Effect of Multi-phase Oxide Particles on TiN Crystallization and Solidification Structure in Ti-Added Ferritic Stainless Steel

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The effect of TiN crystallization on the solidification structure of Ti-added ferritic stainless steel were studied in Ti/Mg, Ti/Ca, Ti/Mg/Al, Ti/Ca/Al, Al/Ti/Ca and Ti/Mg(Ca)/Ca(Mg) deoxidations carried out at 1 600°C using an Fe–17.5(11)%Cr–0.25%Mn–0.20%Si–0.2 to 0.3%Ti–0.01%C–0.003 to 0.04% N alloy on a mass percent basis. Compositional analysis of the oxide particles and TiN layers generated during the deoxidation using scanning electron microscopy in conjunction with an electron probe microanalyzer, coupled with observation of the morphology and homogeneity of complex TiN+oxide particles, revealed that the TiN layers were formed through the postulated mechanism of the co-crystallization of TiN and oxide. Ti/Mg and Ti/Mg/Al deoxidations performed in an Al₂O₃ crucible yielded a very fine solidification structure at high N contents (>200 ppm) because of the presence of complex particles consisting of the TiN layer with a small amount of oxide phases. In the Ti/Ca, Ti/Ca/Al and Al/Ti/Ca deoxidations using an Al₂O₃ crucible, a relatively fine solidification structure was observed when a low oxide content was present in the TiN layer. Ti/Ca/A and Al/Ti/Ca deoxidations carried out using an MgO crucible in the presence or absence of MgO–CaO–Al₂O₃ slag gave rise to solidification structures that were relatively finer in comparison with those obtained using an Al₂O₃ crucible. Very fine structures were observed at low N contents (36 to 80 ppm) in the Ti/Mg/Ca and Ti/Ca/Mg deoxidations using an Al₂O₃ crucible because of the effective surface composition of the oxide particles for δ -phase solidification.

KEY WORDS: ferritic stainless steel; TiN crystallization; deoxidation particles; solidification structure; co-crystallization of TiN and oxide.

1. Introduction

The crucial importance of the nucleation potency of the phases present at the particle surface of Ti-added ferritic stainless steel was illustrated in a previous study,¹⁾ in which the refining of the solidification structure using a nucleation catalyst was explored. That study, focused on the numbers of TiN, TiN+oxide and oxide particles obtained in various complex deoxidations, indicated that the solidification structure was not influenced by the numbers of TiN, TiN+oxide and oxide particles having sizes greater than 1.5 μ m, but rather, was influenced by the deoxidation methods.

The crystallization of TiN occurs on single oxide phases having the cubic structure such as MgO, MgO·Al₂O₃, CaO·TiO₂, 2MgO·TiO₂ and MgO·Al₂O₃–2MgO·TiO₂ solid solutions; however, these particles are difficult to produce by the addition of respective deoxidants. As an alternative, these oxide phases may be generated by first producing homogeneous liquid oxide particles that are saturated with the aforementioned oxide phases and then to crystallize the saturated phase by solidification during the cooling period.

In the present study, the morphology of deoxidation products and the compositions of crystallized and matrix phases of a ferritic alloy were evaluated by using scanning electron

microscopy (SEM), coupled with an electron probe microanalyzer (EPMA). The morphology of the complex TiN+oxide particles and the composition of the TiN layers were studied in an Fe–17.5(or 11)%Cr–0.25%Mn–0.20%Si–0.2 to 0.3%Ti–0.01%C alloy containing 30 to 400 ppm N using an Al₂O₃ or MgO crucible, in the presence or absence of CaO–MgO–Al₂O₃ slag. The deoxidation methods carried out at 1 600°C are classified as Ti/*M* (*M*=Mg, Ca or Zr) and Ti/*M*/*M'* (Ti/Mg/Al, Ti/Al(Ca)/Ca/(Al), Al/T/Ca, Ti/Mg(Ca)/Ca(Mg) or Ti/Zr/Mg) deoxidations. The solidification structure is discussed with particular focus on the compositions of TiN layers crystallized on the oxide particles. The formation of TiN before and after δ -phase solidification is denoted as crystallization and precipitation of TiN, respectively, hereafter.

2. Experimental

2.1. Deoxidation Method

An Fe–17.5(or 11)%Cr–0.25%Mn–0.20%Si–0.01%C alloy (250 g) was melted at 1 600°C in an Al₂O₃ or MgO crucible using an induction furnace (100 kHz) and was then deoxidized with a Ti/Ca/Mg mixture, *e.g.*, Ti(0.3%, initial amount), Ca(0.1%) and Al(0.05%). This method is denoted as “Ti/Ca/Mg deoxidation”. The melt was held at 1 600°C for 1 min, followed by cooling to 1 400°C (1 450 and 1 200°C). The deoxidation methods are summarized in **Table 1**.

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The deoxidation method in the presence of slag was carried out in an Al_2O_3 , MgO or Al_2O_3 crucible with an MgO -ring. Slags (20 g) with compositions of 56% CaO –39% Al_2O_3 –5% MgO (Slag A) and 31% CaO –65% Al_2O_3 –4% MgO (Slag B) were used for the Al/Ti/Ca and Ti/Al/Ca deoxidations as a function of Al content. A more detailed description of the deoxidation methods in the absence or presence of slag is given elsewhere.¹⁾

2.2. Inclusion Analysis and Solidification Structure

The methods of determining the planar and spatial particle size distributions are given elsewhere,¹⁾ along with a description of the technique for observation of the solidification structure.¹⁾ The compositions of the planar particles on the polished metal surface were analyzed using SEM in conjunction with an EPMA. The method of chemical analysis is given elsewhere.^{1,2)}

Table 1. Deoxidation experiments without slag.

Exp. No.		Deoxidant
Ti/Mg		
8 *		0.3%Ti/0.1%Mg (1 400°C)
9 *	M	0.25%Ti/0.1%Mg–1 540°C, 5 min (1 400°C)
10 *	M	0.25%Ti/0.1%Mg–1 540°C, 1 min (1 400°C)
11		0.2%Ti/0.1%Mg (1 400°C)
14		0.2%Ti/0.1%Mg (1 200°C)
16		0.2%Ti/0.1%Mg (1 400°C)
Ti/Mg/Al		
20		0.2%Ti/0.1%Mg/0.003%Al (1 200°C)
Ti/Ca		
21 *		0.3%Ti/0.1%Ca (1 400°C)
24		0.2%Ti/0.1%Ca (1 400°C)
25		0.3%Ti/0.02%Ca (1 400°C)
Al/Ti/Ca		
32		0.003%Al/0.2%Ti/0.1%Ca (450°C)
Ti/Al/Ca		
33		0.25%Ti/0.05%Al/0.1%Ca (1 400°C)
34 *		0.003%O/0.25%Ti/0.05%Al/0.1%Ca–1 540°C, 10 min (1 400°C)
Ti/Al/Ca		
40 *	M	0.25%Ti/0.05%Al/0.1%Ca (1 400°C)
Ti/Ca/Al		
42 *	M	0.25%Ti/0.1%Ca/0.05%Al (1 400°C)
Ti/Mg/Ca		
43 *		0.15%Ti/0.1%Mg/0.15%Ti/0.1%Ca (1 450°C)
44 *		0.3%Ti/0.1%Mg/0.1%Ca (1 400°C)
45 *		0.15%Ti/0.1%Mg/0.15%Ti/0.1%Ca (1 400°C)
46 *		0.15%Ti/0.1%Mg/0.15%Ti/0.1%Ca–1 600°C, 10 min (1 400°C)
47		0.3%Ti/0.1%Mg/0.1%Ca (1 400°C)
48		0.3%Ti/0.1%Ca/0.1%Mg (1 400°C)
49		0.15%Ti/0.1%Mg/0.15%Ti/0.1%Ca–1 600°C, 10 min (1 400°C)
Al/Ti/Ca		
60 *	M	0.05%Al/0.3%Ti/0.1%Ca (1 400°C)

*: 17.5% Cr, without *: 11% Cr.

