Effect of TiN Precipitates on Austenite Grain Size in Fe–1.5%Mn–0.12%Ti–Si(<1.1%)–C(0.05 and 0.15%) Alloy

Hiroki OHTA,¹⁾ Ryo INOUE²⁾ and Hideaki SUIITO³⁾

1) Formerly Institute of Multidisciplinary Research for Advanced Materials, Tohoku University. Now at Iron and Steel Research Laboratories, Kakogawa Works, Kobe Steel, Ltd., Ikeda, Onoue-cho, Kakogawa, Hyogo-ken, 675-0023 Japan.

2) Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira, Aoba-ku, Sendai, Miyagiken 980-8577 Japan.

3) Professor Emeritus, Tohoku University, Katahira, Aoba-ku, Sendai, Miyagiken 980-8577 Japan.

(Received on July 26, 2007; accepted on October 12, 2007)

In order to clarify the effect of non-uniformly dispersed TiN particles on the inhibition of austenite grain growth at non-steady state, an Fe–1.5%Mn–0.12%Ti–Si(<1.1%)–N(20~130 ppm)–C(0.05 and 0.15%) alloy with and without Mg deoxidation has been cooled from 1873 to 1473 K at 50 or 5 K·min⁻¹, followed by quenching. The austenite grain size distributions have been measured as functions of C, N and Si contents, Mg deoxidation and cooling rate. It was found that the γ grain growth is inhibited by the uniformly dispersed TiN particles which are found at 0.05% C. The effect of Si (0~1.1%) content on the γ grain size at given C, N and Ti contents has not been observed. In Mg deoxidation the number of TiN+MgO and TiN particles is about two times larger than that without Mg deoxidation, thus leading to smaller γ grain size. The mean γ grain size, $\bar{D}_A$, decreases with increasing the Zener pinning force at 0.05% C, but is independent of it at 0.15% C. The $\bar{D}_A$ value at 50 K·min⁻¹ is lower than that at 5 K·min⁻¹ at 0.05% C, but the $\bar{D}_A$ value is independent of the cooling rate at 0.15% C. This is explained by the fact that with decreasing cooling rate the number of uniformly dispersed TiN particles decrease considerably at 0.05% C, but only TiN particles at interdendritic region decrease at 0.15% C.

KEY WORDS: Fe–C alloy; TiN precipitation; Mg deoxidation; austenite grain size; Zener pinning force.

1. Introduction

It has been experimentally confirmed that the limiting mean austenite grain size at steady state is considerably smaller than that predicted from the Zener model. This austenite grain size is functions of the volume fraction of particles and the mean size of particles, if oxide particles are uniformly dispersed. The mean austenite grain size at non-steady state has been studied in previous experiments^{1,2)} in which an Fe–1%Mn–1%Ni–0.05~0.30%C alloy containing different oxide particles is cooled to a given temperature, followed by quenching. The γ grain size obtained at 0.05% C in which the δ/γ transformation occurs at δ/δ grain boundaries is found to be independent of the Zener pinning force, Z_p . However, the γ grain sizes at 0.15 and 0.30% C in which the γ phase appears after the peritectic reaction decrease with increasing Z_p .

The effect of non-uniformly dispersed particles on the limiting γ grain size has been studied theoretically^{3,4)} and experimentally.^{5–7)} However, there is little and no report dealing with the effect of non-uniformly dispersed particles such as TiN particles on γ grain size at non-steady state. In previous study,⁸⁾ the crystallization and precipitation behavior of TiN in an Fe–1.5%Mn–0.12%Ti–Si(<1.1%)–C(0.05 and 0.15%) alloy with and without MgO deoxidation has been studied for the samples cooled to 1473 K, followed by quenching. In the sample obtained at 0.05% C, the TiN par-

ticles below 1 μ m are uniformly dispersed in micro segregation domain, but in the sample obtained at 0.15% C, most of TiN particles are located at interdendritic region. In the presence of MgO particles, the TiN+MgO and TiN particles whose number is more than two times larger than that of TiN particles in the absence of MgO are observed and the different behavior of precipitation is also observed between 0.05 and 0.15% C.

In this study, the γ grain size distributions in the samples obtained in previous experiments⁸⁾ have been measured as functions of the contents of N and Si, MgO particles and cooling rate. The factors affecting the γ grain size at non-steady state have been studied, particularly, focusing on the degree of particle dispersion in solidification segregation domain which is influenced by solidification mode.

