Effect of Primary Deoxidation Products of Al_2O_3 , ZrO_2 , Ce_2O_3 and MgO on TiN Precipitation in Fe–10mass%Ni Alloy

Georgy V. PERVUSHIN and Hideaki SUIITO

Institute for Advanced Materials Processing, Tohoku University, Katahira, Aoba-ku, Sendai, Miyagi-ken 980-8577 Japan.

(Received on February 5, 2001; accepted in final form on March 16, 2001)

Effect of Al_2O_3 , ZrO_2 , Ce_2O_3 and MgO particles with mean diameter of 0.8 to 1.5 μm on the precipitation of TiN during solidification and holding at 1400°C has been studied in an Fe–10mass%Ni alloy. The values for the number of particles per unit area, N_A , and the mean diameter, $\bar{d}_A$, of TiN and $\text{TiN} + M_x\text{O}_y$ ($M = \text{Al, Zr, Ce, and Mg}$) particles have been measured as a function of initial contents of Ti (50 to 990 mass ppm) and N (200 to 290 mass ppm), and holding time (0 and 60 min). The N_A values of the $\text{TiN} + \text{MgO}$ particles are considerably higher than those of the $\text{TiN} + M_x\text{O}_y$ ($M = \text{Al, Zr, and Ce}$) particles, while the $\bar{d}_A$ values of the former particles, which are found to be independent of solidification mode, are smaller than those of the latter particles. The $\bar{d}_A$ values of TiN and $\text{TiN} + M_x\text{O}_y$ ($M = \text{Al, Zr, and Ce}$) particles in dendritic solidification are smaller than those in nondendritic one, whereas an opposite trend is observed with respect to the N_A values. The $\bar{d}_A$ values of the TiN and $\text{TiN} + M_x\text{O}_y$ particles were found to remain unchanged, but the N_A values tended to slightly increase with holding time.

KEY WORDS: precipitation; solubility product; microsegregation; deoxidation products; dendritic solidification; TiN; Fe–Ni alloy.

1. Introduction

When the solubility product of TiN precipitation is larger than the equilibrium one, that is, the melt is critically supersaturated with reactants, homogeneous precipitation occurs. In practice, however, titanium nitrides nucleated on primary inclusion particles such as alumina are often observed.^{1–3)} The efficiency of heterogeneous precipitation has been discussed on the basis of the wetting angle, which is a measure of the difference in interfacial energy between the precipitate/catalyst and liquid Fe/catalyst interfaces and the lattice mismatching, which is the disregistry between the lattice parameters of the substrate and the nucleating phase.⁴⁾

The effect of inoculation by primary deoxidation products on the precipitation of TiN during solidification and cooling has not been systematically studied despite of such importance that the grain refinement is strongly influenced by the size, number, and location of precipitated particles. Although it is often observed that the TiN particles are located mostly in interdendritic spaces, it is not ascertained whether the TiN precipitation occurs in liquid or solid state as a result of the microsegregation of titanium which reacts with nitrogen.

The precipitation of TiN during solidification and holding at 1400°C was previously studied in an Fe–10mass%Ni alloy as a function of initial contents of Ti and N under the condition that oxide particles were eliminated as much as possible.⁵⁾ As a result, it was found that the number of particles per unit area, N_A , for the TiN particles increased with increasing the $[\text{Total Ti}] \cdot [\text{Total N}]$ product, and the N_A

value and size of the TiN particles depended on solidification mode such as columnar dendrite and globular cell.

In the present article, the effect of the primary deoxidation products of Al_2O_3 , ZrO_2 , Ce_2O_3 and MgO on the precipitation behavior of TiN is studied in an Fe–10mass%Ni alloy as a function of initial contents of Ti and N, holding time at 1400°C, and solidification mode.

2. Experimental

2.1. Procedure

An Fe–10mass%Ni alloy (70 g) was melted at 1600°C in an alumina crucible under the 46.5vol%Ar–50vol%N₂–3.5vol%H₂ gas flowing atmosphere by using an induction furnace. The initial contents of N and O were controlled to 200 to 290 mass ppm and 100 to 150 mass ppm, respectively. An alloy (Fe–50mass%Al, Fe–50mass%Zr, Ni–10mass%Ce and Ni–10mass%Mg) was added to produce uniformly dispersed fine oxide particles.⁶⁾ Then, immediately an appropriate amount of an Fe–20mass%Ti alloy was added to control the initial Ti level (50 to 990 mass ppm Ti). Thereafter, the melt was immediately cooled to 1400°C at a rate of 0.70°C/s and was held for 0 or 60 min, followed by quenching in water. More detailed description was given in previous article.⁵⁾

2.2. Microscopic Observation

The size, number and composition of the TiN, $\text{TiN} + M_x\text{O}_y$, and $M_x\text{O}_y$ particles in dendritic and nondendritic zones on a polished cross-section were measured by SEM

with EPMA-EDX with a magnification of 3 000 using the technique described elsewhere.⁵⁾ The observed areas of dendritic and nondendritic zones were 0.14 to 0.40 mm² and total numbers of the observed particles in dendritic (nondendritic) zone were 300 (198), 220 (206), 315 (256), and 473 (494) for the Al, Zr, Ce, and Mg deoxidation, respectively. More details on the microscopic observation were given in previous article.⁵⁾