M: MgO crucible, without M: Al_2O_3 crucible.

3. Results and Discussion

3.1. Characteristics of Oxide Particles in Various Deoxidations

3.1.1. Homogeneity and Morphology

Particles with homogeneous composition, denoted as HM, were observed for a single oxide, compound and rapidly cooled liquid phases. If the formation of second phase in liquid particles (denoted as crystallized phase, hereafter) and/or that in solid particles (denoted as precipitated phase, hereafter) are sufficiently small and uniformly dispersed, these particles appear to be apparently homogeneous. The particles, denoted as HT-1 and HT-2(a) in Fig. 1, were observed on cross-sectional view of the alloy. A few large secondary phases due to the growth of the crystallized phase can be observed in HT-1 particles and heterogeneous phases (consisting of the crystallized and precipitated phases) can be observed in the homogeneous matrix in the particles denoted as HT-2(a). Heterogeneous particles, denoted as HT-3, are produced by the following mechanism; spherical particles of ca. $0.5\ \mu\text{m}$ in diameter produced by the Ti/M deoxidation coagulate by collision; this is followed by the reduction of the $\text{TiO}_x\text{--MO}_x$ particles with the third deoxidant M' . Particles, denoted as HT-2(b), are produced by both mechanisms described for HT-2(a) and HT-3. These particles are shown in Fig. 1 and the homogeneity of oxide particles generated during the various deoxidations is summarized in Table 2.

Oxide particles with polyhedral, spherical and irregular morphologies were observed based on the deoxidation mechanisms. Polyhedral particles were observed in the deoxidation products of MgO , $\text{MgO}\cdot\text{Al}_2\text{O}_3$, the binary compounds in the $\text{CaO}\text{--TiO}_2$, $\text{MgO}\text{--TiO}_2$ and $\text{CaO}\text{--Al}_2\text{O}_3$ systems and the $\text{MgO}\cdot\text{Al}_2\text{O}_3\text{--}2\text{MgO}\cdot\text{TiO}_2$ and $\text{TiO}_2\cdot\text{Al}_2\text{O}_3\text{--MgO}\cdot\text{TiO}_2$ solid solutions. Spherical particles were observed in the liquid particles in the complex deoxidation. Liquid regions at 1 500°C are present in the $\text{TiO}_2\text{--CaO}$, $\text{CaO}\text{--Al}_2\text{O}_3\text{--TiO}_2$ and $\text{MgO}\text{--CaO}\text{--TiO}_2$ phase diagrams. In the present Ti deoxidation, Ti_3O_5 is the deoxidation product at 1 600°C and Ti_2O_3 is the component present after solidification. However, the TiO_2 -including phase diagrams are used for discussion, because the Ti_2O_3 -containing phase diagrams mentioned above are not available.

Irregular particles result from particle coagulation by collision. In most cases, the particles are roughly spherical and only the rim is irregular. However, very irregular particles were observed, when large particles coagulate by collision. In the notation used in Table 2, “Irr, Irr+Poly” indicates that the first morphology “Irr” is present to a greater extent than the second one “Irr+Poly”. The notation “Irr+Sph” indicates

Fig. 1. Homogeneity of oxide particles.

Table 2. Characteristics of oxide particles obtained in various deoxidations.

Exp. No.	T. N ppm	Ti %	Solid. type	Morphology		Homogeneity	
				Complex	Oxide	Oxide	TiN layer
Ti/Mg							
8*	64	0.3	C-2(A)	a, b	Poly + Sph	HM	hm
9 (MgO)	176	0.25	C-3	a + a'	Irr	HT-3	ht-irr
10 (MgO)	81	0.25	C-3	b	Irr, Irr + Poly	HM, HT-3	ht-irr
11*	212	0.2	A	a	Poly + Sph	HM, HT-3	hm, ht-cu
14*	248	0.2	A	a	Poly + Sph	HM	hm, ht-cu
16*	204	0.2	A	a, a'	Poly + Irr	HM, HT-3	hm-cu, ht-irr
Ti/Mg/Al							
20*	282	0.2	A	a	Poly + Sph	HM	hm, ht-cu
Ti/Ca							
21	67	0.3	B-1(A)	c, b	Irr, Irr + Poly	HT-3, HT-1	ht-irr
24	37	0.2	B-1(A)	c	Irr, Irr + Sph	HT-3	ht-irr
Ti/Ca							
25*	68	0.3	B-3	c, b	Irr, Irr + Poly	HT-3, HM	hm, ht-cu
Al/Ti/Ca							
32	401	0.2	B-4(A)	a + a'	Irr	HT-2(b)	ht-irr, ht-cu
Ti/Al/Ca							
33	68	0.25	B-3	a'	Irr	HT-3, HT-2(a)	ht-irr
34	121	0.25	B-2	a + a', a'	Irr, Irr + Poly	HT-3, HT-2(a)	hm, hm-cu
Ti/Al/Ca							
40 (MgO)	102	0.25	B-1(A)	b', a'	Irr	HT-3, HM	ht-irr
Ti/Ca/Al							
42 (MgO)	104	0.25	B-1(A)	a', b'	Irr, Irr + Sph	HT-2(a)	ht-irr, ht-cu
Al/Ti/Ca							
60* (MgO)	100	0.3	C-2(A)	b', a'	Irr	HT-3	hm, ht-cu
61 (MgO)	72	0.3	C-2(A)	b', a'	Irr, Irr + Sph	HT-3	ht-irr, ht-cu
Ti/Mg/Ca							
43	75	0.3	A	c'	Irr, Irr + Sph	HT-3, HT-2(a)	
44	70	0.3	A	c', c, b'	Irr, Irr + Sph	HT-2(a), HT-2(b), HT-3	
Ti/Mg/Ti/Ca							
45	80	0.3	A	c	Irr, Irr + Sph	HT-3	
46	56	0.3	A	c, b'	Irr, Irr + Sph	HT-2(a), HT-2(b), HT-3	
Ti/Mg/Ca							
47	36	0.3	A	c, b'	Irr, Irr + Sph	HT-2(a), HT-3	
Ti/Ca/Mg							
48	40	0.3	A	c, b	Irr, Irr + Sph	HT-2(a), HT-3	
Ti/Mg/Ti/Ca							
49	38	0.3	A	b', c'	Irr, Irr + Sph	HT-2(b), HT-3	
Al/Ti/Ca							
SM-1*	92	0.3	B-1(A)	b', c'	Sph + Irr, Irr	HT-3, HT-2(b)	hm-cu
SM-5*	211	0.3	C-2(A)	b', c'	Sph + Irr, Irr	HT-1, HT-2(b)	hm-cu
Ti/Ca/Al							
SM-6*	88	0.3	C-4(A)	b', c'	Sph + Irr, Irr	HT-1, HT-2(b)	hm-cu
Al/Ti/Ca							
SM-7*	86	0.3	C-4(A)	b, c	Sph + Irr, Irr	HT-1, HT-2(b)	hm-cu
Ti/Ca/Al							
SM-8*	77	0.3	C-4(A)	b, c	Sph + Irr, Irr	HT-1, HT-2(b)	hm-cu