2. Experimental

An Fe–1.5%Mn–Si(<1.1%)–C(0.05 and 0.15%) alloy (70 g) was melted in an Al₂O₃ crucible at 1873 K under Ar–N₂ (P_{N_2} =0.03 and 0.1 atm) flowing atmosphere (% represents mass%, hereinafter). An Fe–10%Ti alloy was added to control the initial Ti content (0.12%) and a melt was stirred by an Al₂O₃ rod for 30 min in order to remove oxide particles by flotation. A melt was cooled to 1473 K at 50 or 5 K·min⁻¹. This experiment denotes the TiN experiment, hereinafter. To study the effect of MgO particles on TiN

Table 1. Contents of C, Si, Mg and total N, mean austenite grain size, $\bar{D}_A$, and Z_p values.

Exp. No.	Cooling rate (K·min ⁻¹)	[C] (%)	[Si] (%)	[sol.Mg] (ppm)	[insol.Mg] (ppm)	[T.N] (ppm)	$\bar{D}_A$ (μm)	Z_p × 10 ⁻³
TN-1	50	0.05	—	—	—	126	806	5.33
TN-2	50	0.05	0.52	—	—	122	618	4.44
TN-3	50	0.05	1.10	—	—	130	614	4.57
TN-4	50	0.05	—	—	—	61	915	2.88
TN-5	50	0.05	1.08	—	—	70	751	2.94
TN-6	50	0.05	—	—	—	23	1380	1.89
TN-7	50	0.05	1.07	—	—	20	1170	1.55
TN-8	50	0.15	—	—	—	129	1530	4.30
TN-9	50	0.15	0.57	—	—	124	943	3.45
TN-10	50	0.15	1.09	—	—	115	1820	3.29
TN-11	50	0.15	—	—	—	22	1220	1.19
TN-12	50	0.15	1.01	—	—	20	992	1.12
MT-1	50	0.05	—	< 0.1	67.4	119	565	7.74
MT-2	50	0.05	1.08	0.6	68.2	112	911	7.27
MT-3	50	0.05	—	< 0.1	58.5	70	723	5.18
MT-4	50	0.05	1.05	0.1	52.9	69	550	5.22
MT-5	50	0.15	—	0.5	53.6	122	1010	6.55
MT-6	50	0.15	1.04	< 0.1	58.6	130	1080	7.01
TN-13	5	0.05	—	—	—	93	2310	2.39
TN-14	5	0.05	0.50	—	—	79	2720	1.56
TN-15	5	0.05	1.07	—	—	85	1840	1.55
TN-16	5	0.15	—	—	—	95	1660	1.82
TN-17	5	0.15	0.52	—	—	84	467	1.39
TN-18	5	0.15	1.02	—	—	76	2290	1.30

precipitation, an Fe–1.5%Mn–Si(<1.1%)–C(0.05 and 0.15%) alloy was melted at 1873 K in an Al₂O₃ crucible under the controlled nitrogen gas atmosphere, followed by an Fe–10%Ti addition. A Ni–10%Mg alloy was added and a melt was cooled to 1473 K at 50 K·min⁻¹, followed by quenching in water. This experiment denotes the MT experiment, hereinafter. More details are given elsewhere.⁸⁾ The methods for the measurement of particle size, d_A , particle number, N_A , and γ grain diameter, D_A , and chemical analysis are given in detail elsewhere.⁸⁾ The fraction of solid, f_s , was estimated from the microsegregation of Mn whose content was measured by using a computer-aided X-ray micro-analyzer (the size of one analysis point: 2 μm×2 μm, integration time: 150 ms and irradiation current: 1×10⁻⁶ A). The particle dispersion in microsegregation domain was determined by coupling the fraction of solid.

3. Results and Discussion

The Zener pinning force,⁹⁾ Z_p , calculated from Eq. (1) and the measured values for mean value of the γ grain diameter, $\bar{D}_A$, are summarized in **Table 1**, together with the contents of carbon and total nitrogen.

$$Z_p = 3\sigma V_f / d \dots \dots \dots (1)$$

where σ is the grain boundary energy (6×10⁻⁷ J·mm⁻²), V is the molar volume of Fe (7×10³ mm³·mol⁻¹) and d is the mean particle diameter.

