Sn Segregation at Grain Boundary and Interface between MnS and Matrix in Fe-3 mass%Si Alloys Doped with Tin

S. Suzuki, K. Kuroki, H. Kobayashi
and N. Takahashi

Technical Development Bureau, Nippon Steel Corporation, Futtsu, Chiba 299-12, Japan

Grain boundary segregation in Fe-3 mass%Si alloys doped with tin was investigated by Auger electron spectroscopy (AES), in order to shed light on a fact that tin addition modifies secondary recrystallization of Si steels. It was found that in decarburized specimens tin was segregated at grain boundaries and its segregated amount increased with the bulk tin content. The effective grain boundary segregation energy of tin was estimated from the results, and the kinetics of the grain boundary segregation of tin was discussed.

As related to a phenomenon that the size of precipitates (inhibitors) in silicon steels becomes smaller by tin addition, interfaces between precipitates and matrix were also examined with AES. Significant segregation of tin was found at the interface between MnS and the matrix. This indicates that the tin segregation at the interface can affect morphology or size of the precipitates. The influence of tin on primary recrystallization and secondary recrystallization of Si steels was discussed from these results.

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I. Introduction

Secondary recrystallization in Si steels or iron-silicon alloys has been extensively investigated with respect to the processing of grain-oriented Si steels. The investigation of secondary recrystallization has been focused on mainly analysis of cube-on-edge {110}<001> texture and on the effect of precipitates so-called inhibitors for secondary recrystallization. Further it has been found that a small addition of tin improves the magnetic properties of Si steels⁽¹⁾⁻⁽⁶⁾. From the previous investigations, it has been considered that the improvement may be related to a change of the primary recrystallized grain texture, the grain size, inhibitors and so on.

On the other hand, it is widely accepted that tin is segregated to grain boundaries in steels, inducing intergranular fracture. The typical phenomenon is temper embrittlement in low alloy steels⁽⁷⁾⁻⁽¹⁰⁾. With regard to this phenomenon of tin in Si steels, the grain boundary energy⁽¹¹⁾, the surface segregation⁽¹²⁾⁻⁽¹⁶⁾, the grain boundary segregation⁽¹⁷⁾⁻⁽²²⁾ and the grain boundary diffusion⁽²³⁾⁻⁽²⁵⁾ have been studied with several analytical techniques. The characteristics of tin segregation in iron have been reviewed⁽²⁶⁾⁽²⁷⁾.

Thus, although tin is considered to be a harmful element for structural steels, it has been shown that the addition of tin to silicon steels is beneficial to the development of the secondary recrystallization texture in grain-oriented Si steels. However, grain boundary segregation of tin in Si steels has scarcely been systematically investigated, so that the role of tin in the recrystallization is not clarified. The first purpose of this research was to in-

vestigate the grain boundary segregation of tin in Fe-3 mass%Si alloys with Auger electron spectroscopy (AES).

Second-phase particles or precipitates can serve as grain boundary pinning agents of the primary recrystallized grains in Si steels, which control onset of the secondary recrystallization. Typical precipitates are MnS and AlN in the alloys which are decomposed and disappear in annealing at high temperatures under hydrogen gas, and during the annealing the secondary recrystallization begins. It has been found that tin addition to Si steels reduces the size of the precipitates such as MnS⁽⁴⁾⁽⁵⁾. This may result from the interface-active behavior of tin. Although tin is a typical element segregating to grain boundaries as mentioned above, it has not yet been examined whether segregation of tin occurs at the interface between the precipitates and the matrix. The second aim of the present research was to study tin segregation at the interface by AES. Based on these results, the effect of the grain boundary segregation and the interface segregation between the precipitates and the matrix on primary recrystallization and secondary recrystallization in Fe-3 mass%Si alloys was discussed.

II. Experimental

1. Specimen preparation

Fe-3 mass%Si alloys with AlN and MnS were produced by melting. Sn of 0.1 mass% and 0.3 mass% was added to the alloys. The chemical compositions of ingots are given in Table 1.

The ingots were rolled to 2.8 mm in thickness at 1623 K, and subsequently annealed at 1473 K and quenched

Table 1 Chemical compositions of steels used.

	C	Si	Mn	P	S	s Al	N	Sn
A	0.078	3.07	0.081	<0.002	0.024	0.028	0.0071	<0.005
B	0.077	3.07	0.078	<0.003	0.024	0.029	0.0071	0.10
C	0.077	3.06	0.080	<0.003	0.024	0.028	0.0075	0.30

s Al: Al dissolved in acid.

Table 2 Chemical composition of low carbon steels with MnS or AlN.

