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Effects of Sulfur Segregation on Tertiary Recrystallization Kinetics in Thin-gauged 3% Si-Fe Electrical Strip

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Effect of sulfur segregation on tertiary recrystallization and magnetic induction during final annealing was investigated in a 3% Si-Fe electrical strip containing 6 ppm (LS) and 15 ppm (HS) sulfur. During final annealing, Auger peak height of segregated sulfur on the surface of the strips reached a maximum, and then decreased to low level with increasing annealing time, which is attributed to sulfur segregation and evaporation. The magnetic induction of the thin-gauged 3% Si strip was inversely proportional to the Auger peak height of segregated sulfur on the surface. The overall profile for surface segregation of sulfur and B_{10} was observed, irrespective of sulfur content in Si-Fe strips, but the peaks of LS strips appeared earlier than those of HS strips. The grain growth rate of the LS strips during final annealing was faster than that of the HS strips, which may be attributed to the pinning effects of segregated sulfur. With increasing final annealing temperature, B_{10} value increased rapidly and the saturation level in B_{10} increased.

1. Introduction

3% Si steel strips have been used as core materials of power and distribution transformers due to their excellent soft magnetic properties. The magnetic properties of Si-Fe strips are mainly attributed to a preferred orientation, *i.e.* {110}<001> Goss texture.

The {110}<001> texture in thin-gauged Si-Fe strips has been known to be developed through tertiary recrystallization under a vacuum atmosphere, the driving force of which is the difference in surface free energy between {110} and other planes. In a vacuum, {110} plane of the Si-Fe strips has the lowest surface free energy and {110} grains grow, consuming other grains [1, 2]. On the other hand, under a H_2S atmosphere, {100} grains grow selectively, consuming other grains because the {100} plane has the lowest surface free energy under a sulfur atmosphere [3-6]. Referring to a previous study [7], even under a high vacuum a sulfur atmosphere was formed during final annealing due to sulfur segregated on the Si-Fe strips, resulting in the growth of {100} grains. Therefore, the surface-segregation of sulfur affects on the tertiary recrystallization kinetics and, thus magnetic properties of the thin-gauged Si-Fe strips.

In this study, effects of sulfur content of the Si-Fe strips on surface segregation of sulfur, tertiary recrystallization kinetics and magnetic properties are investigated.

2. Experimental Procedures

Two kinds of 3% Si-Fe alloys, containing 6 and 15 ppm sulfur (hereafter, LS and HS respectively), were prepared through vacuum induction melting. The chemical composition of those steels are listed in Table 1. The ingots were hot-rolled to 2.5 mm plates after holding at 1200 °C for 3.6 ks. The thickness of the plates were finally reduced to 100 μm through three-stage cold rolling process with a reduction ratio of 80%-50%-60%. During cold rolling process intermediate annealing was performed at 800 °C for 1.8 ks. The final annealing was given the thin strips in the temperature range of 1000-1300 °C for 0.02 to 184.2 ks. All the annealing treatments were carried out under a vacuum of 6×10^{-6} Torr.

The microstructure and grain orientation of the Si-Fe strips were measured by an etch-pit method. The strips were etched by using an etchant of 100 ml H_2O + 6 ml H_2O_2 + 0.6 ml HCl for 20 sec and then an etchant of 40 ml $FeCl_3$ + 40 ml H_2O + 40 ml C_2H_5OH for 50 sec, continu-

Table 1. Chemical compositions of the thin-gauged 3% Si-Fe alloys. (wt.%)

	C	S	N	Mn	Si
LS	0.002	0.006	0.013	<0.001	2.92
HS	0.0048	0.0015	0.0005	<0.001	2.98

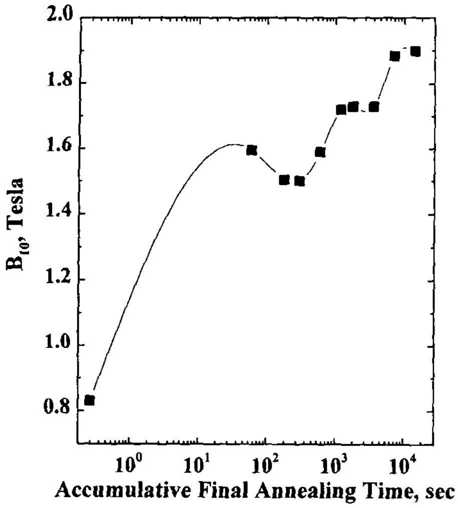

Fig. 1. A change in magnetic induction of the thin-gauged 3% Si steel strip 100 thick with accumulative final annealing time at 1200 °C.