2.3. Chemical Analysis

For the determination of soluble and insoluble Ce, a metal sample (0.2 to 0.4 g) was dissolved with 2v/v% triethanol amine–1w/v% tetramethylammonium chloride–methanol–0.1 to 0.2w/v% Ba by using a potentiostatic electrolytic extraction method. After filtration, the solution and residue were analyzed by using inductively coupled plasma (ICP) emission spectrometry. The method for analyzing other elements was explained elsewhere.⁵⁾

3. Results and Discussion

3.1. Inclusion Content from Chemical Analysis

The contents of total and insoluble deoxidant *M* (*M*=Al, Zr, Ce, and Mg) and Ti and those of total N and total O for the samples obtained at 0 and 60 min at 1 400°C are summarized in **Table 1**. The experiments are classified into two groups depending on high and low contents of total Ti at the nitrogen level between 197 and 285 mass ppm. The experiments for high content of total Ti ranging from 598 to 986 mass ppm (Exp. Nos. 10, 12, 14, 16, 18, 20, 22, and 24) are denoted by $[T.Ti] \cdot [T.N] = (1.5\text{--}2.5) \times 10^{-3} \%^2$ and those for low content of total Ti ranging from 47 to 144 mass ppm (Exp. Nos. 11, 13, 15, 17, 19, 21, 23, and 25) are denoted by $[T.Ti] \cdot [T.N] = (1\text{--}4) \times 10^{-4} \%^2$.

The relationship between total Ti and total N contents and that between soluble Ti and soluble N contents are shown in **Fig. 1**. The method of obtaining soluble N content was described elsewhere.⁵⁾ Total Ti and total N contents represent soluble Ti and soluble N contents at 1 600°C, respectively. It is seen that the data for soluble Ti and soluble N at zero holding time scatter around the solubility line at 1 400°C obtained by Wada and Pehlke,⁷⁾ but those at 60 min holding time fall on the line at 1 400°C reported by Kunze⁸⁾ irrespective to the $[T.Ti] \cdot [T.N]$ value. In the previous experiments⁵⁾ without oxide particles, the data of soluble Ti and soluble N for both zero and 60 min holding times were found to be located on the solubility line at 1 400°C by Wada and Pehlke.⁷⁾ These results reveal that in the presence of oxide particles the precipitation of TiN reaches the equilibrium within 60 min and the equilibrium solubility product of TiN reported by Kunze⁸⁾ seems to be valid in an Fe–10mass%Ni alloy.

The contents of TiN and Ti₂O₃ were estimated from the values for insoluble *M* (*M*=Al, Zr, Ce, and Mg), insoluble Ti, total O and total N by using the method described in detail in previous article.⁵⁾ Consequently, it was found that insoluble Ti corresponded to almost TiN, namely no titanium oxide was present. This was also confirmed by EPMA-EDX. The contents of TiN, *M*_xO_y and Al₂O₃ in inclusions were estimated from a chemical analysis and the results are shown in **Fig. 2** as a function of holding time and

Table 1. Chemical composition in metal phase.

Exp. No.	Insol.Ti	T.Ti	Insol.M	T.M	Insol.Al	T.Al	T.N	T.O
(mass ppm)								
Al deoxidation								
10	206	620	23	200	-	-	264	21
11	67	136	34	297	-	-	251	30
12*	630	735	52	287	-	-	262	46
13*	24	47	59	103	-	-	197	52
Zr deoxidation								
14	413	719	184	186	2	34	202	67
15	4	108	231	231	29	189	214	106
16*	703	752	203	214	4	13	229	75
17*	64	69	207	230	tr.	tr.	234	73
Ce deoxidation								
18	350	598	342	342	tr.	91	229	59
19	22	88	299	300	15	130	237	65
20*	690	705	286	286	7	7	214	55
21*	60	67	286	286	14	14	208	61
Mg deoxidation								
22	727	986	73	88	16	49	239	63
23	113	144	51	56	37	39	285	67
24*	650	666	119	138	16	41	227	93
25*	56	63	70	70	35	154	207	77

M : deoxidant. * : *t* (1400 °C)=60 min. tr. : trace.

Fig. 1. Effect of temperature on equilibrium solubility of TiN and the relation between Ti and N contents.