	C	Si	Mn	S	s Al	N	Sn
G	0.002	3.58	0.10	0.028	0.005	0.001	0.24
H	0.003	3.62	0.003	0.002	0.015	0.003	0.30

into hot water. The sheets were cold rolled to 0.285 mm and annealed in wet hydrogen at 1123 K to remove carbon, which is the heat treatment of primary recrystallization. The sheets were annealed at a heating rate of 0.0042 K/s under hydrogen gas with 25% nitrogen gas and extracted at 1123 K, 1223 K and 1323 K in the finishing annealing. The sheets were cut to AES specimens of 3 mm × 20 mm having a notch.

Fe-Sn alloys with 0.34, 0.58 and 1.01 mass%Sn were also made in order to compare grain boundary segregation of tin in the binary alloys with that in the Fe-Si alloys. The ingots were rolled at 1473 K and shaped to AES specimens of 3 mm × 3 mm × 20 mm.

Fe-Si-Sn alloys with MnS or AlN were prepared, of which carbon concentration was lowered to enhance grain boundary fracture. The chemical compositions are listed in Table 2. The ingots were rolled at 1473 K and shaped to AES specimens of 3 mm × 3 mm × 20 mm. Since it was very difficult to analyze small precipitates on fracture surface in the present Auger measurement, relatively large precipitates of MnS or AlN were produced by annealing at 1273 K.

2. Measurement

Primary recrystallized Fe-3 mass%Si alloys were fractured in impact at low temperatures to check the fracture mode. Fractography was studied by scanning electron microscopy (SEM). The morphology of precipitates on the fractured surface were also observed using high resolution SEM.

In specimens revealing intergranular fracture, grain boundary segregation was investigated by analyzing the intergranular fracture planes by Auger electron spectroscopy (AES). The apparatus employed was PHI type 590. The accelerating voltage was 5 kV and the diameter of the incident electron beam in AES was about 3 micrometers. Figure 1 shows typical Auger spectra from cleavage plane in an Fe-3 mass%Si alloy. The spectrum just after fracture reveals only Fe and Si peaks, and small peaks of carbon and oxygen were detected on the clean surface of the specimen measured after 7.2×10^3 s, which are due to contamination by residual gas. Auger measurements of fracture surfaces were, therefore, performed within 7.2×10^3 s. Relative concentration changes on the

Fig. 1 Auger spectra from cleavage plane in an Fe-3 mass%Si alloy measured (a) just after fracture and (b) after 7.2×10^3 s.

surfaces were evaluated with Auger peaks of Fe 703 eV ($1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$), Si 89 eV and Sn 530 eV. Since each grain boundary plane reveal a variety of segregated degrees, more than twenty points were analyzed and the averages of different specimens were compared.

III. Results

1. Microstructure

Figure 2 shows the cross-section microstructures an Fe-3 mass%Si alloy sheet without Sn, and one with 0.1 mass%Sn and one with 0.3 mass%Sn, which were decarburized and annealed up to 1123, 1223 and 1323 K. Grain size after decarburization is smaller in tin added steels than in tin free steel, which is consistent with a previous result where the primary grain size was analyzed quantitatively⁽⁶⁾. The distribution of the grain size is relatively homogenous in tin added steels. Secondary recrystallization did not begin at 1323 K in the specimen without tin. On the other hand, in the Fe-3 mass%Si alloys doped with tin alloys started secondary recrystallization at the temperature and the secondary recrystallization temperature decreases with the tin concentration.

2. Fractography and grain boundary segregation in Fe-3 mass%Si alloys

Figure 3 shows fractography of the decarburized alloys. The specimen without tin revealed transgranular fracture planes and partially intergranular planes. The degree of the intergranular fracture increases with the tin concentration, and the specimen with 0.3 mass%Sn revealed almost intergranular fracture. In Auger measurements the fractured mode of analyzed area in AES was

Fig. 2 Microstructures of Fe-3 mass%Si alloys without Sn (a), and with 0.1 mass%Sn (b) and 0.3 mass%Sn (c) which were decarburized and annealed up to 1123 K, 1223 K and 1323 K.

