Anomalous Sulfur Segregation Kinetics Governed by MnS Precipitation Reaction and {110} Annealing Texture Development in Al-free and 0.1 % Mn–Added 3% Si–Fe Alloys

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In 0.1 % Mn-added 3 % Si–Fe alloys, the total number of {110} grains increased with increasing bulk sulfur content and with decreasing heating rate. This is contrary to that in Mn-free alloys. During isothermal annealing, the segregation concentration of sulfur for the initial time range was lower in the alloy containing 95 ppm sulfur than that in the other alloy containing 25 ppm sulfur. Also the maximum segregation concentration of sulfur appeared at a later time in the former. Such an annealing texture development and a segregation behavior can be attributed to the MnS precipitation and the subsequent dissolution into the matrix.

KEY WORDS: Mn-added 3 % Si–Fe; MnS precipitation; segregation; selective growth; annealing texture.

1. Introduction

The formation mechanism of {110}<001> Goss texture in 3 % Si–Fe alloys containing MnS and AlN^(1–5) has been explained with secondary recrystallization or abnormal grain growth and has recently been elucidated in Al- and Mn-free 3 % Si–Fe alloys.^(6,7) Following the theories,^(6,7) the crystallographic orientation of a formed nucleus resembles that of the deformed matrix surrounding the nucleus. Also {110} nuclei are formed from a {110}<001> or {111}<112> cold-rolling surface texture due to the surface energy advantage. Among the formed {110} nuclei, the number of {110}<001> Goss nuclei is the most, resulting from the strongest {110}<001> or {111}<112> core intensity in the cold-rolling textures. The number of the {110} nuclei decreases as the deviation angle between the <001> crystal direction placed on the {110} plane and the rolling direction increases. As a result, the orientation distribution of the {110} grains after final annealing is similar to that of the nuclei after nucleation.^(8–13) In Mn-free 3 % Si–Fe alloy strips, the segregation concentration of sulfur shows a convex profile during annealing under a vacuum or hydrogen atmosphere that results from the depleted zone of sulfur formed just below the strip surface, due to the evaporation of segregated sulfur and the H₂S reaction.⁽¹¹⁾ The overall segregation profile of sulfur is generally shifted to a higher temperature range with increasing heating rate. Before the selective growth of {100} or high-index-plane grains containing {111} grains under a high surface segregation atmosphere of sulfur, the size of the {110} grains becomes larger due to their selective growth under a low segregation condition of the higher temperature range.⁽¹⁴⁾ This increases the survival probability of the {110} grains during the subsequent selective growth of the {100} or high-index-plane

grains and so the total number of the {110} grains after final annealing.⁽¹⁴⁾ The total number of the {110} grains increases also with increasing hydrogen flow rate and with decreasing bulk sulfur content. This is due to the lower surface segregation concentration of sulfur that arises from the more active H₂S reaction and the lower bulk sulfur content.⁽⁹⁾ Therefore, the formation of the sharp {110}<001> Goss texture, which is accompanied by the decrease in total number of the {110} grains, is prerequisite for obtaining a high magnetic induction.

It is the purpose of this study to investigate effects of Mn addition on surface segregation kinetics of sulfur and orientation distribution of {110} grains in 3 % Si–Fe alloys containing 25 and 95 ppm sulfur.

2. Experimental

Alloy plates of about 3 mm thickness containing 0.1 % Mn were prepared through vacuum induction melting and hot-rolling. The total quantity of the other impurities containing carbon was below 40 ppm. The plates were solution-heat-treated at 1 280 °C for 15 min in dry hydrogen of 6 N purity and then gas-quenched. Strips with 0.1 mm thickness were produced from the plates, using a triple-stage cold-rolling process. Between each cold-rolling process, intermediate annealing was carried out at 800 °C for 20 min in a high vacuum of about 9×10^{-4} Pa. The cold-rolling process was performed with a rolling lubricant. Final thickness reduction of 60 % was chosen. Before final annealing, all the strips with a dimension (5 mm in width and 100 mm in length parallel to the rolling direction) were pre-annealed for 13 min in a furnace held at 850 °C under the same hydrogen atmosphere. The pre-annealed strips were heated up to 1 200 °C with heating rates of 50, 400 and 10 800 °C/h

Fig. 1. Surface segregation results obtained by an ion-sputtering technique after hydrogen annealing at 1200°C at 10 L H_2 /min: (a) 25 ppm sulfur and 200 s and (b) 95 ppm sulfur and 200 s.