*: TiN layer consisting of small amount of oxide content.

that some part of the rim in a particle is irregular and another part of the rim is spherical. The variation of the homogeneity and morphology with deoxidation methods is discussed, along with the oxide compositions, in the following section.

3.1.2. Oxide Composition

The compositions of the oxide particles on a cross-section of the alloy measured by SEM coupled with EPMA, were plotted in a ternary phase diagram; most of the measured

oxide particles were in the range of 0.5 to 5 μm in particle size. The deoxidation results are described according to the deoxidation methods summarized in Table 1, as follows:

1) Ti/Mg (Al_2O_3 , MgO) and Ti/Mg/Al (Al_2O_3) Deoxidation

The oxide compositions of the TiO_2 -MgO system observed in the Ti/Mg (MgO) deoxidation (Exps. 9 and 10) are considerably scattered, as shown in Fig. 2. The liquid region in the $\text{MgO-Al}_2\text{O}_3\text{-TiO}_2$ (TiO_x) system, which is located in the TiO_2 corner is described elsewhere.^{3,4)} The deoxidation of Exp. 9 generated particles with HT-3 homogeneity, whereas HM and HT-3 particles were generated in Exp. 10. The morphology of the particles produced in Exp. 9 could be classified as Irr and in Exp. 10, Irr and Irr+Poly were observed. The polyhedral morphology arises from the crystal growth of $2\text{MgO}\cdot\text{TiO}_2$ and $\text{MgO}\cdot\text{TiO}_2$ phases.

The oxide compositions obtained from the Ti/Mg (Al_2O_3) (Exps. 14 and 16) and the Ti/Mg/Al (Al_2O_3) (Exp. 20) deoxidations were rich in TiO_2 and contained 5% to 20% Al_2O_3 . The soluble Al contents obtained in Exps. 14, 16 and 20 were 15, 21 and 20 ppm, respectively, as indicated in Table 3. Some oxide particles are located in the liquid regions at 1600°C based on the $\text{MgO-Al}_2\text{O}_3\text{-TiO}_2$ (TiO_x) phase diagram.^{3,4)} The homogeneity (morphology) on the particles obtained in Exps. 14, 16 and 20 were HM (Poly+Sph), HM, HT-3 (Poly+Irr) and HM (Poly+Sph), respectively. The oxide particles obtained after the Ti/Mg deoxidation were homogeneous, but these particles coagulated by collision, thereby leading to the HT-3 homogeneity. During this process, the oxide particles undergo simultaneous reduction with soluble Al. The polyhedral and spherical morphologies are explained by the formation of the $\text{MgO}\cdot 2\text{TiO}_2\text{-TiO}_2\cdot\text{Al}_2\text{O}_3$ solid solution and liquid composition, respectively.

The oxide compositions obtained in Exps. 8 and 11 comprised MgO-rich Al_2O_3 , indicating that the TiO_2 in the initial TiO_2 -MgO particles was completely reduced by soluble Al due to the high Mg addition yield. The homogeneity (morphology) of the particles produced in Exps. 8 and 11 are HM (Poly+Sph) and HM, HT-3 (Poly+Sph), respectively. The polyhedral morphology arises from the formation of MgO and $\text{MgO}\cdot\text{Al}_2\text{O}_3$, but the origin of the spherical morphology is not clear at present. A scatter of compositions was observed not only in the heterogeneous particles (HT-3), but also in the homogeneous particles (HM).

2) Ti/Ca (Al_2O_3) Deoxidation

The oxide compositions observed in Exps. 21 (HT-3, HT-1: Irr, Irr+Poly), 24 (HT-3: Irr, Irr+Sph) and 25 (HT-3, HM: Irr, Irr+Poly) are shown in Fig. 3, in which two liquid regions at 1500°C are plotted in the $\text{CaO-Al}_2\text{O}_3\text{-TiO}_2$ phase

diagram. The oxide compositions were measured for the matrix only in the case of HT-1. It can be seen that the TiO_2 contents in the oxide particles decrease in the order: Exp. 21>Exp. 24>Exp. 25. TiO_2 -rich compositions were observed in Exp. 21, compared with those in Exp. 24, due to a higher initial Ti content (0.3%) in the former. However, TiO_2 -poor $\text{CaO-Al}_2\text{O}_3$ compositions were observed in Exp. 25, despite the fact that the initial Ca contents in Exp. 25 ($\text{Ca}=0.02\%$) was much lower than those in Exps. 21 and 24 ($\text{Ca}=0.1\%$). These results indicate that scatter of the oxide composition arises from the Ca addition yield, along with the variation of initial O content. The HT-3 homogeneity and the irregular morphology observed in these experiments are explained by the coagulation of deoxidation particles by collision, even though melt stirring was eliminated by installing a graphite susceptor in the present experiment.

In a previous study,^{5,6)} the Al and Ti deoxidation equilibria in an Fe-20%Cr alloy were measured at 1600°C using $\text{CaO-Al}_2\text{O}_3\text{-TiO}_2\text{-TiO}_{1.5}$ slag in an Al_2O_3 or a CaO cruci-

Table 3. Compositions of soluble and insoluble Ti, Mg, Ca and Al.

Exp. No.	Ti		Mg		Ca		Al	
	sol.	insol.	sol.	insol.	sol.	insol.	sol.	insol.
	(ppm)		(ppm)		(ppm)		(ppm)	
14	551	16	1	61			15	4
16	487	446	0	82			21	12
20	397	293	0	35			20	19
24	1510	119			5	62	94	27
33	1970	267			34	24	359	28
*40	1920	207	3	3	9	25	375	32
43	2290	78	5	31	28	38	160	33
44	2180	244	2	56	18	47	193	37
47	2200	50	3	53	34	38	57	6
48	1970	77	1	59	16	23	76	10
*60	452	434	24	3	29	38	1484	17
*61	467	228	14	3	29	35	596	8
SM-1	1550	255	4	3	27	37	622	37
*SM-5	1030	464	4	9	25	25	537	22
*SM-6	1410	342	5	7	22	27	438	20
**SM-7	1810	312	4	8	18	29	432	40
**SM-8	1940	143	3	7	19	31	478	46

*, MgO crucible, **: Al_2O_3 crucible with MgO-ring, Without * and **: Al_2O_3 crucible.

