Pinning of Austenite Grain Boundary of Fe–0.09 to 0.53 mass% C–0.02 mass%P Alloys by Primary Inclusions of Ce_2O_3 and CeS

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The effect of the deoxidation and desulfurization products of Ce_2O_3 (the mean planar diameter, $\bar{d}_A = 1.6$ to $2.1 \mu\text{m}$) and CeS ($\bar{d}_A = 2.2$ to $2.8 \mu\text{m}$) particles on the austenite grain growth was studied in Fe–0.20 (0.09 and 0.53) mass% C–0.02 mass% P alloys. The melts at 1873 K were continuously cooled to 1673, 1573 and 1473 K and then were held for 0 to 180 min in the austenite single phase region. Grain growth in the presence of particles was strongly inhibited by the pinning effect and the mean grain size was independent of the carbon content for a given holding time, holding temperature, and volume fraction of Ce_2O_3 particles ($f_V = 0.08$ to 0.12%). The planar limiting grain diameter, $\bar{D}_A$, obtained at holding times of more than 60 min, was found to be significantly smaller than that predicted from the Zener relation, and the deviation from this relation increased with increasing the $\bar{d}_A/f_V$ value. The fraction of particles at the grain boundaries, $\Phi_A = 0.07$ to 0.23 , was about 20 to 60 times higher than that estimated from the random distribution from the Zener limit. Based on these values for Φ_A , the limiting grain size was discussed as a function of f_V value, and the present results for Ce_2O_3 and CeS particles were compared with those obtained for the MgO and ZrO_2 particles in Fe–0.20 mass% C–0.02 mass% P and Fe–10 mass% Ni alloys.

KEY WORDS: austenite grain; grain size; Zener; pinning; Fe–C system; primary inclusion; Ce_2O_3 ; CeS.

1. Introduction

Most previous investigations on the austenite grain refinement in an Fe–C alloy have been made by the heat treatment of a quenched specimen in the austenite region, followed by precipitation of a second phase such as nitride, carbide, and carbonitride. Maehara *et al.*¹⁾ and Pottore *et al.*²⁾ studied the grain growth in samples which were continuously cooled from Fe–C melts through a peritectic reaction to form γ -Fe during cooling, and subsequently, the austenite grain growth started to take place. To the authors' knowledge, however, no published quantitative data, which concern the influence of primary inclusions on the austenite grain refinement in continuously cooled samples, are available, despite the importance of the pinning effect.

Grain growth inhibition by second-phase particles has been studied by a number of investigators, in particular, Hillert³⁾ and Gladman⁴⁾ who refined Zener's original calculation.⁵⁾ All these refinements give the results close to Zener's estimate. A detailed review of the various models for grain growth has been provided by Rymm *et al.*⁶⁾ Although the validity of Zener's assumption has been challenged on theoretical grounds and on the basis of experimental studies, the experimental verification of Zener's prediction is very limited due to difficulties in the accurate analysis of mean size and volume fraction of dispersed particles. This problem was discussed in our previous study,⁷⁾ in which the content of insoluble

elements or oxygen as primary inclusions determined by chemical analysis was compared with that estimated from the inclusion size distribution.

In the present study, Fe–0.09, 0.20 or 0.53 mass% C–0.02 mass% P alloys were continuously cooled from 1873 K to 1673, 1573, and 1473 K and the effect of deoxidation and desulfurization products of Ce_2O_3 and CeS particles on the austenite grain growth was studied in the austenite single phase region as a function of holding time. The fraction of particles at the grain boundaries was measured as a function of volume fraction of particles, grain size, holding time, and carbon contents. The limiting grain size was discussed with special emphasis on the fraction of particles at grain boundaries. The experimental results for the particle size distribution,⁷⁾ the grain size distribution⁸⁾ and the topological features⁸⁾ are described elsewhere. For the purpose of studying the relationship between solidification microstructure and grain structure,⁹⁾ the present alloys contain 0.02 mass% P which is favorable for revealing the solidification structure.