(i.e., isothermal annealing at 1200°C) under the same vacuum or in the same dry hydrogen and subsequently final-annealed at the temperature for 12 h. All the heat treatments were performed without any MgO coating in a quartz tube with the inner and outer diameters of 29 and 33 mm that is enclosed by a three-zone tube furnace. There are several studies^{15–19)} reporting surface segregation behaviors of solutes in the 3% Si–Fe alloy strips. Due to the active evaporation of solutes at a higher temperature that attacks the electron gun, most of these studies were performed *in-situ* below 1000°C in AES (Auger electron spectroscope). In the present study, the surface segregation behavior of the solutes was, therefore, investigated using an ion-sputtering technique.⁹⁾ That is, the strips were first annealed, cooled and then placed in AES for the analysis. The primary beam energy was 2 keV and the sputtering rate corresponded to 5.7 nm of SiO_2 /min. AES spectra were obtained every 15 s during ion-sputtering. Differential peak heights of S 150 and Fe 703 eV were used. In each case, the differential maximum peak heights of S 150 eV were mostly observed after ion-sputtering for 45 s and these peaks were chosen as the segregation concentrations accumulated at the free surface during isothermal annealing. One example obtained by such an ion-sputtering technique is shown in **Fig. 1**. All the differential peak heights of S 150 eV were normalized with the peak height of Fe 703 eV which was obtained after ion sputtering for about 5 min. Here, the carbon and oxygen peaks are mainly due to the air contamination after annealing and are not considered in the analysis. ODFs (orientation distribution functions) for the cold-rolled strips and an etch-pit method for the annealed strips were used for texture analyses. The etchant in the etch-pit method is composed of distilled water 80 mL + H_2O_2 20 mL + three or four droplets of HCl solution. After etching, the annealed strips were cleaned in 15% nital solution for a short time and subsequently in alcohol before drying. Finally, the number of $\{110\}$ grains in the specimen dimension of 5 mm in width and 100 mm in length and the deviation angle between the $\langle 001 \rangle$ crystal direction placed on the $\{110\}$ grains and the rolling direction were measured using a monitor attached to an optical microscope and a protractor.

3. Results and Discussion

Figure 2 shows ODFs obtained from cold-rolled 0.1% Mn-added 3% Si–Fe alloy strips. In the alloy containing 25 ppm sulfur, the main cold-rolling surface texture was

Fig. 2. ODFs (orientation distribution functions) from the cold-rolled alloy strips surface: (a) 25 and (b) 95 ppm sulfur. The symbols represent the orientations of $\{110\}\langle 001 \rangle$ (●), $\{110\}\langle 110 \rangle$ (○), $\{111\}\langle 112 \rangle$ (▲) and $\{100\}\langle 011 \rangle$ (◆), respectively. $\phi_2 = 45^\circ$.

composed of a $\{554\}\langle 225 \rangle$ texture and a $\{100\}\langle 011 \rangle$ texture. The cold-rolled strip containing 95 ppm sulfur showed an intensified $\{554\}\langle 225 \rangle$ surface texture and a weaker $\{100\}\langle uvw \rangle$ surface texture. Following the nucleation theories,^{6,7)} because the $\{110\}$ nuclei can be also formed from the $\{554\}\langle 225 \rangle$ surface texture, the more $\{110\}$ nuclei are obtained from the intensified $\{554\}\langle 225 \rangle$ surface texture of the cold-rolled strip containing 95 ppm sulfur. All the strips were only composed of $\{110\}$ grains after final annealing. Regardless of the bulk sulfur content, the total number of the $\{110\}$ grains was more at a higher hydrogen flow rate, as shown in **Fig. 3**. This is consistent with the results in Mn-free 3% Si–Fe alloys.^{8–14)} As shown in **Fig. 3** and **Fig. 4**, the total number of the $\{110\}$ grains was however rather more in the alloy containing the higher bulk sulfur content and decreased with increasing heating rate even under a different annealing atmosphere. Such results are contrary to those in the Mn-free 3% Si–Fe alloys.^{8–14)} **Figure 5** shows changes in surface segregation kinetics of sulfur with bulk sulfur content during isothermal annealing at 1200°C at 3 L H_2 /min. The overall segregation profile in the alloy containing 25 ppm sulfur was similar to that in the Mn-free 3% Si–Fe alloys containing 30 ppm sulfur.¹¹⁾ In the other alloy containing 95 ppm sulfur, the initial concentration of sulfur was much lower and the position of the maximum sulfur segregation concentration was shifted to a later annealing time in comparison to that of the alloy containing 25 ppm sulfur.