Fig. 3 Scanning electron micrographs of fractured surface of the decarburized (a) Fe-3 mass%Si, (b) Fe-3 mass%Si-0.1 mass%Sn and (c) Fe-3 mass%Si-0.3 mass%Sn.

distinguished by observing secondary electron images. Figure 4 shows tin concentration dependence of Auger peak heights of Si and Sn to Fe in the specimens which were decarburized and annealed up to 1123 and 1223 K. The silicon segregation was not obvious, since Auger peak heights such as Si (89 eV) less than 100 eV tend to

disperse, depending on measuring conditions of the configuration between measured points and the analyzer and so on, and since the silicon segregation may be essentially low. It is obvious that the tin segregation increases with bulk tin concentration, but the degree is hardly dependent on the heat treatment. That point will be discussed

Fig. 4 Sn concentration dependence of Sn and Si Auger peak height ratios from intergranular fractured planes in Fe-3 mass%Si alloys. (○ ● decarburized, △▲ extracted from 1123 K and ▼▼ extracted from 1223 K)

later, taking into account the kinetics of the grain boundary segregation.

Intergranular fracture planes of secondary recrystallized specimens have hardly been investigated so far, and therefore grain boundary segregation has never been analyzed by AES, because the secondary recrystallized structure has very large grains and the grains have similar orientation of $\{110\}\langle 001 \rangle$ with small misorientation. In the present research, we succeeded in analyzing a partially intergranular plane by fracturing the secondary recrystallized specimen along a notch close to a specific grain boundary. Figure 5 shows a secondary electron image and Auger images of Fe, Si and Sn of the fracture plane of a secondary-recrystallized specimen with 0.1 mass%Sn. Since the observed orientation of the fractured specimen is rolling direction, the fracture plane is near (001) which is a preferential recrystallized orientation of the specimen. It coincides with the cleavage plane of body centered cubic metals. Intergranular fracture planes were observed partially, which may appear for misorientation of the orientation between grains. The segregation of tin was observed on the intergranular plane from the Sn Auger image. This indicates that tin can be segregated even at grain boundaries in a secondary-recrystallized specimen having large grains.

3. Grain boundary segregation in Fe-Sn binary alloys

Figure 6 shows plots of Auger peak height ratios of Sn

Fig. 5 Secondary electron image, Fe Auger image, Si Auger image and Sn Auger image of fracture plane of secondary-recrystallized Fe-3 mass%Si alloy.

Fig. 6 Sn concentration dependence of Sn Auger peak height ratio from intergranular fractured planes in Fe–Sn binary alloys.

to Fe in Fe–Sn binary alloys as a function of tin concentration, which were quenched from 1173 K where the specimens are ferritic. The tin segregation increases with the bulk concentration. The segregated amounts are comparable to those obtained in Fe–3 mass%Si alloys as shown in Fig. 4. It may be due to the small effect of silicon on the tin segregation. From the tin concentration dependence of tin segregation, the tendency of the tin segregation may be estimated as discussed below.

4. Change of precipitates size by Sn addition

Figure 7 shows scanning electron microphotographs of fracture planes with precipitates (inhibitors) in Fe–3 mass%Si alloys without and with tin of 0.1 mass% and 0.3 mass%. The size of the precipitates appears to decrease with the addition of tin, although there is a distribution in the size of the precipitates. It is consistent with earlier investigations⁽⁴⁾⁽⁵⁾, where precipitates in the Fe–3 mass%Si alloys were observed by the extracted replica method. They showed by distribution analysis of the precipitates that tin addition decreases the size of the precipitates, although it may be possible that the size changes by chemical treatment during sample preparation of the extracted replica. According to the energy analysis of characteristic X-ray in transmission electron microscopy, no tin has been detected in the precipitates, so that tin should exist in another state.

5. Analysis of interface between MnS and matrix

Figure 8 shows a secondary electron micrograph and Auger electron images of Fe, Si, Sn, Mn and S in an Fe–3.5 mass%Si alloy with MnS which was quenched from 1273 K. The secondary electron image exhibits an intergranular fracture plane with precipitates. From the precipitates strong Mn and S signals were detected. Correspondingly, Auger spectra from (a) a MnS precipitate and (b) a depression missed by MnS are shown in Fig. 9. A large Auger peak of tin was detected at the fractured surface along an interface MnS and the matrix, especially on the side of the depression. The segregated amount is larger than that of tin grain boundary segregation. Since ferritic iron has a large solubility for tin, the detected tin peak originates from the interface segregation of tin.

Analysis of the fractured interfaces between AlN and the matrix was also attempted. However, the significant segregation of tin was not detected in the present measurement, perhaps because of the small size of AlN and/or its low segregation.

Fig. 7 Fractography of specimens (a) without Sn, (b) with 0.1 mass%Sn and (c) with 0.3 mass%Sn which were decarburized.

Fig. 8 Secondary electron micrograph, and Auger electron micrographs of Fe, Si, Sn, Mn and S in an Fe-3.5 mass%Si alloy with MnS.