$[T.Ti] \cdot [T.N]$ product. It is seen that the contents of Al₂O₃ in the Mg deoxidation for low $[T.Ti] \cdot [T.N]$ value is relatively high in comparison with those in Zr and Ce deoxidation. The contents of Al₂O₃ in the Al deoxidation for high $[T.Ti] \cdot [T.N]$ value is small in comparison with those of other oxides. The contents of TiN for high $[T.Ti] \cdot [T.N]$ value which correspond to the content of TiN and TiN+*M*_xO_y particles are considerably higher than those for low $[T.Ti] \cdot [T.N]$ value. It should be noted that although the contents of MgO are lower than those of other deoxidation products, the number of MgO particles per unit area is much higher in comparison with that of other oxide particles ($\bar{d}_A = 1.5 \mu\text{m}$) due to small size of MgO particles ($\bar{d}_A = 0.8 \mu\text{m}$), as will be explained later.

3.2. Solidification Structure

The globular cell and columnar dendrite were observed on a polished cross-section by etching in Oberhoffer solution. The globular cell, which is denoted by nondendrite in this article, was described in details elsewhere.⁹⁾ The

columnar dendrite was observed in the upper part of the cross-section.⁵⁾ The fraction of dendrite area at the observed cross-section was 20 to 30%, which was nearly the same value as observed in the previous experiments⁵⁾ without oxide particles, but the fractions of dendritic areas for Exp. Nos. 18, 22, and 23 were about 70%. No dendritic solidification was observed in the Zr deoxidation (Exp. No. 17) in which the holding time was 60 min and the $[T.Ti] \cdot [T.N]$ product was low. The values for the mean globular diameter, $\bar{d}$, and those for the mean primary, $\bar{d}_1$, and secondary, $\bar{d}_2$, dendrite arm spacings measured at 3 to 4 mm apart from the top surface, which is nearly at the center of the dendritic zone, are $\bar{d}=150$ to 200, $\bar{d}_1=300$ to 400 and $\bar{d}_2=100$ to 150 μm , respectively. The globular cell size

was found to be independent of its location in nondendritic zone.

3.3. Effect of Initial Contents of Ti and N on N_A and $\bar{d}_A$

The numbers of the TiN, $TiN+M_xO_y$ and M_xO_y particles per unit area observed by SEM with EPMA-EDX in dendritic and nondendritic zones, which are given in Table 2, are shown in Figs. 3 and 4, respectively. The M_xO_y and $TiN+M_xO_y$ particles for the Zr, Ce, and Mg deoxidation contain some amount of Al_2O_3 , as shown in Fig. 2. The N_A value for the $TiN+MgO(+Al_2O_3)$ particles (Exp. Nos. 23 and 25) was 20 to 25% of that for the $TiN+MgO$ particles and the N_A values for other $TiN+M_xO_y+Al_2O_3$ particles are considerably small. It can be seen that the data for Exp. Nos. 11, 19, and 23 in the lower diagram of Fig. 3, Exp. Nos. 11, 13, and 19 in the lower diagram of Fig. 4 and Exp. No. 18 in the upper diagram of Fig. 4 contain the M_xO_y particles whose contents are not negligibly small compared with those of the TiN and $TiN+M_xO_y$ particles. This trend is mostly observed in the Al and Ce deoxidation for low $[T.Ti] \cdot [T.N]$ value. From the results in Figs. 3 and 4, it is apparent that the N_A values for the $TiN+M_xO_y$ particles in the Mg deoxidation are considerably higher than those in other deoxidation regardless of solidification mode and $[T.Ti] \cdot [T.N]$ value.

By using the data obtained at zero holding time, the effect of the $[T.Ti] \cdot [T.N]$ product on the mean diameter and the N_A value for the sum of the TiN and $TiN+M_xO_y$ particles is discussed as a function of solidification mode. The results are shown in Fig. 5, in which the results obtained in previous study⁵⁾ in the absence of oxide particles are also indicated by the hatched lines. The error bars represent the standard deviation. As shown in the lower diagram, the N_A values in both solidification modes increase with increasing the $[T.Ti] \cdot [T.N]$ product and those for dendritic solidification are higher than those for nondendritic one in the range of high $[T.Ti] \cdot [T.N]$ value. Furthermore, the N_A values for

Fig. 2. Inclusion contents estimated from chemically analyzed contents of insoluble M (Ti, Al, Zr, Ce and Mg), total N and total O.

Table 2. Mean size, $\bar{d}_A$, and number of TiN and $TiN+M_xO_y$ particles per unit area, N_A , in dendritic and nondendritic zones.