Chemical composition of metal phase (total oxygen, Mn, and soluble and insoluble M (M =Al and Ti)) and number density, N_A , mean particle diameter, $\bar{d}_A$, and volume fraction of particles, f_v , in TN-1~TN-12, MT-1~MT-6 at

50 K·min⁻¹ and TN-13~TN-18 at 5 K·min⁻¹ are already given elsewhere.⁸⁾ In the calculation of Z_p , the $\bar{d}_A$ value is used instead of d in Eq. (1).

Austenite grain size distributions obtained in the samples cooled to 1473 K at 50 K·min⁻¹, followed by quenching are shown in **Figs. 1** and **2** for [T.N]=20~23 and 115~130 ppm at 0.05 and 0.15% C, respectively. As shown in Fig. 1, the γ grain size distributions obtained at 0.05% C are nearly the same at 0.15% C and are independent of Si content up to 1.1%. On the other hand, the modal $\bar{D}_A$ values at 0.05% C are significantly smaller than those at 0.15% C, as shown in Fig. 2. The reason for this can be explained by the difference in the pinning force, if the TiN particles are uniformly dispersed. As observed previously⁸⁾ the TiN particles at 0.05% C are more uniformly dispersed than those at 0.15% C. It should be noted that the number of Al₂O₃ particles are negligibly small compared with the TiN particles.

In previous study⁸⁾ on the crystallization and precipitation of TiN particles in TiN experiments, it was found at [T.N]=115~130 ppm that the number of small TiN particles below 1 μm at 0.05% C is greater than that at 0.15% C. Furthermore, the N_A (120~160 mm⁻²) values at 0.05% C are significantly higher than those (70~110 mm⁻²) at 0.15% C, as shown in **Fig. 3**. This different precipitation behavior with respect to carbon content is explained as follows: The micro segregated Ti at interdendritic region is considerably influenced by the rapid diffusion in δ phase and the redistribution during δ/γ transformation in the case of 0.05% C. This leads to the bimodal particle size distribution in which the TiN particles with above 2 to 3 μm crystallize from the liquid phase, but those with below 0.5 to 1 μm precipitate from δ phase. More details are given

Fig. 1. Austenite grain size distributions obtained in TN experiments (total N=20~23 ppm and cooling rate=50 K·min⁻¹).

Fig. 2. Austenite grain size distributions obtained in TN experiments (total N=115~130 ppm and cooling rate=50 K·min⁻¹).

Fig. 3. Size distribution of TiN particles in TN experiments at 0.05 and 0.15% C and Si<0.005%.

Fig. 4. Number of TiN particles plotted against fraction of solid at 0.05 and 0.15% C and Si<0.005%.

elsewhere.⁸⁾

The reason that the grain size distribution is not affected by Si content is due to the fact that Si does not affect total number of TiN particles, although Si affects the crystallization of TiN particles in liquid phase which cannot be separated from total number of TiN particles.

The effect of nitrogen content on γ grain size distribution at 0.05 and 0.15% C is discussed in the following. The modal $\bar{D}_A$ values at 0.05% C shown on the left-hand side of Fig. 2 is significantly smaller than those shown on the left-hand side of Fig. 1. This is attributed to the fact that the N_A (from 30~40 to 130~160 mm⁻²) and $\bar{d}_A$ (from 1.7 to 2.0~2.4 μ m) values increase with an increase in nitrogen content (from 20~23 to 126~130 ppm), thus leading to the increase in the pinning force. More detailed explanation is made in Sec. 3.3.

The modal D_A values at 0.15% C shown on the right-hand side of Fig. 2 is greater than those shown on the right-hand side of Fig. 1. These results indicate that the modal D_A values increase with an increase in N content. These results are not simply explained by the pinning force, which means that the N_A (from 30~40 to 70~110 mm⁻²) and $\bar{d}_A$ (from 1.7 to 2.5~3.1 μ m) increase with increasing N content (from 20~22 to 115~129 ppm) at a given total Ti content (0.12%). Therefore, this should be explained by another reason.