2. Experimental

2.1. Procedure

In the case of the experiments with the Ce_2O_3 inclusions, an Fe–0.20 mass% C–0.02 mass% P alloy (70 g) was melted at 1873 K in an Al_2O_3 crucible under a deoxidized Ar atmosphere (200 ml/min), by using an induc-

Table 1. Experimental conditions, inclusion and grain characteristics, and metal composition in Fe-0.20 mass% C-0.02 mass% P alloy containing Ce₂O₃ and CeS particles.

Exp. No.	Holding		$\bar{d}_A$ (μm)	N_A (mm^{-2})	f_V (pct)	D_{mean}	D_{max}	D_{min}	n	T. Ce	T. O	T. Al	T. S	insol. Ce	insol. Al	init. O	Φ_A	Inclusion composition
	Time (min)	Temp. (K)																
13-1	0	1673	1.61	262	0.028	1010	2600	399	229	235	49	—	—	210	< 1	113	0.13	Ce_2O_3
13-2	10	1673	1.83	220	0.027	1690	3940	599	127	194	55	—	—	204	< 1	125	0.11	
13-3	60	1673	1.78	260	0.025	2020	4540	901	104	205	50	—	—	186	< 1	105	0.09	
13-4	120	1673	1.69	278	0.027	1880	3640	1240	115	217	41	—	—	201	< 1	94	0.07	
13-5	180	1673	1.85	243	0.024	1900	3450	969	97	200	43	—	—	183	< 1	135	0.12	
14-1	0	1673	1.79	902	0.091	271	613	80	227	776	137	—	—	682	—	176	0.23	Ce_2O_3
14-2	10	1673	2.05	796	0.104	323	824	70	195	832	135	—	—	784	—	142	0.19	
14-3	60	1673	1.94	853	0.081	478	1260	225	164	679	77	—	—	607	—	104	0.15	
14-4	60	1673	1.77	168	0.016	1900	4020	512	98	124	30	—	—	117	—	124	0.10	
14-5	60	1673	2.04	395	0.062	1470	3690	554	108	457	64	—	—	463	—	117	0.09	
14-6	60	1673	2.01	330	0.053	1490	3270	418	114	389	78	—	—	401	—	109	0.08	
15-1*	0	1673	2.39	395	0.076	1300	3890	510	140	499	—	3050	103	468	6	16	0.13	CeS
15-2*	10	1673	2.67	307	0.054	1660	3700	644	163	345	—	3120	108	329	4	18	0.11	
15-3*	60	1673	2.21	323	0.070	2020	4560	624	108	396	—	3100	122	431	11	27	0.08	
16-1*	0	1673	2.45	635	0.143	461	1250	246	217	799	—	2890	178	874	6	22	0.14	CeS
16-2*	10	1673	2.75	504	0.084	855	2540	447	195	587	—	2900	144	518	14	16	0.14	
16-3*	60	1673	2.31	561	0.125	1570	5880	713	94	635	—	2970	150	765	11	19	0.12	
16-4*	120	1673	2.48	533	0.088	1600	3670	754	91	603	—	3110	160	541	17	17	0.12	
17-1*	0	1673	2.49	657	0.128	456	1110	106	255	796	—	3020	260	783	11	19	0.16	CeS
17-2*	10	1673	2.53	639	0.137	693	2950	106	448	829	—	3090	240	838	10	20	0.13	
17-3*	60	1673	2.60	724	0.189	1010	3340	216	382	1201	—	3090	200	1160	4	25	0.11	
18-1	0	1473	1.97	901	0.106	358	1150	79	299	816	155	—	—	797	—	138	—	Ce_2O_3
18-2	10	1473	1.82	878	0.107	412	1500	140	201	894	150	—	—	803	—	127	—	
18-3	60	1473	1.73	923	0.092	478	1500	116	212	740	169	—	—	696	—	144	—	
19-1	0	1573	2.02	826	0.108	290	897	81	276	802	142	—	—	812	—	112	—	Ce_2O_3
19-2	10	1573	2.04	909	0.100	349	1050	98	245	798	139	—	—	756	—	141	—	
19-3	60	1573	1.85	952	0.106	468	1600	187	198	832	131	—	—	801	—	122	—	
20-1*	0	1473	2.51	385	0.069	1400	3100	498	169	441	—	3000	125	423	14	15	—	CeS
20-2*	10	1473	2.61	392	0.075	1650	5000	619	135	485	—	2990	156	459	6	21	—	
20-3*	60	1473	2.39	435	0.078	2000	6010	997	99	509	—	3110	124	481	4	24	—	
21-1*	0	1573	2.45	423	0.064	1360	3590	458	155	502	—	3010	186	401	16	18	—	CeS
21-2*	10	1573	2.56	387	0.064	1600	4900	599	140	431	—	3000	166	391	3	19	—	
21-3*	60	1573	2.42	402	0.069	2010	6000	1040	83	448	—	2950	171	423	8	20	—	