Exp. No.	$\bar{d}_A$ (μm)						N_A (mm^{-2})					
	Dendrite			Nondendrite			Dendrite			Nondendrite		
	TiN	TiN + M_xO_y	Ave.**	TiN	TiN + M_xO_y	Ave.**	TiN	TiN + M_xO_y	Tot.**	TiN	TiN + M_xO_y	Tot.**
Al deoxidation												
10	1.26	1.90	1.33	2.10	2.69	2.23	428	60	488	126	65	201
11	1.33	1.72	1.49	n.o.	1.55	1.35	17	58	183	n.o.	102	167
12*	2.23	2.25	2.22	2.62	2.74	2.65	191	106	307	113	113	237
13*	0.63	1.61	1.35	2.33	1.82	1.86	70	52	124	6	50	103
Zr deoxidation												
14	1.09	1.82	1.45	2.56	2.93	2.82	204	200	404	58	94	152
15	0.43	1.23	1.21	-	1.81	1.77	4	60	67	n.o.	42	56
16*	1.04	1.65	1.37	1.54	2.31	2.14	270	323	594	74	252	327
17*	-	-	-	1.06	1.54	1.51	-	-	-	8	264	280
Ce deoxidation												
18	1.10	2.01	1.65	1.67	2.54	2.01	189	320	541	93	202	425
19	0.92	1.41	1.46	n.o.	1.58	1.48	15	96	357	n.o.	37	334
20*	1.12	2.16	1.61	1.62	2.22	2.04	412	369	781	119	286	405
21*	n.o.	2.01	2.01	n.o.	1.87	1.87	n.o.	158	158	n.o.	136	136
Mg deoxidation												
22	0.88	1.09	1.04	1.14	1.14	1.14	322	871	1193	247	611	858
23	0.51	0.84	0.86	0.73	0.81	0.80	35	376	537	68	556	673
24*	1.05	1.42	1.35	0.99	1.25	1.21	165	703	869	168	870	1028
25*	0.56	0.91	0.85	0.61	1.09	1.05	103	484	617	29	622	685

M : deoxidant. n.o.: not observed. *: t (1400 °C) = 60 min.

**: values of average $\bar{d}_A$ and total N_A for TiN, $TiN+M_xO_y$, and M_xO_y particles.

Fig. 3. Particle number per unit area, N_A , plotted against holding time and 1400°C in dendritic zone for different deoxidants and $[T.Ti] \cdot [T.N]$ products.

Fig. 4. Particle number per unit area, N_A , plotted against holding time at 1400°C in nondendritic zone for different deoxidants and $[T.Ti] \cdot [T.N]$ products.

the MgO particles indicated by the open and solid square marks are significantly higher than those for other oxides and those for “without oxide” are lower than those with oxides in both solidification modes.

The $\bar{d}_A$ values for dendritic mode are independent of the $[T.Ti] \cdot [T.N]$ product, whereas those for nondendritic mode in Al, Zr and Ce deoxidation increase with an increase of the $[T.Ti] \cdot [T.N]$ product. That is, the difference in the $\bar{d}_A$ values between dendritic and nondendritic modes increase with an increase of the $[T.Ti] \cdot [T.N]$ product. The results for “without oxide” show a similar trend. The $\bar{d}_A$ values for the MgO particles, which are independent of the $[T.Ti] \cdot [T.N]$ product, are significantly lower than those for other oxides.

Fig. 5. Mean diameter, $\bar{d}_A$, and particle number per unit area, N_A , for the sum of TiN and $TiN+M_xO_y$ particles plotted against $[T.Ti] \cdot [T.N]$ product in dendritic and nondendritic zones.

Fig. 6. Number of TiN, $TiN+M_xO_y$ and M_xO_y particles per unit area, N_A , plotted against $[T.Ti] \cdot [T.N]$ product in dendritic and nondendritic zones for zero holding time at 1400°C.

The reason for different behavior in the case of MgO particles will be discussed in detail in Sec. 3.6.

In order to understand the reason for the dependence of $[T.Ti] \cdot [T.N]$ product on the $\bar{d}_A$ and N_A values, the dependence on the $[T.Ti] \cdot [T.N]$ product of the N_A values for TiN, $TiN+M_xO_y$ and M_xO_y particles are considered separately, as shown in Fig. 6. The datum point marked by asterisk in the upper diagram corresponds to Exp. No. 10, in which the N_A values of Al_2O_3 and $TiN+Al_2O_3$ particles are small compared with other oxides, as shown in Fig. 3. The reason that

the N_A values for the TiN particles in dendritic mode for a given high $[T.Ti] \cdot [T.N]$ value are higher than those in non-dendritic mode is not clear at present, although the reason is discussed in the previous article.⁵⁾ It can be seen from the middle diagram of Fig. 6 that the heterogeneous precipitation of TiN on the MgO particles occurs more favorably. However, the N_A values for MgO particles in the Mg deoxidation are significantly higher than those in other deoxidation, as shown in Figs. 3 and 4. This will be discussed in Sec. 3.6.

Heterogeneous precipitation of TiN on oxide particles is expected to occur more favorably with increasing the $[T.Ti] \cdot [T.N]$ product regardless of solidification mode. Consequently, as a result of the decrease of soluble Ti and N contents, it is considered that the N_A values of TiN in the presence of oxide particles are lower than those in the absence of oxide particles at a given initial contents of Ti and N. The N_A values for the TiN+MgO particles are considerably higher, but the size of these particles is much smaller than that of other oxide particles, as will be shown below. The N_A values for the TiN particles in the Mg deoxidation of both solidification modes fall on the respective extrapolated lines obtained by other oxides, as shown in the upper diagram of Fig. 6.