IV. Discussion

1. Equilibrium segregation of Sn in iron

The grain boundary segregation of solute atoms in solid solution alloy can be expressed by an equilibrium segregation model⁽²⁸⁾. In an alloy with solute i of concentration X_i , the degree of segregation, X_i^{GB} , that is a fraction of saturated segregation is given by

$$X_i^{GB} / (1 - X_i^{GB}) = X_i / (1 - X_i) \exp (E_i / kT) \quad (1)$$

where E_i is the segregation energy, T an equilibrium temperature and k the Boltzmann constant⁽²⁸⁾. The semi-quantitative segregated level can be estimated using the

relative sensitivity factors for elements in AES⁽²⁹⁾ under a few assumptions⁽³⁰⁾, although there remains problems in strict analysis of grain boundary segregation⁽³¹⁾. The segregated amount of tin can be compared with those of typical previous investigations on the grain boundary segregation⁽³⁰⁾⁽³²⁾. The segregation level of tin is comparable to phosphorus segregation around 1100 K from the approximate comparison. Since the simple analysis of eq. (1) involves uncertain factors related to many grain boundary structures or segregation sites⁽³¹⁾, there is little meaning in exact value for the segregation. However, the segregation energy of tin in Fe-3 mass%Si alloys may be estimated to be about 50 kJ/mol analogous to the phosphorus segregation.

Fig. 9 Auger spectra from (a) a MnS precipitate and (b) depression missed by MnS.

For a ternary system containing two kinds of segregated elements, the site competitive behavior has been observed in an Fe-P-C system⁽³²⁾, an Fe-S-C system⁽³⁰⁾ and so on. It does not always mean that two kinds of segregated elements occupy given sites at grain boundaries and that the same grain boundary structure is taken between the elements, but it suggests that there are a limited number of segregation sites at grain boundaries and that the segregated elements distribute to them effectively. The present Fe-Si-Sn system did not exhibit clear competitive segregation at grain boundaries between silicon and tin. It may be caused by the low segregation of silicon and a lack of accuracy in measurement of low energy Auger electrons of silicon. Actually grain boundary segregation of tin in the Fe-Si-Sn system may be regarded as the Fe-Sn binary alloys.

2. Segregation kinetics of Sn

Let us consider the grain boundary segregation kinetics started from no segregation at a temperature. The degree of the segregation at time, t , is given by

$$\begin{aligned} (X^{\text{GB}}(t) - X^{\text{GB}}(0)) / (X^{\text{GB}}(\infty) - X^{\text{GB}}(0)) \\ = 1 - \exp(Z^2) \operatorname{erfc}(Z) \\ Z = 2\sqrt{Dt}/\alpha d^2 \end{aligned}$$

where D is the diffusion coefficient of segregant, α the enrichment factor and d the thickness of the grain boundary⁽²⁸⁾. The thickness may be assumed to be 0.3 nm, that is approximately equal to the size of unit cell, although it cannot be strictly defined for the complicated atomistic

Fig. 10 Temperature-time-segregation diagram for Sn grain boundary segregation. The number in the figure denotes the degree of the segregation.

structure of grain boundaries. Temperature dependence of the diffusivity of tin is summarized as follows⁽³³⁾.

$$D = 2.24 \times 10^{-4} \exp(-222.2/kT) \text{ (m}^2/\text{s)}. \quad (2)$$

Figure 10 shows temperature-time curves calculated with the above equations in Fe-0.15 at%Sn (0.3 mass%), in which the temperature-time relations to a constant segregation are plotted. At higher temperatures the degree of segregation is lower, and the time to equilibrium become shorter. It should be noted that the temperature dependence of the segregation is strong, because the effect of the many kinds of segregation sites is not taken into account in this simple estimation⁽³¹⁾. As shown in the figure cooling curves of 10 K/s and 50 K/s from 1273 K are plotted, which correspond to the cooling rate when the specimens were extracted in this experiment. Therefore the experimental results that the tin segregation is little dependent on the extracted temperature as shown in Fig. 4 should be attributed to the insufficient cooling rate. The other effect involved in the results would be many kinds of segregation sites at grain boundaries, resulting in the low temperature dependence of the equilibrium segregation⁽³¹⁾.

3. Equilibrium segregation of Sn at interface between MnS and matrix

The present results clearly indicate that the considerable tin segregation occurs at the interface as shown in Fig. 9. Figure 11 illustrates fracture along a grain boundary with an MnS precipitate. The degree of tin segregation at the interface is larger than at grain boundaries, meaning that the segregation energy for the interface segregation may be higher than that for grain boundary segregation. It may be estimated to be more than 65 kJ/mol if the segregated amounts are compared at 1273 K. Therefore, the segregation at the interface may easily reach a saturation level with the tin addition at high temperatures.