Fig. 2. Compositions of oxide particles in Ti/Mg (Exps. 8, 11, 14 and 16, Al_2O_3 crucible and Exps. 9 and 10, MgO crucible) and Ti/Mg/Al (Exp. 20, Al_2O_3 crucible) deoxidation experiments.

Fig. 3. Compositions of oxide particles in Ti/Ca deoxidation experiments (Exps. 21, 24 and 25, Al_2O_3 crucible).

ble. The slag compositions, denoted as CAT-1 and CAT-2, herein, have composition of 30~34%CaO–56~59%Al₂O₃–1~4%TiO_{1.5}–6~9%TiO₂–0.1~3%Cr₂O₃ and 11~13%CaO–28~35%Al₂O₃–14~35%TiO_{1.5}–23~34%TiO₂–0.7~12%Cr₂O₃, respectively. The slag compositions, denoted as CA and AC refer to the CaO–Al₂O₃ system saturated with CaO and Al₂O₃ crucibles, respectively, at 1600°C. The relationships between $\underline{\text{Al}}$ and $\underline{\text{O}}$ and between $\underline{\text{Ti}}$ and $\underline{\text{O}}$ are shown in the upper and lower diagrams of Fig. 4, respectively. The compositions of CAT-1, CAT-2, CA and AC are plotted in the CaO–Al₂O₃–TiO₂ phase diagram, as shown in Fig. 3.

The soluble Ti and Al contents in Exp. 24 were 0.151% and 94 ppm, respectively, as shown in Table 3. The soluble oxygen content for Exp. 24 was estimated to be in the range of 30 to 40 ppm, intermediate between the compositions of CAT-1 and CAT-2. The oxygen contents could not be estimated from the results of CAT-2 and CAT-1, CA and AC in the case of Exps. 21 and 25 because the soluble Ti and Al contents were not measured.

3) Al/Ti/Ca (Al₂O₃) and Ti/Al/Ca (Al₂O₃) Deoxidation

The oxide compositions obtained in Exps. 32 (HT-2(b): Irr), 33 (HT-3, HT-2(a): Irr) and 34 (HT-3, HT-2(a): Irr, Irr+Poly) are shown in Fig. 5. The oxide compositions were measured for the matrix, the respective crystallized phases in the case of HT-2(a) and the coagulated particles in the case of HT-3 and HT-2(b). There was no correlation between the Al/Ti/Ca (Exp. 32) and the Ti/Al/Ca (Exps. 33 and 34) deoxidations. Larger compositional scatter was observed with these deoxidations compared with the Ti/Ca (Al₂O₃) deoxidation (shown in Fig. 3) attributed to the fact that the deoxidation products of the Al/Ti (Exp. 32) and Ti/Al (Exps. 33 and 34) deoxidations are solid, whereas some of them are liquid in the Ti/Ca (Exps. 21, 24 and 25) deoxidation. The size of oxide particles in the Al/Ti/Ca deoxidation was significantly larger than those obtained in the Ti/Al/Ca deoxidation because of cluster formation during the initial Al addition in the former. The initial size of the TiO_x–Al₂O₃ particles in the Ti/Al deoxidation (Ti/Al/Ca: Exps. 33 and 34) was relatively small with a value below 0.5 μm and after the Ca addition, larger particles consisting of these small particles were produced by coagulation, as shown in

Fig. 4. Relationship between soluble Al and O (upper diagram) and between soluble Ti and O (lower diagram) in Fe-20% Cr alloy equilibrated with AC, CA, CAT-1 and CAT-2 slags at 1600°C.^{5,6)}

Fig. 1 (HT-3). These results are in line with prior results, in which the particle size was found to increase in the order of Ti/Mg<Ti/Ca<Ti/Al deoxidation.¹⁾ The scatter of the oxide composition in the Ti/Al/Ca and Al/Ti/Ca deoxidations is larger than that of the Ti/Ca deoxidation in which Al is dissolved due to the reduction of the Al₂O₃ crucible with soluble Ca in the metal. It can be deduced that the TiO₂-poor CaO–Al₂O₃ composition obtained in Exp. 33 may be attributed to the high content of soluble Al (359 ppm) and Ti (0.197%). Based on these high soluble Ti and Al contents, an oxygen content in the range of 10 to 30 ppm can be estimated from the curves of CAT-1, CA and AC, shown in Fig. 4.

4) Ti/Al/Ca (MgO), Ti/Ca/Al (MgO) and Al/Ti/Ca (MgO) Deoxidation

The oxide compositions from Exps. 40 (HT-3, HM: Irr), 42 (HT-2(a): Irr, Irr+Sph), 60 (HT-3: Irr) and 61 (HT-3: Irr, Irr+Sph) are plotted in Fig. 6 for the CaO(+MgO)–Al₂O₃–TiO₂ phase diagram, in which the liquid regions at 1500°C in the CaO–Al₂O₃–TiO₂ phase diagram are included. The oxide compositions were measured for the matrix and crystallized phases in the case of HT-2(a) and HT-2(b). The MgO content was in the range of 1% to 6%. The TiO₂ contents in Exps. 40, 60 and 61 were about 20% to 80%, whereas the TiO₂ contents in Exp. 42 were almost zero. The soluble Al (Ti) contents in Exps. 40, 60 and 61 were 375 ppm (0.192%), 1484 ppm (0.0452%) and 596 ppm (0.0467%), respectively. The results in Fig. 4 show that the soluble Al contents in Exps. 40, 60 and 61 were considerably high,

Fig. 5. Compositions of oxide particles in Al/Ti/Ca (Exp.32, Al₂O₃ crucible) and Ti/Al/Ca (Exps.33 and 34, Al₂O₃ crucible) deoxidation experiments.

Fig. 6. Compositions of oxide particles in Ti/Al/Ca (Exps.40 and 42, MgO crucible) and Al/Ti/Ca (Exps.60 and 61, MgO crucible) deoxidation experiments.

whereas the soluble Ti contents appear reasonable judging from the oxide compositions having relatively high TiO_2 . These observations suggest that the Al-O equilibrium was not attained, but the Ti-O equilibrium was attained with respect to the particles containing high TiO_2 . It can thus be deduced that oxygen was supersaturated with respect to the equilibrium between soluble Al and Al_2O_3 in oxide particles.

In the Ti/Ca/Al deoxidation (Exp. 42), some $\text{TiO}_x\text{-CaO}$ particles obtained in the initial Ti/Ca deoxidation were in the liquid state, thereby leading to the favorable formation of $\text{CaO-MgO-Al}_2\text{O}_3$ particles through the reduction of liquid $\text{TiO}_x\text{-CaO}$ particles with soluble Al. On the other hand, the $\text{TiO}_x\text{-Al}_2\text{O}_3$ particles obtained in the initial Ti/Al (Ti/Al/Ca: Exp. 40) and initial Al/Ti (Al/Ti/Ca: Exps. 60 and 61) deoxidations were solid, with consequent difficulty in the reduction of solid $\text{TiO}_x\text{-Al}_2\text{O}_3$ particles with soluble Ca. The compositions of these particles were thus rich in TiO_x content.