The $\bar{d}_A$ values for the TiN and TiN+ M_xO_y particles in dendritic and nondendritic solidification are shown in Figs. 7 and 8, respectively, for zero holding time. It is apparent that the $\bar{d}_A$ values for the TiN and TiN+ M_xO_y particles in dendritic mode are almost independent of the $[T.Ti] \cdot [T.N]$ product, as shown in Fig. 7, whereas those in nondendritic mode increase significantly with an increase of $[T.Ti] \cdot [T.N]$ product, as shown in Fig. 8. In the case of low $[T.Ti] \cdot [T.N]$ value and nondendritic mode, no TiN particles were observed at the zero holding time except for the Mg deoxidation, as shown in the lower diagram of Fig. 4. These findings are consistent with those for the TiN particles observed in the experiments without oxide particles,⁵⁾ as shown in the upper diagrams of Figs. 7 and 8 by the hatched lines.

At high $[T.Ti] \cdot [T.N]$ value and zero holding time, the large size of the TiN and TiN+ M_xO_y ($M=Al, Zr$, and Ce) particles and the small size of the TiN and TiN+ M_xO_y particles were observed in the interglobular region mostly in nondendritic solidification. A similar trend was observed in the absence of oxide particles at high $[T.Ti] \cdot [T.N]$ value and zero holding time. These large particles observed in the experiments with and without oxides at zero holding time are considered to precipitate during solidification at the interglobular space. The small particles for TiN and TiN+ M_xO_y observed in dendritic solidification at high and low $[T.Ti] \cdot [T.N]$ values and those in nondendritic solidification at low $[T.Ti] \cdot [T.N]$ value are considered to precipitate in solid state. This should be confirmed based on the microsegregation model by which the TiN precipitation can be predicted from the value of cooling rate and the critical velocity of the solid-liquid interface for the pushing/engulfment of the particles. This discussion will be made in a separate article.

The $\bar{d}_A$ values for TiN in the presence of oxide particles are lower than those without oxide particles in both solidification modes. This may be interpreted by the fact that solu-

Fig. 7. Mean diameter, $\bar{d}_A$, of TiN and TiN+ M_xO_y particles for different deoxidants M ($M=Al, Zr, Ce$ and Mg) plotted against $[T.Ti] \cdot [T.N]$ product in dendritic zone.

Fig. 8. Mean diameter, $\bar{d}_A$, of TiN and TiN+ M_xO_y particles for different deoxidants M ($M=Al, Zr, Ce$ and Mg) plotted against $[T.Ti] \cdot [T.N]$ product in nondendritic zone.

ble contents of Ti and N decrease, as a result of heterogeneous precipitation of TiN on oxide particles, thus leading to the lowering of the driving force of TiN particle growth. The finding that the $\bar{d}_A$ values for the TiN+MgO particles in both solidification are much lower than those for the TiN+ M_xO_y ($M=Al, Zr$, and Ce) particles can be explained by not only the high N_A value of MgO particles, but also the misfit parameters, which will be discussed in Sec. 3.6.

A similar trend was observed for the results obtained at 60 min holding time.

3.4. Effect of Holding Time on N_A and $\bar{d}_A$

In the previous sections, the N_A and $\bar{d}_A$ values of the TiN

Fig. 9. Numbers of TiN and $TiN+M_xO_y$ particles per unit area, N_A , plotted against holding time at 1400°C in dendritic and nondendritic zones for high $[T.Ti] \cdot [T.N]$ product.

and $TiN+M_xO_y$ particles obtained at zero holding time are discussed as a function of solidification mode and $[T.Ti] \cdot [T.N]$ product. In this section the dependence of holding time on the N_A and $\bar{d}_A$ values is discussed based on the results obtained at high $[T.Ti] \cdot [T.N]$ value. The N_A values for the TiN and $TiN+M_xO_y$ particles are plotted against holding time in **Fig. 9**, in which the results obtained in the absence of oxide particles are shown by hatched lines.⁵⁾ It is clear that the N_A values for the TiN particles in Al, Zr and Ce deoxidation experiments remain unchanged in nondendritic solidification, but those in dendritic one increase for Ce and Zr deoxidation. However, those obtained in the absence of oxide particles increase to a significant degree in both solidification modes. The N_A values for the $TiN+M_xO_y$ particles tend to slightly increase with holding time. No systematic trend observed for MgO and Al_2O_3 particles. Similar trend was observed for low $[T.Ti] \cdot [T.N]$ value shown in **Fig. 9**.

The $\bar{d}_A$ values of TiN and $TiN+M_xO_y$ particles are plotted against deoxidants in **Fig. 10**. It can be seen that the $\bar{d}_A$ values of TiN and $TiN+M_xO_y$ particles do not show a systematic trend with respect to holding time in both solidification modes. The $\bar{d}_A$ values of TiN and $TiN+M_xO_y$ particles in the Mg deoxidation are significantly smaller than those of other oxide particles. Furthermore, the $\bar{d}_A$ values of TiN and $TiN+M_xO_y$ ($M=Al, Zr, \text{ and } Ce$) particles are different in both solidification, but those in Mg deoxidation are independent of solidification mode. A trend similar to the results shown in **Fig. 10** was observed for low $[T.Ti] \cdot [T.N]$ value, in which the standard deviation is much smaller than that indicated in **Fig. 10**.