It was found in previous study⁸⁾ that the TiN particles at 0.05% C are dispersed more uniformly in solidification segregation domain compared with those at 0.15% C, as shown in Fig. 4. The number of TiN particles was measured at three different ranges ($f_s=0\sim0.5$, $0.5\sim0.9$ and $0.9\sim1$) of fraction of solid. Since segregated Ti easily homogenizes in δ phase due to rapid diffusion in the case of 0.05% C, as shown in the upper diagram, the precipitation of TiN tends to occur uniformly. In the case of 0.15% C, however, most of the TiN particles are located at interdendritic region which corresponds to the initial δ grain boundaries. This different degree of dispersion of TiN particles influences the inhibition of γ grain growth, which will be discussed in detail in Sec. 3.3.

Although it is well known that the γ grain growth is re-

Fig. 5. Austenite grain size distributions obtained in MT experiments (total N=112~130 ppm and cooling rate=50 K·min⁻¹).

Fig. 6. Number of particles (MgO, TiN+MgO and TiN) obtained in TN and MT experiments at 0.05 and 0.15% C and Si<0.005%.

tarded during the two-phase region, this retardation effect¹⁰⁾ is disregarded in the present discussion. This is because the present carbon content (0.15%) is close to the peritectic carbon content (0.17%) in which no two-phase region is present.

3.1. Effect of MgO

The γ grain size distributions in MT experiments are shown in Fig. 5, as functions of the contents of carbon and Si at [T.N]=112~130 ppm. It can be seen that the modal D_A values at 0.05% C are smaller than those at 0.15% C. These results are in agreement with those in TN experiments even in the presence of MgO+TiN and TiN particles whose N_A values are about two times greater than those in TN experiments, as shown in Fig. 6. It was found in previous study⁸⁾ in MT experiments that the N_A values for MgO+TiN and TiN particles at 0.05 and 0.15% C are nearly the same, as is clear in Fig. 6. However, the number of small TiN particles below 1 μ m increases at 0.05% C, as shown in Fig. 7. This trend is similar to that observed in TN experiments, as shown in Fig. 3. Typical morphologies of TiN, MgO and TiN+MgO particles, and crystallization and precipitation of TiN particles at interdendritic region are shown in Fig. 8.

The MgO+TiN particles at 0.05 and 0.15% C are uni-

Fig. 7. Size distribution of particles (MgO, TiN+MgO and TiN) in MT experiments at 0.05 and 0.15% C, 119~122 ppm total N and Si<0.005%.

Fig. 8. Typical morphologies of (a) TiN, (b) MgO, (c) TiN+MgO and (d) interdendritic TiN particles.

formly dispersed in solidification segregation domain, as shown in Fig. 9. The number of TiN particles was measured at three different ranges ($f_s=0\sim0.5$, $0.5\sim0.9$ and $0.9\sim1$) of fraction of solid. However, as to the TiN particles the TiN particles at interdendritic region are high in the case of 0.15% C, whereas the TiN particles tend to be more uniformly dispersed in the case of 0.05% C, as shown in the upper diagram of Fig. 9. This is the reason that the modal D_A values at 0.05% C are smaller than those at 0.15% C.

When the grain size distributions at 0.15% C in MT experiments shown on the right-hand side of Fig. 5 are compared with those at 0.15% C in TN experiments at

Fig. 9. Number of TiN, TiN+MgO and MgO particles plotted against fraction of solid at 0.05 and 0.15% C and Si<0.005%.

[T.N]=115~130 ppm, shown on the right hand side of Fig. 2. The modal $\bar{D}_A$ values in the former are smaller than those in the latter. This can be explained by the difference in the N_A values between TN and MT experiments, as shown on the right-hand side of Fig. 6.

When the grain size distributions at 0.05% C in MT experiments shown on the left-hand side of Fig. 5 are compared with those at 0.05% C in TN experiments at [T.N]=115~130 ppm shown on the left-hand side of Fig. 2, the modal $\bar{D}_A$ values are nearly the same despite of the fact that the N_A values in the former are about two times greater than those in the latter, as shown on the right-hand side of Fig. 6. Furthermore, the number of particles in segregation domain in MT experiments shown in Fig. 9 are higher than those in TN experiments shown in Fig. 4. The reason that the modal $\bar{D}_A$ values at 0.05% C in TN and MT experiments are nearly the same cannot be explained simply by the number of particles only. This can be explained by the pinning force which will be discussed in next section.