* Al deoxidation

tion furnace (100 kHz). Pure Ce metal (0.04 to 0.14 g) was added to the melt containing the initial oxygen level of 90 to 180 mass ppm and immediately was stirred for 30 sec by using an Al₂O₃ rod. Then, the melt was cooled to 1673, 1573 and 1473 K at the rate of 1.02 K/s and was held for 0 to 180 min, followed by quenching in water.

In the case of the experiments with the CeS inclusions, an Fe-0.20 mass% C-0.02 mass% P alloy (70 g) was melted at 1873 K under an Ar-7 vol% H₂ gas atmosphere (200 ml/min). An Fe-0.50 mass% Al alloy (0.44 g) was added to decrease the oxygen level to 16 to 25 mass ppm and then was held for 30 min in order to remove Al₂O₃ particles by flotation. Total sulfur level was controlled in the range between 100 and 260 mass ppm by adding an Fe-38 mass% S alloy. After addition of pure Ce metal (0.07 to 0.28 g), the melt was cooled to 1673, 1573 and 1473 K at the rate of 1.02 K/s and then was held for 0 to 120 min, followed by quenching in water.

2.2. Fraction of Particles at Grain Boundaries

The fraction of particles at grain boundaries, Φ_A , was measured as follows: The mark by scratching was made in a polished cross-section prior to etching in 3 v/v % nital solution. The photomicrographs were taken at a magnification of 1000 for total observed area of 0.27

mm². By superimposing the photomicrographs taken before and after etching at the marked region of a cross-section, the particles at the grain boundaries and in the interior of the grain were counted separately. The Φ_A values were calculated from the $N_{A(g)}/N_A$ ratio where $N_{A(g)}$ and N_A are the number of particle sections at the grain boundaries and total number of particle sections per unit area, respectively. The measurement of particle size and number,⁹⁾ that of grain size,¹⁰⁾ and chemical analysis⁹⁾ are described elsewhere.

3. Results and Discussion

The experimental conditions, inclusion and grain characteristics, and metal composition in an Fe-0.20 mass% C-0.02 mass% P alloy containing Ce₂O₃ or CeS particles are given in Table 1. The results for Fe-0.1 (0.5) mass% C-0.02 mass% P alloys containing Ce₂O₃ particles are given in Table 2. The results for an Fe-0.20 mass% C-0.02 mass% P alloy without Ce addition obtained at holding times of 1473, 1573, and 1673 K are already given in a previous report.¹⁰⁾

3.1. Isothermal Grain Growth

An Fe-0.20 mass% C-0.02 mass% P alloy containing the Ce₂O₃ or CeS particles was cooled from 1873 to 1673 K at the rate of 1.02 K/s and then was held for 0

Table 2. Experimental conditions, inclusion and grain characteristics, and metal composition in Fe-0.1 (or 0.5)mass% C-0.02 mass%P alloys containing Ce₂O₃ particles.