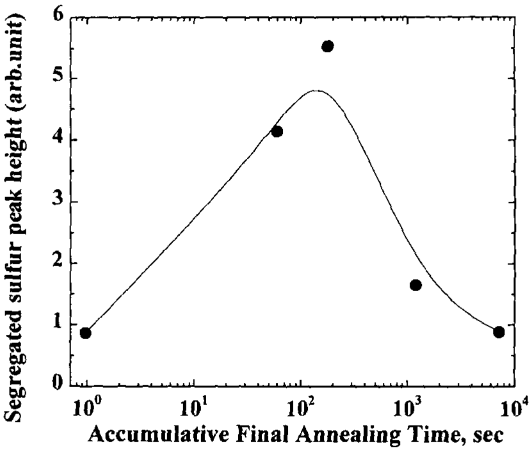

Fig. 3. A change in Auger peak height of segregated sulfur with accumulative final annealing time at 1200 °C.

ously. Auger Electron Spectroscopy (AES) was used for surface analysis. Surface phenomena on the thin-gauged 3% Si strips during final annealing were investigated with ion sputtering technique after final annealing. Magnetic induction at 10 Oe (B_{10}) was measured using a loop tracer (Model TRF-5AH1, Toei Co., Japan).

3. Results and Discussion

Figure 1 shows a change in B_{10} of LS strip with final annealing time at 1200 °C. Here, one sample was only used, and was repeatedly annealed to remeasure the B_{10} values up to 14.4 ks. It can be seen in Fig. 1. that during final annealing, B_{10} passed through a maximum and a minimum, and then increased up to 1.90 Tesla after final annealing to 14.4 ks. The result of ion-sputtering is shown in Fig. 2, which has been obtained from the sample finally annealed at 1200 °C for 0.06 ks. Prior to ion-sputtering, strong oxygen and carbon peaks were observed while sulfur peak was very weak. After ion-sputtering for 0.015 ks, the carbon adsorbed on the surface from atmosphere was removed, but the oxygen peak became stronger, relatively. This result may imply the presence of an iron oxide layer of atomic scale on the surface, which can be supported by the data [8]. A sulfur peak appeared with increasing ion-sputtering time, and showed a maximum after ion-sputtering for 0.045 ks. Figure 3 shows a change in Auger peak height of segregated sulfur in LS strip with final annealing time at 1200 °C. After final annealing for 0.18 ks, the sulfur peak height reached a maximum, and then decreased to a low level with increasing annealing time. It is shown from a combining Figs. 1 and 3 into Figure 4 that a trough in magnetic induction appeared during final annealing, and the minimum corresponded to the maximum peak height of sulfur. This result is in good agreement with the results of some other researches [9, 10], which reported that sulfur on strip surface was the main factor inhibiting the formation of (110)[001] Goss texture.

It has been reported that the segregation kinetics of a species is largely influenced by evaporation occurring at a solid-vapor or solid-vacuum interface [11, 12] or by a precipitation reaction related to the segregating species [13,

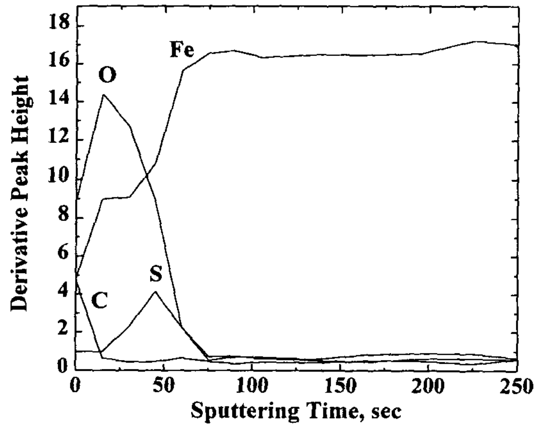

Fig. 2. Ion-sputtering result obtained from the sample finally annealed at 1200 °C for 0.06 ks.

