and the grain size data, Fig. 3, we notice that, in the case of high S content (0.017 % S), the grain growth promoted by an increase in Mn content induces a remarkable increase in the {222} intensity. In the case of ultra-low S content (0.0003 % S), however, an increase in Mn content also resulted in an increase in the {222} intensity despite of a retardation of grain growth.

Fig. 6 shows the relationship between the grain size and the pole intensity of {222} or {110} component. Generally the {222} intensity increases and the {110} intensity decreases with an increase in the grain size. In the case of ultra-low S content (0.0003 % S), a higher Mn content leads to a higher {222} intensity and a lower {110} intensity.

3.3. Observation of Precipitates Existing before Cold Rolling

Fig. 7 shows the electron micrographs of the precipitates observed in the hot-bands annealed for 1 h at 800°C. In the low Mn steels (Steels A-1, B-1 and C-1), fine precipitates, the amount of which increases with an increase in S content, are observed. These precipitates were identified by electron diffraction as α -MnS. In the high Mn steels (Steels A-4, B-4 and C-4), fine MnS particles are rarely observed and instead large polygonal precipitates (1 000–3 000 Å in size), the amount of which is independent of the S content, are observed. These large precipitates were identified as MnSiN_2 of an orthorhombic structure⁸⁾ as shown in Fig. 8. When the Mn content is higher, less fine MnS precipitates are observed even at a high

Fig. 6. Relationship between grain size and texture.

S content (0.017 % S). As mentioned previously,¹³⁾ the solubility of S in austenite at the slab-heating temperature will become lower by an addition of Mn, resulting in less amount of fine MnS precipitates during the hot rolling process.

Fig. 9 shows a result of quantitative analysis of nitride contained in the hot-band before and after annealing at 800°C using the extraction method with bromine-ester. The ordinate gives the ratio of the quantity of N as nitride to the total amount of N. Here again, considering the chemical composition of the steels, we can confirm that the nitride precipitated is MnSiN_2 . Fig. 9 indicates obviously that the MnSiN_2 was precipitated during the process of hot-band annealing. The amount of MnSiN_2 after hot-

band annealing increases with an increase in Mn content. This result agrees with that of TEM observation.

4. Discussion

4.1. Effects of MnS and MnSiN_2 on the Grain Growth

According to Zener's theory of the pinning of grain boundaries by second phase particles, the restraining force on the grain boundary (F) is proportional to the volume fraction of precipitates (f) and inversely proportional to the mean radius of precipitates (r).^{11,12)} That is $F \propto f/r$. In the present study it is necessary to consider the effects of two kinds of precipitates, which are MnS and MnSiN_2 . The effect of MnSiN_2 will become more dominant with an increase in the Mn content irrespective of the S content. This is a natural consequence led from the fact that the amount of MnSiN_2 increase in the Mn content and does not depend on the S content, in particular for high Mn contents. The restraining force of MnSiN_2 particles on the grain boundary is, however, much weaker than that of MnS particles, because the radius of MnSiN_2 particles is larger than that of MnS particles and, moreover, the solubility product of MnSiN_2 is larger than that of MnS.

The effect of MnS on the grain boundary migration depends on both S and Mn contents. An increase in the S content suppresses the grain growth as a result of an increase in the volume fraction of MnS. As for the effect of Mn content, an increase in the Mn content leads to a weaker restraining force on the grain boundary in conventional steels containing com-

(a) Steel A-1 (b) Steel B-1 (c) Steel C-1
(d) Steel A-4 (e) Steel B-4 (f) Steel C-4

Fig. 7. Observation of precipitates after hot-band annealing. (Blank replica method)

Fig. 9. Effect of Mn content on nitride precipitation in hot-band.

Fig. 8. Identification of MnSiN_2 after hot-band annealing. (Steel A-4)

paratively high S as a result of the decreasing of fine MnS particles. The amount of fine MnS particles is considered to decrease with an increase in Mn content, because Mn addition decreases the solute S content during slab heating, which precipitates as fine MnS particles during hot rolling.¹³⁾ In ultra-low S steels containing less than 0.001 % S, however, S dissolves perfectly at 1 250°C regardless of Mn content according to the solubility product of MnS by Turkdogan *et al.*¹⁵⁾ Therefore, in ultra-low S steels the precipitation condition of MnS does not depend on Mn content and of course the effect of MnS is smaller than in high S steels.