Exp. No.	Holding time at 1673 K (min)	$\bar{d}_A$ (μm)	N_A (mm^{-2})	f_V (pct)	D_{mean} (μm)	D_{max} (μm)	D_{min} (μm)	n	C	T. Ce	T. O	insol. Ce	init. O	ϕ_A
(mass ppm)														
22-1	0	—	—	—	1450	4120	546	157	890	—	32	—	—	—
22-2	60	—	—	—	2590	6940	869	98	997	—	27	—	—	—
23-1	0	—	—	—	935	2370	398	123	5190	—	25	—	—	—
23-2	60	—	—	—	2200	5900	1030	95	5270	—	21	—	—	—
24-1	0	1.75	912	0.118	331	760	112	239	1080	864	148	889	169	0.20
24-2	60	2.05	799	0.108	771	1680	160	238	991	837	159	812	178	0.09
25-1	0	1.88	893	0.111	274	492	92	284	4960	801	165	833	98	0.22
25-2	60	1.94	835	0.120	741	1730	336	220	4940	934	134	901	94	0.12

Fig. 1. Grain growth in the experiments with and without inclusions as a function of holding time at 1673 K in Fe-0.20 mass% C-0.02 mass% P alloy.

to 180 min, followed by quenching in water. The mean grain diameter, $\bar{D}_A$, in a cross-section is plotted against holding time as a function of insoluble Ce content in **Fig. 1**. The error bars represent the range between the maximum and the minimum values, and the solid circles represent the results without Ce addition. The inclusion diameter, $\bar{d}_A$, and the content of dissolved Ce are given in Table 1. The experimental numbers except for Exp. No. 7-1 to 7-3 (Table 1 in Ref. 10)) shown in the figure correspond to those given in Table 1. Since the content of dissolved Ce (<90 mass ppm) is considerably small in this study, the effect of the solute drag on grain growth is supposed to be neglected, judging from the previous results.¹⁰⁾ Furthermore, in this study, the precipitates of CeP_x were not observed even at holding time of 60 min, although in the previous work,¹⁰⁾ in which the content of dissolved Ce is in the range between 140 and 800 mass ppm, the precipitation of CeP_x occurred at the Ce₂O₃

Fig. 2. Mean grain size obtained at holding times of 0 and 60 min plotted against carbon content in the experiments with and without Ce₂O₃.

particles located at the grain boundaries. It can be seen from **Fig. 1** that the grain growth inhibition occurs with increasing the content of insoluble Ce and the limiting grain size is observed in the range of holding time of more than 60 min. It should be pointed out that the particle size and number did not change with holding time at 1673 K.⁷⁾

An Fe-0.09 to 0.53 mass% C-0.02 mass% P alloy with and without Ce₂O₃ particles was cooled from 1873 to 1673 K and then was held for 0 and 60 min, followed by quenching in water. The mean grain size is plotted against carbon content in **Fig. 2**, in which the results represented by the open symbols correspond to those without Ce addition. It can be seen that the $\bar{D}_A$ values for the samples containing the Ce₂O₃ particles are significantly smaller than those without particles and furthermore, they are independent of carbon content. The reason that the $\bar{D}_A$ values for the sample without Ce₂O₃ particles have the maximum at about 0.2 mass% carbon is already explained by Maehara *et al.*¹⁾ as follows: When the melt with the peritectic composition of 0.17 mass% in Fe-Fe₃C system is cooled to a certain temperature in

Fig. 3. Mean grain size plotted against holding time at 1473, 1573, and 1673 K in Fe-0.20 mass% C-0.02 mass% P alloys with and without Ce_2O_3 or CeS.

γ -region, the time during cooling in this single phase region is the longest if the comparison is made for the same cooling rate. This results in the maximum grain size at the peritectic composition, because the grain in two-phase region is strongly pinned. It is of interest to note that in the presence of second-phase particles, the mean grain size at this composition does not have the maximum grain size.

A liquid Fe-0.20 mass% C-0.02 mass% P alloy with and without Ce_2O_3 or CeS was cooled to 1673, 1573, and 1473 K at the rate of 1.02 K/s and then was held for 0, 30, and 60 min. The mean grain size is plotted against holding time as a function of holding temperature in Fig. 3. As shown in the top diagram for the experiments without Ce addition, the $\bar{D}_A$ values at different holding temperatures increase with holding time, and do not have the same value at 60 min. On the other hand, the $\bar{D}_A$ values for the samples containing Ce_2O_3 or CeS particles shown in the middle and bottom diagrams, respectively, have almost the same value at 60 min for different holding temperatures. The reason that the $\bar{D}_A$ values for the holding times of 0 and 10 min are higher at a lower holding temperature compared with those at a higher holding temperature, is due to the fact that the time to the corresponding holding temperature from the start of the austenite crystallization is longer, although the growth rate is slower at a lower holding temperature. In the experiments with the CeS particles, no distinct trend was observed. It was confirmed experimentally that the limiting grain size was independent of holding temperature for a given insoluble Ce content; namely, a given volume fraction of particles and particle size.