3.5. Particle Size Distribution

3.5.1. Effect of Holding Time

The size distributions of TiN and $TiN+Ce_2O_3(+Al_2O_3)$ particles obtained at high $[T.Ti] \cdot [T.N]$ value in Ce deoxida-

Fig. 10. Mean diameter, $\bar{d}_A$, of TiN and $TiN+M_xO_y$ particles for different deoxidants, holding times at 1400°C for high $[T.Ti] \cdot [T.N]$ product in dendritic and nondendritic zones.

Fig. 11. Size distribution of TiN and $TiN+Ce_2O_3(+Al_2O_3)$ particles in Ce deoxidation as a function of holding time at 1400°C for high $[T.Ti] \cdot [T.N]$ products.

tion are shown in **Fig. 11** for dendritic and nondendritic solidification. It can be seen that the maximum d_A value in dendritic mode is smaller than that in nondendritic mode regardless of holding time. This trend is similar to the results of TiN particles obtained in the previous experiment⁵⁾ without oxide particles whose results are indicated by broken lines. The maximum size for the TiN particles is also smaller than that for the $TiN+Ce_2O_3(+Al_2O_3)$ particles in both solidification modes. It is clear that the mode values for the TiN particles are smaller than those for the $TiN+Ce_2O_3(+Al_2O_3)$ particles regardless of solidification mode. Furthermore, the peak height increases with holding time for both different particles and solidification modes.

Fig. 12. Size distribution of TiN and TiN+MgO(+Al₂O₃) particles in Mg deoxidation as a function of holding time at 1400°C for high [Ti]_T·[N]_T products.

This trend in the size distribution curve is also observed for Zr and Al deoxidation.

The size distribution curves for TiN and TiN+MgO(+Al₂O₃) particles are shown in **Fig. 12**, indicating completely different behavior from the case of Ce deoxidation shown in **Fig. 11**. The maximum d_A value for the TiN particles is slightly smaller than that for the TiN+MgO(+Al₂O₃) particles, but the mode value is almost independent of solidification mode and kind of particles. No systematic trend with respect to the peak height with holding time is observed, which indicates that the precipitation of TiN little occurs during holding time.

3.5.2. Log-normal Probability Graph

In the previously cited article¹⁰⁾ the relationships between cumulative frequency and particle size were plotted in a probability graph for the size distributions obtained in an Fe-10mass%Ni-0.2mass%M ($M = \text{Zr}$ and Ce). It was found that the log-normal distribution was a good approximation. The data for Ce and Mg deoxidation shown in **Figs. 11** and **12** are plotted in the log-normal probability graphs in **Figs. 13** and **14**, respectively, along with the data⁵⁾ for high [Ti]_T·[N]_T value obtained in the absence of oxide particles. All the lines for the TiN and TiN+M_xO_y particles are approximately linear.

In the case of Ce deoxidation, the slopes of the lines for TiN and TiN+Ce₂O₃(+Al₂O₃) particles in dendritic mode are steeper than those in nondendritic one. Furthermore, the large particles in the range of $d_A > 5 \mu\text{m}$ are present in nondendritic mode without respect to the holding time. The slopes of the lines for TiN particles in the absence of oxides, which are represented by plus marks, are lower than those in the Ce deoxidation and the number of large particles in the former is higher than that in the latter in both solidification modes and holding times. A similar trend was observed for the data in the Zr deoxidation in the log-normal probability graph.

Fig. 13. Size distribution of TiN and TiN+Ce₂O₃(+Al₂O₃) particles in Ce deoxidation experiment in the log-normal probability graph.

Fig. 14. Size distribution of TiN and TiN+MgO(+Al₂O₃) particles for Mg deoxidation experiment in the log-normal probability graph.

In the case of Mg deoxidation shown in **Fig. 14**, the lines for TiN and TiN+MgO(+Al₂O₃) particles almost agree with each other for both solidification modes and holding times. However, the slopes of lines for both particles are steeper and the number of large particles is much smaller compared with those for TiN particles in the absence of oxides in both solidification modes and holding times. These results suggest that the presence of large number of MgO particles decreases the number of large TiN and TiN+MgO(+Al₂O₃) particles in nondendritic mode. This is different from the behavior of other oxides. This will be discussed in next section.

3.6. Effect of Deoxidation Products

3.6.1. Misfit Parameter

As shown in Figs. 7 to 9, the size of TiN and TiN+ M_xO_y particles in the Mg deoxidation is smaller and the number of these particles per unit area is higher in both solidification modes in comparison with the results obtained in other deoxidation. The reasons for this are discussed in the following.