3.2. Zener Pinning Force

The values for the mean γ grain size, $\bar{D}_A$, observed at 0.05 and 0.15% C are plotted against $1/Z_p$ in Figs. 10 and 11, respectively, together with the values obtained at $5 \text{ K} \cdot \text{min}^{-1}$ (half-filled triangles) which will be discussed in next section. The data for different total N contents at a given total Ti content (0.12%) are represented by different marks. It is reasonable to assume that the $\bar{D}_A$ values observed at non-steady state for given cooling rate and quenching temperature are related to the Zener pinning force if the particles are randomly dispersed. The results shown in Fig. 10 for $50 \text{ K} \cdot \text{min}^{-1}$ reveal that the $\bar{D}_A$ values at 0.05% C decrease with increasing Z_p values. However, the $\bar{D}_A$ values at 0.15% C for $50 \text{ K} \cdot \text{min}^{-1}$ are independent of Z_p , as shown in Fig. 11, although the data points scatter considerably in comparison with those shown in Fig. 10.

As mentioned previously, the TiN particles in TN experiments and the TiN+MgO and TiN particles in MT experi-

Fig. 10. Effect of Zener pinning force on γ grain size at 0.05% C as functions of total nitrogen content and cooling rate.

Fig. 11. Effect of Zener pinning force on γ grain size at 0.15% C as functions of total nitrogen content and cooling rate.

ments at 0.05% C are more randomly dispersed in comparison with those at 0.15% C. Therefore, the $\bar{D}_A$ values shown in Fig. 10 for $50 \text{ K} \cdot \text{min}^{-1}$ can be well related to the Zener pinning force. The $\bar{D}_A$ values shown in Fig. 11 for $50 \text{ K} \cdot \text{min}^{-1}$ are interpreted by the fact that the particles located at interdendritic region do not effectively pin the austenite grain growth in a manner similar to those for randomly dispersed particles. This effect of non-randomly dispersed particles on γ grain-growth-inhibition is basically different from that due to the particle dragging in presence of dissolved Ce.^{5,6,7)}

3.3. Effect of Cooling Rate

The austenite grain size distributions obtained at $5 \text{ K} \cdot \text{min}^{-1}$ at [T.N]=76~95 ppm are shown in Fig. 12 as functions of the contents of C and Si. Compared with the γ grain size distributions obtained at $50 \text{ K} \cdot \text{min}^{-1}$ for [T.N]=115~130 ppm shown in Fig. 2, it is clear that the modal $\bar{D}_A$ values at $5 \text{ K} \cdot \text{min}^{-1}$ are greater than those at $50 \text{ K} \cdot \text{min}^{-1}$ for 0.05% C, while those at 5 and $50 \text{ K} \cdot \text{min}^{-1}$ are nearly the same for 0.15% C. It was found previously⁸⁾ that the N_A values decrease and the $\bar{d}_A$ values increase con-

Fig. 12. Austenite grain size distributions obtained in TN experiments (total N=76~95 ppm and cooling rate=5 K·min⁻¹).

siderably under nearly constant volume fraction of particle with decreasing the cooling rate from 50 to 5 K·min⁻¹. These results explain the behavior for 0.05% C, but that for 0.15% C cannot be explained from the change of particle number and size arising from the cooling rate.

The mean values of γ grain size, $\bar{D}_A$, obtained at 5 and 50 K·min⁻¹ are plotted against Si content in Fig. 13. It can be seen from the upper diagram for 0.05% C that the $\bar{D}_A$ values for 5 K·min⁻¹ are more than two times greater than those for 50 K·min⁻¹ ([T.N]=122~130 ppm). However, the $\bar{D}_A$ values for 5 K·min⁻¹ ([T.N]=76~95 ppm) and 50 K·min⁻¹ ([T.N]=115~129 ppm) agree well with each other for 0.15% C, although the data points scatter considerably. The reason of such scatter for the $\bar{D}_A$ values at 0.15% C must be clarified in further study. The completely different behavior with respect to carbon content can be explained in terms of particle size distribution as well as the particle dispersion in solidification micro segregation domain.