Fig. 4. Limiting grain diameter in two dimensions plotted against $\bar{d}_A/f_v$ ratio.

3.2. Limiting Grain Size and Particle Pinning

The relationship between $\bar{D}_A$ and $\bar{d}_A/f_v$ is shown in Fig. 4 for the data obtained at a steady state, that is, the holding times of more than 60 min.

The Zener relation¹¹⁾ for the limiting grain diameter in two dimensions is given by

$$\bar{D}_A = (\pi/4) \cdot (\bar{d}_A/f_v) \quad \dots\dots\dots(1)$$

It can be seen from the results shown in Fig. 4 that the data points fall below the line given by Eq. (1), and particularly those for the Ce_2O_3 particles tend to deviate markedly with increasing the $\bar{d}_A/f_v$ value. The f_v values obtained from chemical analysis were used in this study, rather than those estimated from the inclusion characteristics on spatial size distribution, as discussed in a previous article.⁷⁾

The validity of the Zener approach concerning the grain growth inhibition by second-phase particles has been theoretically discussed based on the pinning force and the fraction of particles at the grain boundaries by Doherty *et al.*¹¹⁾ The computer simulations in two¹²⁾ and three¹³⁾ dimensions have indicated that particles are much more effective at inhibiting normal growth than would be expected on the basis of the Zener analysis. A review by Olgard and Evans¹⁴⁾ showed a wide scatter in the experimentally determined data of the particle pinned grain size and also showed a consistent trend in which pinned grain size were found to be much smaller than those predicted by the Zener analysis of low volume fractions.

The relationship between the $\bar{D}_A/\bar{d}_A$ ratio and f_v value is shown on logarithmic scales in Fig. 5, in which the relation given by Eq. (1) is also indicated. All data points correspond to those obtained at a steady state, which are used for the plot shown in Fig. 4. It can be seen that the data points for the Ce_2O_3 particles fall below the line given by Zener's limit in two dimensions and the slope is less than that predicted from Eq. (1). Those for the CeS particles tend to fit the line. The results¹⁵⁾ for an Fe-0.20 mass% C-0.02 mass% P alloy containing the

Fig. 5. Relationship between the ratio of limiting grain diameter to particle diameter and volume fraction of particles in logarithmic form for Ce₂O₃ and CeS particles in Fe-0.10 to 0.49 mass% C-0.02 mass% P alloys.

Fig. 6. Relationship between the ratio of limiting grain diameter to particle diameter and volume fraction of particles in logarithmic form.¹⁵⁾

MgO or ZrO₂ particles and those¹⁵⁾ for an Fe-10 mass% Ni alloy containing the MgO, ZrO₂ or Ce₂O₃ particles are shown in Fig. 6. The data points for the MgO particles in Fe-0.20 mass% C-0.02 mass% P and Fe-10 mass% Ni alloys follow the dash-dotted line obtained for the Ce₂O₃ and CeS particles in Fe-0.20 mass% C-0.02 mass% P alloy, as shown in Fig. 5. On the other hand, the data points for the ZrO₂ particles in Fe-0.20 mass% C-0.02 mass% P and Fe-10 mass% Ni alloys and the data points for the Ce₂O₃ particles in an Fe-10 mass% Ni alloy have a different behavior, that is, the $\bar{D}_A/\bar{d}_A$ value for a given f_V is significantly smaller. The reason for this different behavior with respect to the kind of particles is not certain at present.

Fig. 7. Fraction of particles at grain boundaries in two dimensions for random and nonrandom distributions plotted against mean grain diameter.