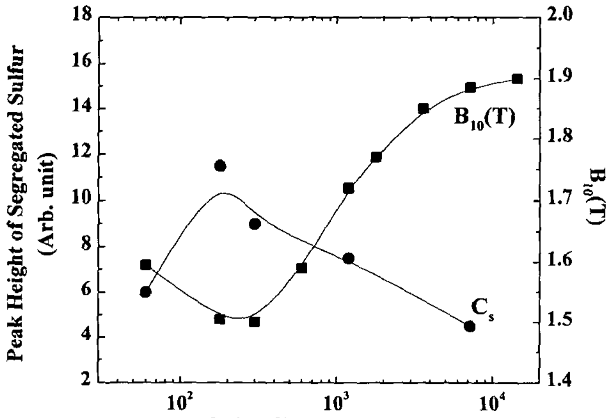

Fig. 4. Changes in magnetic induction and Auger peak height of segregated sulfur with final annealing time in LS alloy strip.

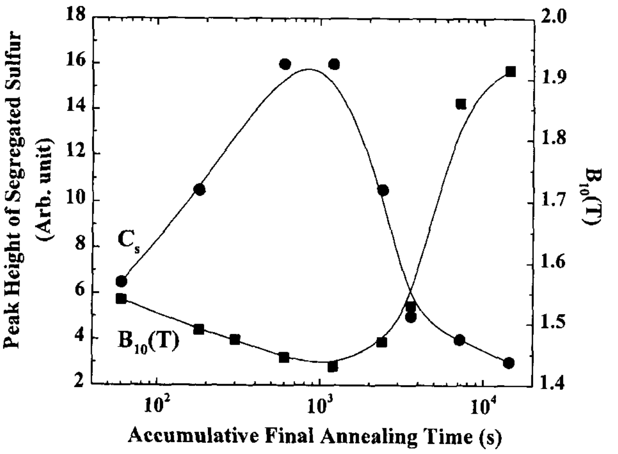

Fig. 5. Changes in magnetic induction and Auger peak height of segregated sulfur with final annealing time in HS alloy strip.

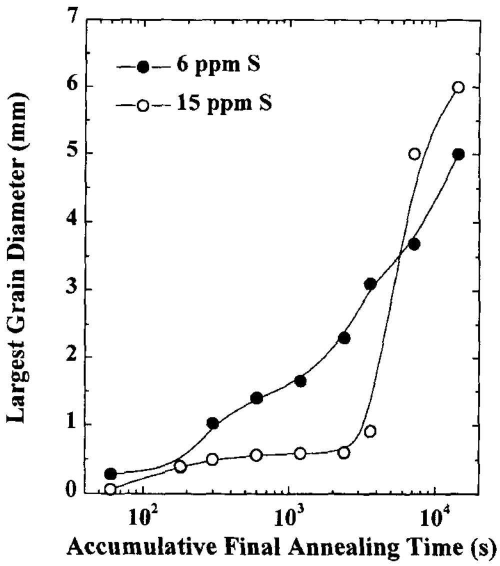

Fig. 6. Changes in grain size during final annealing at 1200 °C.

14]. Lea and Seah found evaporation of tin to be significant in their Auger study of surface segregation kinetics in an Fe-Sn system, and treated the free surface segregation including evaporation theoretically. Following their results, the surface coverage at short times increases as if there were no evaporation. With increasing time, the evaporative loss term becomes dominant so that the surface coverage passes through a maximum, and then decreases to a very low value. Likewise, such a maximum appears also in segregation kinetics accompanying a precipitation reaction [11, 12]. Considering the extremely high vapor pressure of sulfur [15], such an evaporation phenomenon can possibly occur in the present annealing condition. As a result, the maximum point in sulfur concentration, as shown in Fig. 3, means a turning point, after which the evaporation of sulfur becomes dominant, relatively.

Figure 5 shows changes in B_{10} values and normalized Auger peak height of segregated sulfur with final annealing time in the HS strip. The overall profile for surface segregation of sulfur and magnetic induction was similar to Fig. 4. The segregated sulfur was, however, observed in the annealing time 3.6 ks, the range of which was wider than that in the LS alloy. The maximum in segregation concentration of sulfur, which was larger than that in the LS alloy, appeared at about 1.2 ks, while the LS alloy showed the maximum at 0.18 ks.