5) Ti/Mg/Ti/Ca (Al_2O_3), Ti/Mg/Ca (Al_2O_3) and Ti/Ca/Mg (Al_2O_3) Deoxidation

The oxide compositions obtained in Ti/Mg/Ti/Ca (Al_2O_3), Ti/Mg/Ca (Al_2O_3) and Ti/Ca/Mg (Al_2O_3) deoxidations were measured for the matrix and crystallized phases for oxide particles of homogeneity types HT-2(a) and HT-2(b). The oxide compositions obtained in Exp. 47 (Ti/Mg/Ca) (HT-2(a), HT-3: Irr, Irr+Sph) belonged to the CaO-MgO-TiO_2 system. Those in Exp. 43 (Ti/Mg/Ca) (HT-3, HT-2(a): Irr, Irr+Sph), Exp. 45 (Ti/Mg/Ti/Ca) (HT-3: Irr, Irr+Sph) Exp. 46 (Ti/Mg/Ti/Ca) (HT-2(a), HT-2(b), HT-3: Irr, Irr+Sph) and Exp. 49 (Ti/Mg/Ti/Ca) (HT-2(b), HT-3: Irr, Irr+Sph) belonged to the $\text{TiO}_2\text{-CaO-MgO-Al}_2\text{O}_3$ system. The oxide compositions in Exp. 44 (Ti/Mg/Ca) (HT-2(a), HT-2(b), HT-3: Irr, Irr+Sph) and Exp. 48 (Ti/Ca/Mg) (HT-2(a), HT-3: Irr, Irr+Sph) belonged to the $\text{CaO-MgO-Al}_2\text{O}_3$ system. In these deoxidations, the particles obtained were of the HT-2(a), HT-3 and HT-2(b) homogeneity types and irregular and irregular+spherical morphologies were observed. The soluble Al contents in Exp. 47 (CaO-MgO-TiO_2), Exp. 43 ($\text{TiO}_2\text{-CaO-MgO-Al}_2\text{O}_3$) and Exps. 44 and 48 ($\text{CaO-MgO-Al}_2\text{O}_3$) were 57, 160, 197 and 76 ppm, respectively, consistent with the relative TiO_2 content. It is reasonable to assume that the oxygen content decreases with a decrease in the TiO_2 content, as explained in the next section.

It was found that the particle compositions were independent of the order of deoxidant addition such as in the case of Ti/Mg/Ca and Ti/Ca/Mg and Ti/Mg/Ti/Ca. The liquid region was present in the TiO_2 -rich corner in the CaO-MgO-TiO_2 system in Exp. 47 and in the $\text{CaO-Al}_2\text{O}_3$ system containing a small amount of MgO in Exps. 44 and 48. Therefore, liquid particles could be obtained by the initial Ti/Ca deoxidation step of in the Ti/Ca/Mg deoxidation process, but liquid particles were not obtained in the Ti/Mg and Ti/Mg/Ca deoxidations. Furthermore, the number density of small particles below $1\text{ }\mu\text{m}$ in the Ti/Mg deoxidation is significantly higher than that in the Ti/Ca deoxidation.¹⁾ These differences in behaviors influenced the final composition of the particles as a result of particle coagulation by collision and crystallization of the primary phase. The oxide composition consisting of the $\text{TiO}_2\text{-CaO-MgO-Al}_2\text{O}_3$ system (Exps. 43, 45, 46 and 49) is discussed in a later section.

6) Al/Ti/Ca and Ti/Ca/Al Deoxidation in the Presence of Slag

Oxide particles containing MgO were prepared by carrying out the Al/Ti/Ca and Ti/Al/Ca deoxidations using the $\text{CaO-MgO-Al}_2\text{O}_3$ slag in crucibles made of an Al_2O_3 (Exp. SM-1), MgO (Exps. SM-5 and -6) or an Al_2O_3 crucible with an MgO-ring (Exps. SM-7 and -8). The oxide compositions obtained in Exps. SM-1 (HT-3, HT-2(b): Sph+Irr, Irr) and SM-5 to SM-8 (HT-1, HT-2(b): Sph+Irr, Irr) comprised the $\text{TiO}_2\text{-CaO-MgO-Al}_2\text{O}_3$ system and the compositions of oxide in the matrix and crystallized phases are shown in Fig.

Fig. 7. Compositions of oxide particles in Al/Ti/Ca (Exp. SM-1, Al_2O_3 crucible, Exp. SM-5, MgO crucible and Exp. SM-7, Al_2O_3 crucible with MgO ring) and Ti/Al/Ca (Exp. SM-6, MgO crucible and Exp. SM-8, Al_2O_3 crucible with MgO-ring) deoxidation experiments with slag.

7. The composition of oxide particles with homogeneity types of HT-1 and HT-2(b) was assayed for the matrix and crystallized phases. The majority of the particles with HT-1 type homogeneity consisted of a few large crystallized phases grown from the particle surface, as shown in Fig. 1. It can be seen from Fig. 7 that most of the matrix compositions are present in the liquid region at 1600°C and the compositions of the crystallized phases are present between the $\text{MT}_2\text{-AT}$ and $\text{M}_2\text{T-MA}$ solid solutions ($\text{M}=\text{MgO}$, $\text{A}=\text{Al}_2\text{O}_3$ and $\text{T}=\text{TiO}_2$). The oxide particles in Exp. SM-1 exhibit no crystallized phase due to a low MgO content in the matrix phase. The MgO content in the matrix phase increases in the order: Al_2O_3 crucible (2% to 4%) < Al_2O_3 crucible with MgO-ring (12% to 23%) < MgO crucible (33% to 52%). Because the sizes of the crystallized phases are nearly the same, the MgO content in particles is the highest in the deoxidation using an MgO crucible. The MgO content in the Ti/Al/Ca deoxidation in the absence of slag using an MgO crucible, the results of which are shown in Fig. 4, was in the range of 1% to 7%. This value was slightly higher than the MgO content (2% to 4%) in the Al/Ti/Ca deoxidation (SM-1) in the presence of slag using an Al_2O_3 crucible.

The soluble Al and Ti content of the particles obtained in SM-1 and SM-5 to SM-8 were 432 through 622 ppm and 0.103 through 0.194%, respectively. The oxygen contents estimated from the results of the Ti-O (Al-O) relationships delineated in Fig. 4 are about 30 (10) ppm at CAT-2 and 20 (20) ppm at CAT-1. There are two liquid regions at high and low TiO_2 contents and the corresponding soluble oxygen contents are high and low, respectively, as shown in Fig. 7. Liquid particles with a low TiO_2 content have a high MgO content in the particles and a high soluble Al content in the metal. Similar results were observed for the $\text{TiO}_2\text{-CaO-MgO-Al}_2\text{O}_3$ particles during Ti/Mg/Ca deoxidation in the absence of slag (Exps. 43, 45, 46 and 49) using an Al_2O_3 crucible.