3.3. Fraction of Particles at Grain Boundaries

3.3.1. Dependence of $\bar{D}_A$, Holding Time, Carbon Level, and f_V

If the boundaries are distributed randomly with respect to the position of the particles, the fraction of particles at grain boundaries in two dimensions, $\Phi_{R(2-D)}$, will be given by¹¹⁾

$$\Phi_{R(2-D)} = 2\bar{d}_A/\bar{D}_A \quad \dots\dots\dots (2)$$

The fraction of particles at grain boundaries, Φ_A , was determined experimentally for an Fe-0.09 to 0.53 mass% C-0.02 mass% P alloy containing the Ce₂O₃ or CeS particles. These values along with the $\Phi_{R(2-D)}$ values given by Eq. (2) are plotted against mean grain diameter in Fig. 7 for different holding times at 1 673 K. The results¹⁵⁾ for the Ce₂O₃ particles in Fe-10 mass% Ni alloy, which are indicated by a broken line, are also included for comparison. It can be seen that the Φ_A values, which tend to decrease with an increase in the $\bar{D}_A$ value, are 20 to 60 times greater than the $\Phi_{R(2-D)}$ values. The Φ_A values for an Fe-10 mass% Ni alloy for a given $\bar{D}_A$ value are significantly smaller than those for an Fe-0.20 mass%-0.02 mass% P alloy. These findings suggest that a very high correlation between boundaries and particles is present in comparison with the random distribution for the Zener limit. The four data points marked by asterisk obtained for small grain size at holding times of 0 and 10 min indicate higher value of $\Phi_A > 0.19$. There is no difference between Ce₂O₃ and CeS particles and no effect of carbon content on the relationship, which will be discussed later in this section.

It is evident that the number of particles at the grain boundaries for a given number of particles per unit area, which corresponds to the fraction of particles at grain boundaries, increases with decreasing grain size. The grain size depends upon the volume fraction of particles under constant value of particle size according to the classical Zener model. In the present study, the f_V values are in the range between 0.02 and 0.19% and the f_V

Fig. 8. Time dependence of fraction of particles at grain boundaries.

Fig. 9. Fraction of particles at grain boundaries as a function of carbon content.

values for the data showing $\Phi_A > 0.19$ are 0.09 to 0.12 %.

The relationship between Φ_A and holding time at 1673 K is shown in Fig. 8 for the different values of f_v and $\bar{d}_A$. The Φ_A values for a given value of f_v and $\bar{d}_A$ tend to decrease with holding time and the Φ_A values for a given holding time tend to increase with an increase in the $f_v/\bar{d}_A$ values.

The Φ_A values are plotted against carbon content in Fig. 9 for the data obtained in the experiments with the Ce₂O₃ particles at the holding times of 0 and 60 min. It is obvious that the Φ_A values tend to be independent of carbon level under constant values of $\bar{d}_A$ and f_v , although the data points scatter to a considerable degree.

The relationship between Φ_A and f_v is shown in Fig. 10 for different holding time at 1673 K. The four data points marked by asterisk showing $\Phi_A > 0.19$, which correspond to the data having a small $\bar{d}_A$ value shown in Fig. 7, are higher than the others. Although the Φ_A values except for these data points seem to be independent of f_v values within the limit of experimental uncertainty. The results¹⁵⁾ for the MgO and ZrO₂ particles in an

Fig. 10. Dependence of volume fraction of particles on fraction of particles at grain boundaries.

Fig. 11. Relationship between fraction of particles at grain boundaries and that for random distribution.

Fe-0.20 mass%C-0.02 mass%P alloy and those¹⁵⁾ for the MgO, ZrO₂, and Ce₂O₃ particles in an Fe-10 mass% Ni alloy are shown in Fig. 10. It can be seen that the Φ_A values for the MgO and ZrO₂ particles in Fe-0.20 mass% C-0.02 mass%P and Fe-10 mass%Ni alloys are considerably lower than those for the Ce₂O₃ and CeS particles. Further work is necessary to clarify the reason that the Φ_A values for the Ce₂O₃ and CeS particles are considerably higher than those for the MgO and ZrO₂ particles without respect to an alloy system.