In order to understand the effects of bulk sulfur content on the annealing texture development of **Fig. 3** and the segregation kinetics of sulfur of **Fig. 5** in the 0.1% Mn-added 3% Si–Fe alloys, the MnS precipitation and dissolution reactions need to be considered. In the 0.1% Mn-added 3% Si–Fe alloys, the solubility of sulfur is nearly null below 900°C, referring to **Fig. 6**.²⁰⁾ During heating, the dissolved sulfur content decreases due to the MnS reaction at a temperature below 900°C and at the same time the remaining sulfur dissolved in the alloys can segregate to grain boundaries or free surface. Also the more active MnS reaction occurs in the alloy containing 95 ppm sulfur due to the higher bulk sulfur content. As the annealing temperature increases subsequently to a temperature above 900°C, some of the MnS particles begin to dissolve into the matrix in order to satisfy the solubility of sulfur at the temperature. As shown

Fig. 3. Changes in total number and orientation distribution of {110} grains with bulk sulfur content and hydrogen flow rate after isothermal hydrogen annealing at 1200°C: (a) 3 and (b) 10 L H₂/min. Here, $N_{\{110\}}$ means the total number of {110} grains.

Fig. 4. Changes in total number and distribution of {110} grains with heating rate after final annealing: (a) 25 and (b) 95 ppm sulfur.

in Figs. 1 and 5, during isothermal annealing at 1200°C the sulfur peak was much lower in the alloy containing 95 ppm sulfur for the initial annealing time range. This implies that the interface between the formed MnS precipitates and the surrounding matrix may trap strongly the sulfur which segregates toward the grain boundaries or the free surface. Therefore, the MnS precipitation and dissolution reactions in the Mn-added alloy containing 95 ppm sulfur have two

opposite effects on the sulfur segregation kinetics and consequently the selective growth. The first one is the formation of the lower surface segregation concentration for the initial time range which is helpful for the selective growth of the {110} grains. The second one is the formation of a maximum segregation concentration at a later annealing time which is disadvantageous for the survival of the {110} grains. As shown in Fig. 3, the total number of the {110}

Fig. 5. Changes in surface segregation concentration of sulfur with bulk sulfur content during isothermal annealing at 1 200°C at 3 L H₂/min.

Fig. 6. The solubility of sulfur in the 0.1% Mn-added 3% Si-Fe alloys.

grains was more in the alloy containing 95 ppm sulfur. This can be therefore attributed to the stronger first effect of the MnS precipitation reaction as well as the stronger {554} surface texture of Fig. 2 which can supply the more {110} nuclei.

The grain boundary pinning effect of the MnS precipitates is discussed in order to understand the reason why the total number of the {110} grains at a given bulk sulfur content decreases with increasing heating rate, as shown in Fig. 4. From the present result and the previous research,¹¹⁾ the segregation concentration profile of sulfur in the Mn-added alloys is also shifted to a lower temperature range with decreasing heating rate. In this case, the selective growth of {100} or high-index-plane grains around the maximum segregation concentration of sulfur is strongly inhibited by the MnS precipitates due to the relatively lower temperature. As a result, the more {110} grains survive after the selective growth of the {100} or high-index-plane grains and grow selectively at the expense of the {100} or high-index-plane grains under a low segregation condition of sulfur. As the heating rate increases, the maximum segregation concentration of sulfur is formed in a higher temperature range and the grain boundary pinning effect of the MnS precipitates is relatively weakened due to the higher temperature condition. Following the nucleation theories,^{6,7)} the total number of the {110} nuclei which are formed from the same cold-rolled strips is the same, if the strip dimension is the same. Due to the weakened grain boundary pinning ef-

fect in the higher temperature range, the selective growth of the {100} or high-index-plane grains occurs more actively at the expense of the {110} grains under a relatively high segregation condition of sulfur. This causes the decrease in number of the {110} grains surviving during the selective growth. Also the surviving {110} grains grow selectively at the expense of the {100} and high-index-plane grains under the low segregation condition of sulfur, but the total number of the {110} grains after final annealing is relatively decreased.

4. Summary

Effects of Mn addition on surface segregation kinetics of sulfur and orientation distribution of {110} grains have been investigated in 3% Si-Fe alloys containing 25 and 95 ppm sulfur. The total number of the {110} grains in the 0.1% Mn-added alloys increased with increasing bulk sulfur content and with decreasing heating rate. The increase in total number of the {110} grains with increasing bulk sulfur content is probably attributed to the role of MnS precipitate interfaces as a sinker of sulfur which segregates toward grain boundaries or free surface. The increase in total number of the {110} grains with decreasing heating rate is due to the strong grain boundary pinning effect of the MnS precipitates which inhibits the selective growth of {100} or high-index-plane grains. During isothermal annealing, the segregation concentration for the initial time range was lower in the alloy containing the higher bulk content of sulfur. The maximum segregation concentration of sulfur appeared at a later annealing time in the alloy. Such a segregation behavior of sulfur can be understood in the light of the MnS precipitation and the subsequent dissolution into the matrix.

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