During final annealing under sulfur atmosphere, the increase in planar density of {100}<110> grain, which results in the decrease of magnetic induction, is followed by the increase in size of the grain. On the contrary, the increase itself in grain size acts as a positive factor [16] on magnetic induction. It can, therefore, be suggested from Figs. 4 and 5 that, to the annealing time corresponding to the maximum in sulfur concentration, the decrease in magnetic induction is attributed to the dominant effect of the former and at times under sulfur atmosphere after the maximum sulfur level, the increase in magnetic induction is probably due to the effect of the latter which overwhelms the increase effect in planar density of {100}<110> grain.

Figure 6 shows changes in the grain size during final annealing at 1200 . In the LS alloy, the grain size increased gradually with increasing time, while in the HS alloy the grain size increased little within 3.6 ks, after which the grain size increased rapidly with further annealing. This means that, while the grain boundary pinning effect of segregated sulfur is very weak in the LS alloy, the grain boundaries in the HS alloy are strongly pinned by the segregated sulfur.

Figure 7 shows changes in growth rate with final annealing time, which was obtained from Fig. 4. Under H_2S atmosphere [3-6], a semiquantitative relation of the linear growth rate, G, has been derived for secondary grain growth in strips, given by

$$G(t)=M(t)\cdot\left[\frac{\gamma_B}{\gamma(t)}+\frac{2\Delta\gamma_s}{d}+C(t)\right] \qquad (1)$$

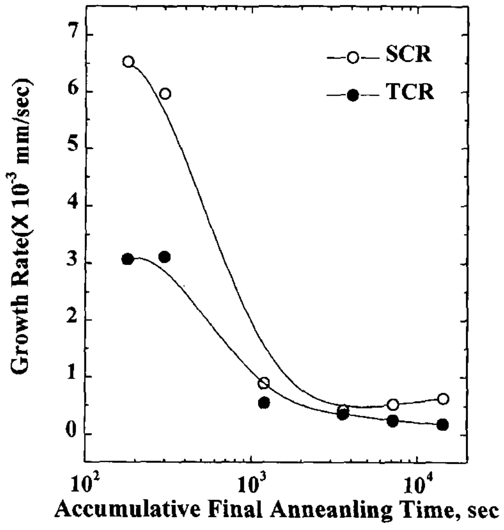

Fig. 7. Changes in growth rate with final annealing time.

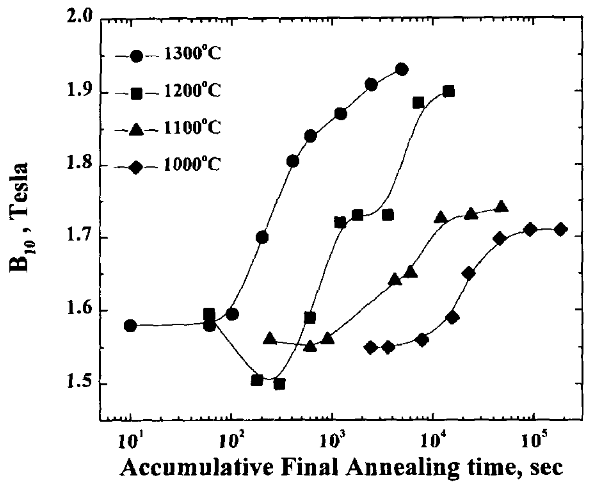

Fig. 8. Changes in magnetic induction of thin-gauged strip with accumulative final annealing time at several temperatures.

where M is the grain boundary mobility, γ_B is the grain boundary free energy, d is the sheet thickness, and C is a term acting as a negative driving force. The Zener's term C is generally related to inclusions at grain boundaries. In the present alloys with few inclusions, the C is mainly related to the segregated sulfur which shows a strong effect of grain boundary pinning. The surface free energy term, $\{2\Delta\gamma_s/d\}$, is trivial in contribution to growth rate, because $\Delta\gamma_s/g_B$ is about 0.03. The growth rate at time t is, therefore, governed by the grain radius r and the Zener's term C. Ignoring the Zener's term in eqn. (1), the growth rate is governed by the grain radius. As a result, the growth rate in the LS alloy should be much slower because the grain size is 1-5 times larger within the annealing time of 3.6 ks. However, the growth rate in the LS alloy is rather 6-16 times faster than that in the HS alloy. This implies that under relatively high sulfur atmosphere the growth rate of {100} grain is absolutely governed by the Zener's term. The grain boundary pinning effect followed by the decrease in sulfur segregation concentration and the relatively small grain size.