3.3.2. Comparison with Previous Study

The relationship between Φ_A and $\Phi_{R(2-D)}$ obtained in Fe-0.09 to 0.53 mass%C-0.02 mass%P alloys containing the Ce₂O₃ or CeS particles is shown in Fig. 11 for different holding times of 0, 10, and 60 to 180 min, along with the data point of the Ce₂O₃ particles in an Fe-10 mass%Ni alloy,¹⁵⁾ which are indicated by a broken line. It is seen that the Φ_A values increase with increasing the $\Phi_{R(2-D)}$ values.

Fig. 12. Relationship between fraction of particles at grain boundaries and that for random distribution.¹⁵⁾

Fig. 13. Ratio of observed fraction of particles at grain boundaries to random one in two dimensions plotted against volume fraction of particles.

The same relationship for the ZrO_2 and MgO particles in Fe-0.20 mass% C-0.02 mass% P and Fe-10 mass% Ni alloys is shown in Fig. 12.¹⁵⁾ These results are obtained when the grain growth is at a steady state. It can be seen that the Φ_A values are considerably smaller than those shown in Fig. 11, but they are slightly greater than the $\Phi_{R(2-D)}$ values.

The relationships between $\Phi_A/\Phi_{R(2-D)}$ ratio and f_V in logarithmic form are shown in Fig. 13 for the data obtained at a steady state shown in Figs. 11 and 12. It is seen that the $\Phi_A/\Phi_{R(2-D)}$ ratios tend to decrease with an increase in the f_V value, but these ratios for the Ce_2O_3 and CeS particles are considerably higher than those¹⁵⁾ for the MgO and ZrO_2 particles regardless of an alloy system, as mentioned previously.

Ohnuma *et al.*¹⁶⁾ derived the empirical relation between $\Phi_A/\Phi_{R(2-D)}$ and f_V based on the results from the two-dimensional computer simulation as follows:

Fig. 14. A plot for the relation derived by Doherty *et al.*¹¹⁾ considering the fraction of particles at grain boundaries.

$$\Phi_A/\Phi_{R(2-D)} = m \cdot f_V^{-1/2} \quad \text{.....(3)}$$

where m is a constant and Ohnuma *et al.* reported $m = 0.60$.

The relation given by Eq. (3) is also plotted in Fig. 13. The $\Phi_A/\Phi_{R(2-D)}$ ratios for the Ce_2O_3 and CeS particles in Fe-0.10 to 0.49 mass% C-0.02 mass% P alloys fall above this line. These results indicate that a very high correlation between boundaries and particles in the case of the Ce_2O_3 and CeS particles is present in comparison with that in the Zener limit.

Doherty *et al.*¹¹⁾ derived the following relation in two dimensions by taking into consideration the fraction of particles at grain boundaries.

$$\bar{D}_A = (\pi/2)^{1/2} \cdot (\Phi_A)^{-1/2} \cdot (\bar{d}_A/f_V^{1/2}) \quad \text{.....(4)}$$

When the pinning force exerted by a single particle is not the maximum force, F_{max} , and it is assumed to be given by the equation $F = \alpha \cdot F_{\text{max}}$ ($0 \leq \alpha \leq 1$), the following relation can be deduced:

$$\Phi_A^{1/2}/\Phi_{R(2-D)} = (\pi/8)^{1/2} \cdot \alpha^{-1/2} \cdot f_V^{-1/2} \quad \text{.....(5)}$$

The $\Phi_A^{1/2}/\Phi_{R(2-D)}$ ratios are plotted against $f_V^{-1/2}$ in Fig. 14, in which the lines for $\alpha = 0.05, 0.10$, and 1 are plotted based on the slope predicted from Eq. (5). The results for the Ce_2O_3 particles in Fe-0.010 to 0.49 mass% C-0.02 mass% P alloys are located between $\alpha = 0.05$ and 0.1 and those for the CeS particles fall above the line of $\alpha = 0.05$. However, those¹⁵⁾ for the MgO and ZrO_2 particles fall roughly on the line of $\alpha = 1$, and those for Ce_2O_3 particles in an Fe-10 mass% Ni alloy fall above the line of $\alpha = 1$, although the data points scatter to a considerable degree. On the basis of this analysis by using the relation proposed by Doherty *et al.*¹¹⁾ and $F = \alpha \cdot F_{\text{max}}$, it can be said that the Ce_2O_3 and CeS particles have much less pinning force exerted by a single particle, as compared with Zener's maximum force. Further work is necessary to clarify the reason for the higher value of Φ_A and the lower value of α in the case of the Ce_2O_3 and CeS particles in Fe-C alloy.