3.2. Effect of Oxide Composition on TiN Crystallization and Solidification

3.2.1. Morphology of Complex Particles

The morphologies of the complex TiN+oxide particles (denoted simply as “complex particles” hereafter) are classified into polyhedral (a, b and c) and irregular (a', b' and c') complex particles. The distinction between a (a'), b (b') and c (c') particles is due to the thickness of the outer layer of the complex particles; the three primary classifications refer to thick, thin and partially covered layers formed on the oxide particles, respectively. The conditions under which the various morphologies of the complex particles are generated can be explained as follows.

The Type a morphology is observed under the conditions

of high nucleation potency for TiN crystallization, high $[\text{Ti}]:[\text{N}]$ solubility product, a small number density of oxide nuclei for TiN crystallization and slow cooling rate. The Type a' morphology is observed when TiN crystallization occurs preferentially because of the non-uniform composition of the oxide surface. The Type b morphology is observed when there is a low nucleation potency for TiN crystallization, low $[\text{Ti}]:[\text{N}]$ solubility product, a large number density of oxide nuclei and high cooling rate. The Types c and c' morphologies are observed under similar (but more severe) conditions than those indicated for Types b and b', respectively.

It is generally accepted that the primary complex particles exhibit Types a (a') and b (b') morphologies and the Type c (c') morphology is observed for secondary complex particles. This arises from the difference between the equilibrium⁷⁾ and experimental $[\text{Ti}]:[\text{N}]$ solubility product under specific conditions of a given number of oxide nuclei and cooling rate. The primary and secondary complex particles are hereafter denoted as the particles crystallized before solidification and precipitated after solidification, respectively.

The morphology of the complex particles arising from the various deoxidation methods fall mainly into three groups based on this notation, as shown in Table 2; these are Types a (a'), c (c') and (a', b'), with a few exceptions. The order of the notations is based on content, for example, b, c indicates that b is present in greater amounts than c. The Type a (a') group was observed in the Ti/Mg, Ti/Mg/Al and Ti/Zr deoxidations, in which the N content is in the range of 66 to 282 ppm. The Type c (c') group was observed in the Ti/Ca, Ti/Mg/Ti/Ca, Ti/Mg/Ca, Ti/Ca/Mg and Ti/Zr/Mg deoxidations, in which the N content were in the range of 35 to 80 ppm. The (a', b') group was observed in the Al/Ti/Ca, Ti/Al/Ca, Ti/Ca/Al, SM-1 and SM-5 to SM-8 deoxidations in an Al_2O_3 or MgO crucible, in which the N content is in the range of 72 to 121 ppm. On the basis of these results, it can be concluded that the morphology of the complex particles is primarily influenced by the $[\text{Ti}]:[\text{N}]$ solubility product and the deoxidation method.

3.2.2. Mechanism of Formation and Homogeneity of TiN Layer

It was found that the composition of the outer layers crystallized on the oxide particles (TiN layers, hereafter) was not always homogeneous and pure TiN. The composition of the TiN layer was found to be related to the oxide compositions. The homogeneities of the TiN layers, denoted as hm, ht-cu, ht-irr and hm-cu are presented in Table 2. The notation hm represents the homogeneous TiN layer composition consisting of one or two polyhedral layers in the complex particles. The notation hm-cu represents the homogeneous TiN layer composition, consisting of several independent polyhedral layers in the complex particles. The notations ht-irr and ht-cu represent the heterogeneous compositions in the TiN layers, consisting of the irregular and several independent polyhedral layers, respectively.

The mechanism of formation of the TiN layer comprising a mixture of TiN, Ti_2O_3 , CaO, Al_2O_3 and MgO is explained as follows; if a soluble oxygen content is high, which means that the soluble Al content is low, the simultaneous crystallization of TiN and oxide components, particularly Ti_2O_3 , occurs on the oxide particle surface during cooling to solidification. In this study, the mechanism of the co-crystallization of TiN and oxide is postulated. The diffusion mechanism of oxide component to the outer TiN layer and the coagulation mechanism of oxide particles with outer TiN layer by collision are considered. However, the former mechanism cannot be accepted because the diffusion of oxide components such as Al_2O_3 , CaO *et al.*, whose crystal structures are different from that of TiN, is improbable. The latter mechanism is also difficult to accept because the presence of homogeneous

oxide phase in the outer TiN layer cannot be explained by this mechanism. If the oxide particles are in equilibrium with the metal phase, the oxide composition of the TiN layer is directly related to the composition of the oxide particles. Of note, therefore, is the fact that the composition of the TiN layer in the co-crystallization process is influenced by the composition of the metal phase, regardless of the particle/metal equilibrium.

3.2.3. Composition of TiN Layer and Solidification Structure

The observed solidification structures are summarized in Table 4. The photographs of the typical solidification structures on half of an ingot are shown in Fig. 8. Fine equiaxed crystals are observed throughout the cross-sectional area of Type A structure. The solidification structures with and without the presence of the equiaxed crystals in the final solidification region represent Types B and C structures, respectively and the notation (A) represents the solidification structure consisting of small equiaxed crystals, small columnar grains or columnar grains with small width and length.

The solidification structures observed in the various deoxidations are discussed by focusing on the composition and homogeneity of the TiN layer as outlined below.

1) Ti/Mg (Al_2O_3 , MgO) and Ti/Mg/Al (Al_2O_3) Deoxidation

The compositions of the oxide particles and the TiN layer in the Ti/Mg deoxidation using an MgO crucible (Exp. 9)

Table 4. Solidification structure.

A	Fine EC in whole area
B-1(A), C-4(A)	Small CR and small EC
B-4(A)	Small CR
C-2(A)	CR with small width and length
B-2	Large EC
B-3, C-3	Large CR

CR: Columnar grains

EC: Equiaxed crystals

B: Presence of EC in final solidification area

C: Absence of EC in final solidification area

Fig. 8. Typical solidification structure: (a) A, (b) C-1, (c) C-2(A) and (d) B-2.

are shown in the upper diagram of **Fig. 9**. The oxide compositions belong to the MgO–TiO₂ system, as shown in Fig. 2 and the TiN layer consists of Ti₂O₃, TiN and a small amount of MgO. A similar result was observed in Exp. 10. It is to be noted that although TiO₂ is used in the ternary phase diagram, the composition of the oxide and TiN layer contain Ti₂O₃. In the case of a high soluble O content, the TiN layer is formed by co-crystallization of TiN and oxide. Heterogeneous TiN layers with irregular shape, denoted as ht-irr, were observed in this deoxidation. The observed Type C-3 solidification structure is attributed to the large amount of oxide phases in the TiN layers; however, despite the presence of a large number of complex particles, these are ineffective as solidification nuclei.