Fig. 11 Schematic of a grain boundary with a MnS precipitate before and after fracture.

4. Effect of Sn on size of MnS precipitates

The fact that tin segregates at the interface between MnS and the matrix may influence the precipitates at high temperatures in the following manners.

(1) Effect of equilibrium Sn segregation on interfaces

Small precipitates become larger with annealing at high temperatures, which is called Ostwald ripening. It is caused by the reduction of free energy of the interface between the precipitates and the matrix⁽³⁴⁾. In the present case, the tin segregation may act to decrease of the interfacial energy and stabilize the small precipitates.

(2) Kinetics effect of Sn segregation on shape change of MnS

Morphology or size change of precipitates proceeds with atomistic reaction at interfaces and bulk diffusion of the component elements. Coverage of tin around MnS precipitates can prevent the reaction, that is the decomposition or the growth of MnS, so that the size of the precipitates may be kept small in the tin-added specimens.

Through the above effects, the size of primary recrystallized grains is considered to become small and homogeneous by tin addition because small particles may act to suppress the mobility of grain boundaries⁽³⁵⁾.

5. Effect of Sn on recrystallization

On the basis of the above discussion, let us consider the role of tin segregation in the primary recrystallization and secondary recrystallization in Si steels.

The effect of tin on the primary recrystallization can be classified as follows:

(1) The tin segregation occurs at grain boundaries, the degree of which depends on the concentration and temperature. By the effect of solute drag effect on grain boundary migration, the segregation can suppress the growth of gain boundaries, reducing the primary grain size. A similar result was also observed in non-oriented silicon steels with low carbon and very low precipitates which were added with tin⁽³⁶⁾.

(2) Considerable interface segregation of tin takes place between MnS as inhibitors and the matrix at high temperatures, which may cause the small precipitates.

Since the morphology of inhibitors is almost determined at high temperature treatment or hot rolling, the small precipitates may effectively inhibit the grain boundary migration or the grain growth of the primary grains after the treatment⁽⁴⁾⁽⁵⁾.

The contribution of these factors to primary grain size reduction and homogenization should be considered qualitatively. It has been shown that the tin segregation energy for the MnS-matrix interface is higher than that for grain boundary segregation, interface segregation may more strongly occur at high temperatures or in a low tin alloy. Nevertheless, grain size reduction by tin addition was observed in higher concentration alloys in the previous study⁽⁵⁾ and the present investigation. Therefore the reduction of the grain size may be mainly dominated by the tin grain boundary segregation.

Next we focused on the effect of tin on secondary recrystallization. The fact that the secondary recrystallization temperature decreases with the tin addition can be explained by the primary grain size reduction, corresponding to the increase of the stored energy for secondary recrystallization. The secondary recrystallization is also closely related to the inhibition effect, so that the size reduction of the inhibitors due to the tin addition can act to decrease the secondary recrystallization temperature.

Moreover, it is to noted that the secondary recrystallization temperature can be affected by annealing atmosphere. For instance, it has been shown by Yoshitomi *et al.*⁽³⁷⁾ that the secondary recrystallization temperature depends on annealing atmosphere such as hydrogen gas and nitrogen-hydrogen gas, which means that the gas elements influence the decomposition of inhibitors or the inhibitor effect at grain boundaries. The present results also suggest that the tin segregation can compensate for reduction of the inhibitor effect, and keep the stored energy for secondary recrystallization. Consequently, these effects may reduce the secondary recrystallized temperature in Fe-3%Si alloys doped with tin.

In addition, primary texture improvement by the tin addition, that is increase of a texture component $\{110\}\langle 001 \rangle$, can serve as the improvement of the preferential evolution of the secondary recrystallization. It must be responsible for the excellent magnetic properties of grain-oriented Si steels.

V. Conclusion

The grain boundary segregation and the interface segregation between precipitates and the matrix in Fe-3 mass%Si alloys doped with tin were investigated, and the effect of tin on the recrystallization was also discussed as follows.

(1) Decarburized specimens revealed intergranular fracture. Tin segregation was detected at grain boundaries, and the amount increased with the bulk concentration.

(2) The segregation energy of tin was considered to

be about 50 kJ/mol. From the segregation energy and the temperature dependence of tin diffusivity, the kinetics of grain boundary segregation was estimated.

(3) Significant segregation of tin was found at the interface between MnS and the matrix in AES experiment. The interface segregation may influence the size of the precipitates.

(4) The grain boundary segregation of tin may mainly contribute to inhibition and homogenization of primary grain growth. The effect and the tin segregation itself can lower the secondary recrystallization temperature in Fe-3 mass%Si alloys.

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