The lattice misfit parameter δ between M_xO_y /TiN interface is estimated from the following relation¹¹⁾:

$$\delta = \frac{|l_{M_xO_y} - l_{TiN}|}{1/2 \cdot (l_{M_xO_y} + l_{TiN})} \dots\dots\dots (1)$$

where $l_{M_xO_y}$ and l_{TiN} are the distance between neighboring atoms for various lattice orientations in M_xO_y and TiN crystal systems, respectively.

These values are calculated at 1400°C using the values for the lattice parameter and thermal expansion listed in Table 3, in which the thermal expansion values for ZrO₂ (monoclinic and tetragonal) and Ce₂O₃ (hexagonal) are assumed to be $10 \times 10^{-6} \text{ K}^{-1}$. The minimum values for the misfit parameter calculated from Eq. (1) are summarized in Table 3. It can be seen that the δ value of MgO (0.0002) are extremely small compared with those for other oxides except for Ce₂O₃ (0.014). From these results it follows that the precipitation of TiN on MgO particles occurs easily compared with other oxides. In addition to the difference in the misfit parameters among oxides, it should be noted that the N_A value and size of MgO particles are considerably larger and smaller, respectively, compared with those of other oxides in the present experiment. Therefore, it is necessary to consider whether the difference in the size and number of oxides may affect the precipitation behavior of TiN.

3.6.2. Effect of Number of Oxide Particles

In Fig. 15, the mean diameters of TiN+ M_xO_y and TiN particles obtained at high $[Ti] \cdot [N]$ value are plotted against the N_A values for oxides, $N_A(\text{oxide})$, which are the sum of the number of M_xO_y particles per unit area and that of the TiN+ M_xO_y particles. However, it is pointed out that the N_A value for M_xO_y particles is negligibly small in the case of high $[Ti] \cdot [N]$ value except for Exp. No. 18 (nondendrite) compared with that of the TiN+ M_xO_y particles, as shown in the upper diagrams of Figs. 3 and 4. The $\bar{d}_A$ values for TiN+ M_xO_y and TiN particles in nondendritic mode tend to decrease with the $N_A(\text{oxide})$ value for M_xO_y ($M = \text{Al, Zr and Ce}$) and the $\bar{d}_A$ values for the TiN+MgO particles are lower and do not fall on the extrapolated line. The $\bar{d}_A$ values for TiN+ M_xO_y and TiN particles in dendritic mode have a similar trend. However, the $\bar{d}_A$ values for Al, Zr and Ce deoxidation are independent of the N_A value.

In the upper diagrams of Fig. 16, the ratios of the N_A values of the TiN+ M_xO_y particles, $N_A(\text{TiN}+M_xO_y)$, to those for total particles, $N_A(\text{total})$, which are shown in the lower diagrams, are plotted against the $N_A(\text{oxide})$ value at high $[Ti] \cdot [N]$ value. It is apparent that these ratios increase with an increase in the $N_A(\text{oxide})$ value. The number of particles per unit area for TiN, $N_A(\text{TiN})$, and the $N_A(\text{TiN})/N_A(\text{TiN}+M_xO_y)$ ratio decrease with the $N_A(\text{oxide})$ value, as

Table 3. Physical properties and misfit parameter between oxide and TiN at 1400°C.

Inclusions	Crystal system	Lattice parameter (Å)		Thermal expansion ($\times 10^{-6} \text{ K}^{-1}$)	Misfit parameter δ
		a	c		
TiN	cubic	4.24	—	7.75	—
Al ₂ O ₃	hexagonal	4.76	12.99	8	0.115
ZrO ₂	monoclinic	5.15	5.31	10	0.119
	tetragonal	3.64	5.27	10	0.126
Ce ₂ O ₃	hexagonal	3.89	6.06	10	0.014
MgO	cubic	4.21	—	13	0.0002

Fig. 15. Mean diameter, $\bar{d}_A$, of TiN and TiN+ M_xO_y particles for different deoxidants M ($M = \text{Al, Zr, Ce and Mg}$) plotted against number of M_xO_y particles per unit area in dendritic and nondendritic zones.

Fig. 16. Effect of number density of oxide, $N_A(\text{oxide})$, on $N_A(\text{TiN}+M_xO_y)/N_A(\text{total})$ and $N_A(\text{total})$.

Fig. 17. Effect of number density of oxide, $N_A(\text{oxide})$, on $N_A(\text{TiN})/N_A(\text{TiN}+M_x\text{O}_y)$ and $N_A(\text{TiN})$.

shown in the lower and upper diagrams of Fig. 17, respectively. It can be seen that the $N_A(\text{TiN})/N_A(\text{TiN}+M_x\text{O}_y)$ ratios in both solidification modes drastically decrease with increasing the $N_A(\text{oxide})$ value in the range below 200 mm^{-2} .