4. Summary

The effect of the deoxidation and desulfurization products of Ce_2O_3 and CeS particles on the austenite grain growth in Fe–0.09, 0.20, or 0.53 mass% C–0.02 mass% P alloys was studied at 1 673, 1 573, and 1 473 K as a function of holding time. The results are summarized as follows:

(1) The grains in the sample without Ce_2O_3 particles had the maximum size at about 0.20 mass% carbon for a given holding time at 1 673 K. On the other hand, the mean grain size in the sample containing the Ce_2O_3 particles, which was strongly reduced by the pinning effect, was independent of carbon level.

(2) The planar limiting grain diameter obtained at holding times of more than 60 min was found to be much smaller than that predicted from the Zener relation and the deviation increased with increasing the $\bar{d}_A/f_V$ values.

(3) The fraction of the Ce_2O_3 and CeS particles at grain boundaries, Φ_A , was measured as a function of holding time, grain diameter, carbon content, and volume fraction of particles. The Φ_A values at a steady state, which were slightly dependent on f_V values in the range between 0.02 and 0.19 %, were significantly higher than those estimated from the random distribution for the Zener limit.

(4) The fraction of particles at the grain boundaries

for the Ce_2O_3 or CeS particles in Fe–0.09 to 0.53 mass% C–0.02 mass% P alloys was significantly greater than that observed for the MgO and ZrO_2 particles in Fe–0.20 mass% C–0.02 mass% P and Fe–10 mass% Ni alloys.

REFERENCES

- 1) Y. Maehara, K. Yasumoto, Y. Sugitani and K. Gunji: *Trans. Iron Steel Inst. Jpn.*, **25** (1985), 1045.
- 2) N. S. Pottore, C. I. Garcia and A. J. Deardo: *Metall. Trans. A.*, **22A** (1991), 1871.
- 3) M. Hillert: *Acta Metall.*, **13** (1965), 227.
- 4) T. Gladman: *Proc. Roy. Soc.*, **A294** (1966), 298.
- 5) C. Zener: see C. Smith: *Trans. AIME*, **175** (1948), 47.
- 6) N. Ryum, O. Hunderi and E. Nes: *Scripta Metall.*, **17** (1983), 1281.
- 7) M. Guo and H. Suito: *ISIJ Int.*, **39** (1999), 680.
- 8) M. Guo and H. Suito: *ISIJ Int.*, **39** (1999), 1297.
- 9) M. Guo and H. Suito: *ISIJ Int.*, **39** (1999), 724.
- 10) M. Guo and H. Suito: *ISIJ Int.*, **39** (1999), 1169.
- 11) R. D. Doherty, D. J. Srolovitz, A. D. Rollet and M. P. Anderson: *Scripta Metall.*, **21** (1987), 675.
- 12) D. J. Srolovitz, M. P. Anderson, G. S. Grest and P. S. Sahni: *Acta Metall.*, **32** (1984), 1429.
- 13) M. P. Anderson, G. S. Grest, R. D. Doherty, K. Li and D. J. Srolovitz: *Scripta Metall.*, **23** (1989), 753.
- 14) D. L. Olgsard and B. Evans: *J. Am. Ceram. Soc.*, **69** (1986), C227.
- 15) K. Sakata and H. Suito: *CAMP-ISIJ*, **10** (1997), 129.
- 16) K. Ohnuma, H. Ohtani, K. Ishida, and T. Nishizawa: *J. Jpn. Inst. Met.*, **58** (1994) 1133.