The compositions of the oxide particles and TiN layer in the Ti/Mg (Exp. 16) deoxidation, using an Al₂O₃ crucible, are shown in the lower diagram of Fig. 9. Similar results were observed in Exp. 14 (Ti/Mg) and Exp. 20 (Ti/Mg/Al) deoxidations. The oxide compositions fall within the TiO₂ rich MgO–Al₂O₃ system, as shown in Fig. 2. Despite the high soluble O content, the oxide contents of the TiN layers are significantly smaller than those obtained in Exps. 9 and 10, due to the high N content of the former (204 ppm in Exp. 16 and 282 ppm in Exp. 20). Consequently, the TiN layer was largely homogeneous (hm) in composition. The observed Type A solidification structure is attributed to the relatively small amount of oxide phases in the composition of the TiN layers; these phases function effectively as solidification nuclei.

In the Ti/Mg (Al₂O₃) deoxidations of Exps. 8 and 11, oxide systems of the MgO–Al₂O₃ composition were observed, as shown in Fig. 2. The contents of MgO and Al₂O₃ in the TiN layers were considerably small because the soluble O content in the MgO–Al₂O₃ system is low. The difference in the solidification structures observed in Exp. 11 (Type A) and that observed in Exp. 8 (Type C-2(A)) is explained by the difference in the N contents employed in both experiments (Exp. 11 (212 ppm) and Exp. 8 (64 ppm)), in addition to a very low soluble O content, thereby leading to the formation of TiN layers consisting of a small amount

of oxide phases.

It can be concluded that the Type A solidification generated in homogeneous TiN layers consisting of a small amount of oxide phases under conditions of high N and low O contents. On the other hand, Types C-3 and C-2(A) solidification structures are generated for TiN layers consisting of a large amount of oxide phases under conditions of low N and high O contents.

2) Ti/Ca (Al₂O₃) Deoxidation

Complex particles with Types c and b morphologies were observed for the Ti/Ca (Al₂O₃) deoxidation because of the low N content (37 to 68 ppm). It is reported that the equilibrium N content is 90 (100) ppm at Ti=0.3% in an Fe–10 (20)%Cr alloy at 1550°C.⁷⁾ The compositions of the TiN layer could be measured for the Type b complex particles only in the Ti/Ca deoxidation. Because the oxide compositions in Exps. 21 and 24 are rich in TiO₂, as shown in Fig. 3, the soluble O contents are high. Consequently, it was found that the Ti₂O₃, CaO and Al₂O₃ contents in the TiN layers having the irregular morphology (het-irr) observed in these experiments were considerably high in the region of 70 to 90% due to the co-crystallization of oxide and TiN; the Type B-1(A) solidification structure was observed. Because most of the complex particles exhibit the Type c morphology, it can be deduced that the solidification structure was influenced by the oxide surface composition. Though it is uncertain whether the crystallized CaO·TiO₂ cubic phase works as effective nuclei for the δ -phase solidification, the particle number in the Ti/Ca deoxidation was notably small relative to that of the Ti/Mg deoxidation.

Exp. 25 gave rise to TiN layers with low oxide contents, in the range of 10% to 20%, because of the low TiO₂ content in the oxide composition, as shown in Fig. 3. The Type B-3 solidification structure observed in this deoxidation is explained by the presence of a small number of complex particles with the Type c morphology, as well as the ineffective surface compositions of the oxide particles for δ -phase solidification.

3) Ti/Al/Ca (Al₂O₃) and Al/Ti/Ca (Al₂O₃) Deoxidation

The compositions of the oxide particles and TiN layers in

Fig. 9. Compositions of oxide and TiN layer in complex particles in Ti/Mg deoxidation experiments (Exps. 9 MgO crucible and 16, Al₂O₃ crucible).

Fig. 10. Compositions of oxide and TiN layer in complex particles in Ti/Al/Ca deoxidation experiments (Exps. 33 and 34, Al₂O₃ crucible).

Fig. 11. Compositions of oxide and TiN layer in complex particles in Ti/Al/Ca (Exp.42, MgO crucible) and Al/Ti/Ca (Exp.61, MgO crucible) deoxidation experiments.

Fig. 12. Compositions of oxide and TiN layer in complex particles in Ti/Mg/Ca (Exp.44, Al₂O₃ crucible) and Ti/Ca/Mg (Exp.48, Al₂O₃ crucible) deoxidation experiments.

the Ti/Al/Ca deoxidations using an Al₂O₃ crucible (Exps. 33 and 34) are shown in the upper and lower diagrams of Fig. 10, respectively. The oxide compositions belong to the CaO–Al₂O₃–TiO₂ system, as shown in Fig. 5. The upper diagram of Fig. 10 shows that the TiN layer has two phases having high and low CaO and Al₂O₃ contents, respectively. The fact that the oxide content in the TiN layer is considerably low is attributed to a low soluble O content, which corresponds to a very low TiO₂ content in the oxide particles, as shown in Fig. 5. The observed Type B-3 solidification structure is explained in terms of the small number of complex particles with Type a' morphology, which are effective to the *d*-phase solidification.

It can be seen from the results of Exp. 34, as shown in the lower diagram of Fig. 10 that the Ti₂O₃ content in the TiN layer is considerably high and the TiO₂ content in the oxide particles is also high. This leads to the favorable co-crystallization of Ti₂O₃ and TiN. A similar result to the Ti/Al/Ca deoxidation of Exp. 34 was observed in Al/Ti/Ca deoxidation of Exp. 32. The B-2 (Exp. 34) and B-4(A) (Exp. 32) solidification types observed in the respective experiments are attributed to the presence of a small number of complex particles with the Type a+a' morphology, having TiN layers consisting of a high Ti₂O₃ content.

4) Ti/Al/Ca (MgO) and Al/Ti/Ca (MgO) Deoxidation

The compositions of the oxide particles and TiN layers in the Ti/Al/Ca and Al/Ti/Ca deoxidations using an MgO crucible (Exps. 42 and 61) are shown in the upper and lower diagrams of Fig. 11, respectively. The oxide compositions obtained in Exp. 61 were rich in TiO₂ and belonged to the CaO–Al₂O₃–TiO₂ system, whereas those of Exp. 42 fall in the CaO–0%–7%MgO–Al₂O₃ system, as shown in Fig. 6. The CaO and Al₂O₃ contents in the TiN layers are high, as shown in the upper diagram, even though the soluble O contents in Exp. 42 are expected to be very low. These results are different from those in Exps. 25 (Ti/Ca (Al₂O₃) shown in Fig. 3) and 33 (Ti/Al/Ca (Al₂O₃) shown in Fig. 5), in which the oxide contents in the TiN layer are smaller than those in Exp. 42. Therefore, these results can be explained in terms of the supersaturated O content with respect to the

Al/(Al₂O₃) equilibrium. The Type B-1(A) solidification structure was observed.

The results of Exp. 61 are shown in the lower diagram of Fig. 11, indicating the TiO₂-rich compositions of the obtained oxide particles and TiN layers. Similar results were obtained for Exp. 61 and Exp. 40. However, it was found that the oxide composition in Exp. 60 was relatively rich in TiO₂, whereas the Ti₂O₃ content in the TiN layer was very low and the CaO and Al₂O₃ contents were also relatively low. Notably, high soluble Al contents were obtained in Exps. 40 (375 ppm), 60 (1 484 ppm) and 61 (596 ppm), as shown in Table 3, even though the oxide compositions were rich in TiO₂, as shown in Fig. 6.