With increasing annealing time, the sulfur-free atmosphere is formed after 1.2 ks in the LS alloy and after 3.6 ks in the HS alloy. Finally the surface energy induced tertiary recrystallization [6] occurs under this atmosphere, and {110} grain, which has survived, grows, consuming {100} as well as other grains. Through such a recrystallization process, a complete {110}<001> Goss texture is formed, and B_{10} higher than 1.9 Tesla was, as shown in Figs. 4 and 5, obtained in both alloys after final annealing for 14.4 ks.

Figure 8 shows changes in magnetic induction of the LS strip during final annealing at several temperatures. It can be seen in Fig. 8 that B_{10} value increased rapidly with increasing final annealing temperature, which may be attributed to high evaporation rate of sulfur from the strip surface with increasing annealing temperature. Also the saturation level in B_{10} increased with increasing final annealing temperature, and amounted to 1.93 Tesla after annealing at 1300 °C for 4.9 ks. However, the saturation value in B_{10}, 1.71 Tesla, obtained after final annealing at 1000 °C for 184.2 ks was much lower than that at 1300 °C. This may be attributed to the formation of silicon oxide films on the strip surface, which was published elsewhere [7].

4. Conclusions

A correlation between sulfur segregation during final annealing and magnetic induction have been investigated in thin-gauged 3% Si-Fe strips containing 6 ppm (LS) and 15 ppm (HS) sulfur. During final annealing, B_{10} passed through a maximum and a minimum, and then increased up to 1.90 Tesla with increasing annealing time while Auger peak height of segregated sulfur on the surface of the strips reached a maximum, and then decreased to low level with increasing annealing time. The overall profile for surface segregation of sulfur and B_{10} was observed, irrespective of sulfur content in Si-Fe strips, but the peaks of LS strips appeared earlier than those of HS strips.

The grain growth rate of the LS strips during final annealing was faster than that of the HS strips, which may be attributed to the pinning effects of segregated sulfur. Under the relatively higher sulfur atmosphere appearing in the alloy with higher bulk content of sulfur, the growth rate of {100} grain is absolutely governed by the Zener's term related to the segregation concentration of sulfur. In the alloy with higher bulk content of sulfur, the increase in growth rate up to 3.6 ks after 1.2 ks can be attributed to two factors : the increase in grain boundary pinning effect followed by the decrease in sulfur segregation concentration and the relatively small grain size. With increasing annealing time, surface energy induced tertiary recrystallization resulted from a sulfur-free atmosphere, and {110} grain growed, consuming {100} as well as other grains. Through such a recrystallization process, a complete {110}<001> Goss texture was formed, and magnetic induction higher than 1.9 Tesla was obtained in both alloys after annealing for 14.4 ks.

With increasing final annealing temperature, B_{10} value increased rapidly and the saturation level in B_{10} increased.

References

[1] J. L. Walter, Acta Met., **7**, 424 (1959).
[2] J. L. Walter and C. G. Dunn, Trans. AIME, **218**, 914 (1960).
[3] G. W. Wiener, J. Appl. Phys., **35**, 856 (1964).
[4] W. L. Elban, M. A. Hebbar and J. J. Kramer, Metall. Trans., **6A**, 1929 (1975).
[5] K. Detert, Acta Met., **7**, 589 (1959).
[6] J. L. Walter and C. G. Dunn, Trans. AIME, **215**, 465 (1959).
[7] N. H. Heo, K. H. Chai, J. G. Na and J. S. Woo, J. Appl. Phys., **83**, 6480 (1998).
[8] D. R. Gaskell, Introduction to Metallurgical Thermody-

namics, 2nd ed. (1981), p. 287.
[9] D. Koehler, J. Appl. Phys., **31**, 4085 (1960).
[10] K. Foster, J. J. Kramer and G. W. Wiener, Trans. TMS-AIME **227**, 185 (1963).
[11] C. L. Lea and C. Molinari, J. Mater. Sci., **19**, 2336 (1984).
[12] C. L. Lea and M. P. Seah, Phil. Mag., **35**, 213 (1977).
[13] N. H. Heo and H. C. Lee, Metall. Trans., **27A**, 3059 (1996).
[14] N. H. Heo, Acta Mater., **44**, 1581 (1996).
[15] R. E. Honig and D. A. Kramer, RCA Rev., **30**, 285 (1969).
[16] R. E. S. Walters, Acta Met., **5**, 628 (1957).