If the preferential precipitation of TiN on oxide particles does not occur, that is, the heterogeneous precipitation is independent of the value such as the misfit parameter, the $N_A(\text{TiN}+M_x\text{O}_y)/N_A(\text{total})$ ratio for a given initial $[\text{T.Ti}] \cdot [\text{T.N}]$ value is expected to continuously increase with increasing the number of oxide particles per unite area, $N_A(\text{oxide})$, and consequently, the size of the $\text{TiN}+M_x\text{O}_y$ particles decrease. Therefore, the reason that the $\bar{d}_A$ values for the $\text{TiN}+\text{MgO}$ particles are smaller and the values of their N_A are higher compared with those of other oxides can be explained by smaller size ($\bar{d}_A=0.8 \mu\text{m}$ for MgO and $1.5 \mu\text{m}$ for other oxides) and higher number of the initial MgO particles. It cannot be definitely concluded from the present results, however, that the efficiency of oxide particles on the heterogeneous precipitation of TiN is dependent on only the number of oxide particles, not on the kind of particles. The reason why the $N_A(\text{TiN})$ value in the Mg deoxidation is higher in nondendritic mode, as shown in the right-hand side of the lower diagram of Fig. 17 is not certain at present.

4. Conclusions

The precipitation behavior of TiN on primary deoxidation products has been studied as a function of initial contents of Ti and N, and holding time from the measurements

of the number of particles per unite area, mean size, and size distribution of TiN and $\text{TiN}+M_x\text{O}_y$ particles in dendritic and nondendritic solidification.

The effects of the $[\text{T.Ti}] \cdot [\text{T.N}]$ product, solidification mode, and holding time on the values for the N_A and $\bar{d}_A$ of TiN and $\text{TiN}+M_x\text{O}_y$ particles in Al, Zr, and Ce deoxidation experiments are summarized as follows:

1. The N_A values for TiN and $\text{TiN}+M_x\text{O}_y$ ($M=\text{Al}$, Zr and Ce) particles increase with an increase of $[\text{T.Ti}] \cdot [\text{T.N}]$ product. The N_A values for TiN in dendritic mode are higher than those in nondendritic mode.

2. The $\bar{d}_A$ values for the TiN and $\text{TiN}+M_x\text{O}_y$ ($M=\text{Al}$, Zr and Ce) particles in dendritic mode are almost independent of the $[\text{T.Ti}] \cdot [\text{T.N}]$ product, but those in nondendritic mode increase with increasing the $[\text{T.Ti}] \cdot [\text{T.N}]$ product. The $\bar{d}_A$ values of the TiN and $\text{TiN}+M_x\text{O}_y$ particles at high $[\text{T.Ti}] \cdot [\text{T.N}]$ value in dendritic mode are smaller than those in nondendritic mode.

3. The N_A values for the TiN and $\text{TiN}+M_x\text{O}_y$ ($M=\text{Al}$, Zr, and Ce) particles tend to slightly increase with holding time, but the $\bar{d}_A$ values remain mostly unchanged.

The different behavior of TiN precipitation observed between Mg and other deoxidation is summarized as follows:

4. The N_A values for the TiN and $\text{TiN}+\text{MgO}$ particles in Mg deoxidation are considerably higher than those in other deoxidation regardless of the $[\text{T.Ti}] \cdot [\text{T.N}]$ product and solidification mode. The $\bar{d}_A$ values in Mg deoxidation are smaller than those in other deoxidation.

5. The presence of MgO particles decreases the number of the TiN and $\text{TiN}+\text{MgO}$ particles in the range of $\bar{d}_A > 5 \mu\text{m}$ in both solidification modes. The presence of other oxide particles decreases the number of large TiN particles in both solidification modes, however, it does not decrease the number of large $\text{TiN}+M_x\text{O}_y$ particles in nondendritic mode.

6. The observation that the N_A values of $\text{TiN}+\text{MgO}$ particles are considerably higher and their values are smaller compared with those of other oxides, are discussed based on the preferential precipitation of TiN on MgO particles and the higher N_A values for MgO particles. However, the reason for this cannot be clarified.

REFERENCES

- 1) A. Ostrowski and E. W. Langer: *Scand. J. Metall.*, **8** (1979), 153.
- 2) G. N. Heintze and R. Mc Pherson: *Weld. J.*, **65** (1986), 715.
- 3) J. C. Villafuerte, E. Pardo and H. W. Kerr: *Metall. Trans. A*, **21A** (1990), 2009.
- 4) B. L. Bramfitt: *Metall. Trans.*, **1** (1970), 1987.
- 5) G. V. Pervushin and H. Suito: *ISIJ Int.*, **41** (2001), 728.
- 6) A. Karasev and H. Suito: *Metall. Mater. Trans. B*, **30B** (1999), 249.
- 7) H. Wada and R. D. Pehlke: *Metall. Trans. B*, **16B** (1985), 815.
- 8) J. Kunze: *Met. Sci.*, **16** (1982), 217.
- 9) K. Sakata and H. Suito: *Metall. Mater. Trans. A*, **31A** (2000), 1213.
- 10) A. Karasev and H. Suito: *Metall. Mater. Trans. B*, **30B** (1999), 259.
- 11) H. I. Aaronson, C. Laird, and K. R. Kinsman: *Phase Transformation*, ASM, Metals Park, OH, (1970), 313.