The particle size distributions obtained at 0.05 ([T.N]=79~93 ppm) and 0.15% C ([T.N]=76~95 ppm) are shown in the upper and lower diagrams of Fig. 14, respectively, for 5 K·min⁻¹ at different Si contents. In previous study⁸⁾ it was found that the significant effect of Si on crystallization and precipitation of TiN is not observed. Thus it is considered that the particle size distributions at different Si contents are nearly the same. The present authors consider that the presence of Si influences the crystallization of TiN before complete solidification which can be experimentally confirmed by rapidly quenching at solidification temperature for the samples with and without Si content under constant Ti and N contents. The particle size distributions obtained at 0.05% C ([T.N]=61 ppm for TN-4) and 0.15% C ([T.N]=129 ppm for TN-8) for 50 K·min⁻¹ and [%Si]<0.005 are included in the figure for comparison. It can be seen from the upper diagram that the number of TiN particles below 1 μ m which precipitate in intragranular γ region becomes drastically smaller with decreasing cooling rate, although the number of TiN particles above 1 μ m which precipitate at interdendritic region also decreases drastically due to the particle growth. These small TiN particles with below 1 μ m which are dispersed uniformly pin the γ grain

Fig. 13. Effect of cooling rate on γ grain size at 0.05 and 0.15% C plotted against Si content.

Fig. 14. Size distribution of TiN particles in TN experiments at 0.05% C and 79~93 ppm total N, and 0.15% C and 76~95 ppm total N.

growth, while the larger TiN particles which are dispersed non-uniformly do not pin effectively the γ grain growth. It was found in previous study⁸⁾ that the small particles below 1 μ m at 0.15% are located at the interdendritic region in both cooling rates, although total number of TiN particles decrease and the mean particle size increases to a considerable degree with a decrease in cooling rate. These results indicate that the $\bar{D}_A$ values for 0.15% C shown in the lower diagram of Fig. 13 are independent of the cooling rate.

4. Conclusions

The inhibition of austenite grain growth by TiN and/or TiN+MgO particles has been studied in an Fe–1.5%Mn–0.12%Ti–Si(<1.1)–C(0.05 and 0.15%) alloy with and without Mg deoxidation. The following conclusions are drawn:

(1) At 115~130 ppm total N content the modal D_A value at 0.05% C is lower than that at 0.15% C. This can be explained by the fact that the number of TiN particles below 1 μm which are uniformly dispersed at 0.05% C is higher than that at 0.15% C due to the different behavior of solute micro segregation at different carbon content.

(2) The effect of Si(0~0.11%) content on γ grain size at a given C, Si and Ti contents has not been observed.

(3) The modal D_A values at 0.05 and 0.15% C in Mg deoxidation become smaller, since the number of TiN+MgO and TiN particles at 119~129 ppm T.N is about two times greater than that without Mg deoxidation at 115~130 ppm T.N.

(4) The mean γ grain size decreases with increasing Z_p at 0.05% C, but that at 0.15% C is independent of Z_p . This

is because the TiN particles at 0.05% C are uniformly dispersed, but those at 0.15% C are mostly present at interdendritic region.

(5) The modal D_A value at 5 K·min⁻¹ for 0.05% C is larger than that at 50 K·min⁻¹, because the number of uniformly dispersed TiN particles decreases considerably. The modal D_A value at 5 K·min⁻¹ for 0.15% C is nearly the same as that at 50 K·min⁻¹, because the TiN particles are located mostly at interdendritic region which do not effectively pin the γ grain growth.

REFERENCES

- 1) H. Suito, H. Ohta and S. Morioka: *ISIJ Int.*, **46** (2006), 840.
- 2) S. Morioka and H. Suito: *ISIJ Int.*, **48** (2008), 286.
- 3) E. Nes and J. A. Wert: *Scr. Metall.*, **18** (1984), 1433.
- 4) R. Elst, J. Van. Humbeeck: *Acta Metall.*, **36** (1988), 1723.
- 5) M. Guo and H. Suito: *ISIJ Int.*, **39** (1999), 1289.
- 6) K. Sakata and H. Suito: *Metall. Mater. Trans. A*, **31A** (2000), 1213.
- 7) H. Ohta and H. Suito: *ISIJ Int.*, **46** (2006), 832.
- 8) H. Ohta and H. Suito: *ISIJ Int.*, **47** (2007), 197.
- 9) C. Zener (quoted by C. S. Smith): *Trans. AIME*, **178** (1948), 15.
- 10) Y. Maehara, K. Yasumoto, Y. Sugitani and K. Gunji: *Trans. Iron. Steel. Inst. Jpn.*, **25** (1985), 1045.