Considering the relative effects of MnS and MnSiN₂ as mentioned above, we can illustrate schematically the restraining force on the grain boundary with Fig. 10 as a function of Mn content for two levels of S content. For ultra-low S steels, the effect of MnS is independent of the Mn content and is considerably small, while the effect of MnSiN₂ increases gradually with an increase in the Mn content. For conventional steels containing a higher S content, the effect of MnS is predominant but decreases with an increase in the Mn content as its restraining force on the grain boundary becomes weaker by the decreasing of fine MnS precipitates.

Fig. 11 shows the solubility product of MnSiN₂ in the ferrite phase for 0.5 and 1.5 % Mn steels at 800°C after Mortimer and Svedung.¹⁶⁾ The solubility product of MnSiN₂ is much larger than that of MnS and MnSiN₂ will dissolve perfectly in the ferrite matrix at temperatures higher than 800°C. In the present study, however, MnSiN₂ did not dissolve perfectly at 800°C, because the integrated diffusion distance is limited in such a short period of the isochronal an-

nealing. There remains a problem that P lowers the solubility product of MnSiN₂. The effect of P on the solubility product of MnSiN₂ should be investigated in further studies.

4.2. Effect of MnSiN₂ on the Recrystallization Texture

The effects of Mn and S contents on the changes in texture components are most remarkable in the grain growth process. In general, the {222} component increases and the {110} component decreases during the grain growth. For ultra-low S steels, however, the development of these components during the grain growth was not governed only by the grain size.

Okamoto¹⁷⁾ reported that the increase in {110} component and the decrease in {222} component during primary recrystallization can be correlated with an increase in solute N as a result of the interaction between Mn and N. Ushioda and Abe¹⁸⁾ reported in their study of warm rolling between 300 and 400°C that a similar recrystallization texture as that of Okamoto's study was developed by nucleation along deformation bands which were formed more frequently with an increase in solute N.

On the basis of these previous reports and the pole intensity data given in Fig. 5, the effect of Mn on the changes of texture components in the present study can be considered to arise from the existence of solute N. The amount of MnSiN₂ will increase and that of solute N will decrease with an increase in the Mn content. Consequently the development of the {110} component by primary recrystallization will be suppressed by increasing Mn content. Therefore, by an addition of Mn, in spite of the deterioration of the grain growth, the {222} component was able to develop by the grain growth in the case of ultra-low S steels with an increase in Mn content. For high S steels, an addition of Mn influences the development of {222} component through promotion of the grain growth.

As shown in Fig. 9, the amount of dissolved nitrogen become much larger in the ultra-low S steel than the high S steel with decreasing Mn content. As shown in Fig. 5, however, in the case of low Mn content, the ultra-low S steel has a higher {222} intensity than the high S steel at temperatures of 650–700°C where the primary recrystallization just completes. The high {222} intensity of the ultra-low S steel may be explained by the fact that the ultra-low S steel contained less C than the high S steel. As in the case of solute N, solute C also suppresses the formation of the {222} component during primary recrystallization through the interaction with Mn.¹⁹⁾ It is concluded that the ultra-low S steel containing 0.05 % Mn had a high {222} intensity after primary recrystallization in spite of the larger amount of solute N, because the steel contained a less amount of solute C than the high S steel.

Phosphorus is added in the steels in order to control the hardness. In cold rolled sheet steels which contain a negligible amount of Si, the effect of P on a recrystallization texture has been investigated by several researchers.^{20,21)} Matsudo *et al.*²⁰⁾ reported

Fig. 10. Schematic representation of the pinning effects of MnS and MnSiN₂ on grain growth.

Fig. 11. Solubility of MnSiN₂ at 800°C after Mortimer and Svedung.¹⁶⁾

that, in an ultra-low C steel containing less than 0.01 % C, the {200} component was increased and the {222} component was suppressed with an increase in P content. Whether the same effect of P on a recrystallization texture holds or not in the steels containing 0.50 % Si remains to be investigated in future.

5. Conclusion

The effects of Mn and S on the grain growth and the texture development have been investigated using ultra-low C steels containing 0.5 % Si. The following conclusions were obtained.

(1) The grain growth rate is influenced by the precipitates of MnS and MnSiN₂. When the steel contains 0.004 to 0.017 % S, the effect of MnS is predominant and the grain growth is promoted with an increase in Mn content through decreasing of fine MnS particles. When the S content of the steel is less than 0.001 % S, the effect of MnSiN₂ is predominant and the grain growth is retarded with an increase in Mn content by an increase in the volume fraction of MnSiN₂ precipitates.

(2) The changes in texture components during the grain growth is governed not only by the grain growth rate but also by the texture formed by primary recrystallization. In general, the {222} component develops in ultra-low S steels in which a marked grain growth takes place. An addition of Mn influence the development of {222} component through a decrease in solute N by the formation of MnSiN₂.

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