The contrastingly low oxide content in the TiN layer and high Ti₂O₃ content in the oxide particles obtained in Exp. 60 can be explained by the fact that the soluble O content was low due to a high soluble Al content. On the other hand, the rationale for the high Ti₂O₃ contents in the TiN layers in Exps. 40 and 61 is explained in terms of a high soluble O content, in spite of a high Al content, that is, the presence of the supersaturated oxygen.

Type B-1(A) solidification structures were obtained in Exps. 40 and 42, and Type C-2(A) solidification structure were observed in Exps. 60 and 61. The Type b' (a') morphology of the complex particles was observed in the presence of ca. 100 ppm N, except in the case of Exp. 61 (N=72 ppm) at 0.25% to 0.3%Ti. A homogeneous TiN layer (hm) with low oxide content was observed in Exp. 60. However, a heterogeneous TiN layer (ht-irr) with high oxide content was observed in Exps. 40, 42 and 61. These results support the validity of the postulated co-crystallization mechanism for the formation of the TiN layer.

5) Ti/Mg/Ti/Ca (Al₂O₃), Ti/Mg/Ca (Al₂O₃) and Ti/Ca/Mg (Al₂O₃) Deoxidation

The morphologies of the complex particles obtained in the Ti/Mg/Ti/Ca (Al₂O₃), Ti/Mg/Ca (Al₂O₃) and Ti/Ca/Mg (Al₂O₃) deoxidations were primarily Types c and c' because of the low N content, which was the range of 36 to 80 ppm at Ti=0.3%. In addition, the particle number was large in the Ti/Mg/Ca deoxidation. The Type A solidification structure

Fig. 13. Compositions of oxide and TiN layer in complex particles in Ti/Mg/Ti/Ca (Exp.46, Al_2O_3 crucible) and Ti/Mg/Ca (Exp.47, Al_2O_3 crucible) deoxidation experiments.

was observed in all of these deoxidation experiments, despite the fact that the morphologies of the complex particles were mostly Types c and c'.

The compositions of the oxide particles in Exps. 44 and 48 ($\text{CaO-MgO-Al}_2\text{O}_3$ system) are shown in the upper and lower diagrams of Fig. 12, respectively. The compositions of the TiN layer are also shown, but these data points are limited because of the Type c complex particle morphology. The solidification structure is influenced by the surface composition of the oxide particles and most of the complex particles with Types c and c' morphologies are considered to be secondary complex particles. The observed fine solidification structure is attributed to the presence of a crystallized MgO or $\text{MgO} \cdot \text{Al}_2\text{O}_3$ phase on the oxide surface, in addition to the large number of particles.

The compositions of the oxide particles obtained in Exp. 46 are shown in the upper diagram of Fig. 13. Similar results were observed in Exps. 43, 45 and 49 ($\text{TiO}_2\text{-CaO-MgO-Al}_2\text{O}_3$ system). Because some of these oxide particles are liquid at 1600°C , the crystallization of $2\text{MgO} \cdot \text{TiO}_2\text{-MgO} \cdot \text{Al}_2\text{O}_3$ solid solution occurs during the period of cooling to solidification, thereby leading to the formation of a fine solidification structure. The compositions of the oxide particles in Exp. 47 ($\text{TiO}_2\text{-CaO-MgO-Al}_2\text{O}_3$ (<3.6%) system) are shown in the lower diagram of Fig. 13. A fine solidification structure is observed due to the formation of the crystallized $\text{CaO} \cdot \text{TiO}_2$ or MgO phase. These results in the Ti/Mg/Ca deoxidation suggest that an increased number of oxide particles having effective surface compositions for δ -phase solidification is necessary for improved solidification structures.

6) Al/Ti/Ca and Ti/Ca/Al Deoxidation in the Presence of Slag

As shown in Fig. 7, crystallized phases having the compositions between $\text{MT}_2\text{-AT}$ and $\text{M}_2\text{T-MA}$ solid solutions

was observed except in the case of Exp. SM-1. Types b' and c (c') morphologies of the complex particles were observed in the N contents of 77 to 92 ppm, except for Exp. SM-5 (211 ppm). The MgO contents in oxide particles decrease in the order: SM-6 (MgO) > SM-8 (Al_2O_3 crucible with MgO-ring) > SM-1 (Al_2O_3) at nearly constant contents of soluble Al and N. The oxide contents in the TiN layer are not high, notably, the Ti_2O_3 content is zero, in spite of a high Ti_2O_3 content in the oxide particles.

The solidification structure of Types B-1(A) (SM-1), C-2(A) (SM-5) and C-4(A) (SM-6, -7 and -8) were observed. It can be concluded that the MgO content in oxide particles in the Ti/Ca/Al deoxidation can be increased to a considerably degree by using the $\text{MgO-CaO-Al}_2\text{O}_3$ slag in an MgO crucible; it is nonetheless difficult to increase the particle number to the same degree as that observed in the Ti/Mg/Ca deoxidation carried out in the absence of the slag.

4. Conclusions

The conclusions drawn with respect to the solidification structure generated by Ti/M and Ti/M/M' deoxidations of a ferritic alloy containing 30 to 400 ppm N using an Al_2O_3 or MgO crucible, in the presence or absence of $\text{CaO-MgO-Al}_2\text{O}_3$ slag can be summarized in the following three deoxidation categories:

(1) Ti/Mg and Ti/Mg/Al deoxidations using an Al_2O_3 crucible generated very fine solidification structures at a high N content (>200 ppm); the oxide contents of the TiN layers of these structures were low, whereas the solidification structure was not fine at a low N content because of a high oxide content in the TiN layers.

(2) Ti/Ca, Ti/Ca/Al and Al/Ti/Ca deoxidations using an Al_2O_3 crucible produced relatively fine solidification structures even for low oxide content in the TiN layers because of a small number of complex particles. In the Ti/Ca/Al and Al/Ti/Ca deoxidations using an MgO crucible, the solidification structures were finer, in comparison with those in the deoxidation using an Al_2O_3 crucible. In the Ti/Al/Ca and Ti/Ca/Al deoxidations using an Al_2O_3 crucible in the presence of $\text{CaO-MgO-Al}_2\text{O}_3$ slag, the solidification structures were relatively finer, compared with those observed in the same experiments carried out in the absence of the slag using an Al_2O_3 crucible.

(3) Ti/Mg/Ca and Ti/Ca/Mg deoxidations using an Al_2O_3 crucible yielded very fine solidification structures at a low N content (36 to 80 ppm), as observed in the Ti/Mg and Ti/Mg/Al deoxidations at high N content (>200 ppm) using an Al_2O_3 crucible. The mechanism of formation of this solidification structure differs from that observed in the Ti/Mg and Ti/Mg/Al deoxidations using an Al_2O_3 crucible in that the former is attributed to the effective surface compositions for solidification of the oxide particles and the latter is explained by the presence of the complex particles in which the crystallized TiN layers consist of a small amount of oxide phases.

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