Formation and Evolution of Al–Ti Oxide Inclusions during Secondary Steel Refining

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The process of Al deoxidation and Ti alloying during RH degassing treatment was studied under an Ar atmosphere at secondary steelmaking temperature (1 600–1 650°C) in an induction furnace equipped with an oxygen probe and a steel sampler. The formation of inclusions during partial Al deoxidation and Ti addition, and the reduction of Ti–Al–O inclusions by second Al addition are discussed using thermodynamic calculations. Specific attention is given to inclusion size and the compositional relation between the inclusions and the steel. The combination of experimental and calculated results shows that, in order to prevent Ti oxidation in liquid steel, it is essential to control [Al] in liquid steel to a level of approximately 200 ppm prior to Ti addition to achieve around 500 ppm [Ti] with minimal Ti loss during the alloying process.

KEY WORDS: IF steel; Al–Ti deoxidation; Ti alloying; Al–Ti–O inclusions; Fe–Al–Ti–O equilibrium diagram.

1. Introduction

Ti stabilized IF (interstitial free) steel is commonly produced by the combination of primary (BOF) and secondary steelmaking (RH degassing treatment), during which Ti is added as an alloying element. Since Ti is substantially more expensive than Al, it is added after Al deoxidation in order to minimize losses through reaction with oxygen. However, if thermodynamic and kinetic conditions allow, Ti will react with oxygen in the molten steel and/or with Al_2O_3 during the Ti alloying process. These reactions lead to the formation of Ti containing inclusions, which influence Ti yield during alloying and also steel cleanliness. The formation of non-metallic inclusions such as Al_2O_3 , TiO_x , and Al–Ti–O oxides might cause both nozzle clogging during continuous casting and loss of final product quality.¹⁾ From the viewpoint of “oxide metallurgy”, Ti containing complex oxides can be utilized as nuclei for MnS precipitation,²⁾ which can serve again as nucleation site for acicular ferrite after welding or heat treatment, hence improving steel toughness and strength.^{3,4)} It is, therefore, of great concern to study the combined oxidation of [Al] and [Ti] in order to try to understand the formation mechanisms of Ti containing oxides. The symbol [] refers to concentration in liquid steel.

Several authors^{5–8)} have investigated Al/Ti and Ti/Al deoxidation using sampling techniques. Kunisada *et al.*^{5,6)} reported that in the case of Ti/Al deoxidation, the oxygen content in the liquid steel is lower than in the case of single Ti deoxidation but higher than in case of single Al deoxidation. Hence, there is no advantage of Ti/Al deoxidation for reducing the oxygen content compared with single Al deox-

idation. They observed that angular Al_2O_3 inclusions that had been formed during Al deoxidation, changed after Ti addition to spherical inclusions containing a small amount of Ti, while, in the case of Ti/Al deoxidation, TiO_x resulting from Ti deoxidation was reduced by the second Al addition. Ruby-Meyer *et al.*⁷⁾ performed inclusion analyses in Ti-deoxidized steel and multiphase equilibrium calculations based on the IRSID slag model (code CEQCSI). They observed that Al_2O_3 inclusions were formed at high [Al] content, whereas inclusions containing both Ti oxides and Al_2O_3 were formed at low Al contents. There was a good correlation between the analyzed oxide composition and that predicted by the calculated Fe–Al–Ti–O inclusion diagram. More recently, Matsuura *et al.*⁸⁾ investigated the inclusion evolution at 1 600°C during Al and/or Ti additions to molten Fe with constant total oxygen concentration. They reported that Al_2O_3 inclusions were formed at first after Al and Ti additions, followed by Ti oxide formation on the existing particles. The latter were then reduced by [Al], resulting in a change of particle morphology from spherical inclusions formed immediately after Al deoxidation to polygonal inclusions.

Park *et al.*¹⁾ studied the reoxidation of Al–Ti containing steel in the tundish by $\text{CaO–Al}_2\text{O}_3\text{–MgO–SiO}_2$ slag at 1 550°C with an initial [Al] of 820 ppm and [Ti] varying from 100 to 500 ppm. They observed that [Al] and [Ti] were simultaneously oxidized by SiO_2 from the slag, and that dissolved oxygen was supersaturated with respect to the Al–O– Al_2O_3 equilibrium. The oxygen supersaturation caused the formation of inclusions with a two-layer complex structure, consisting of an Al_2O_3 core surrounded by

Al–Ti–O oxides.

In the present study, Al/Ti and Al/Ti/Al deoxidation experiments are carried out under Ar atmosphere at secondary steelmaking temperatures (1 600–1 650°C) in an induction furnace equipped with an oxygen probe and a steel sampler. The influences of the amount of Ti addition and the oxygen level in liquid steel prior to Ti alloying on the formation mechanism of complex Al–Ti–O inclusions are highlighted in association with inclusion composition and compared with thermodynamic calculations. The purpose is to simulate the influence of locally high [O] and high [Ti] in the ladle on the type and chemistry of inclusions. The subsequent reduction of Ti-containing inclusions through a second Al addition was evaluated in order to investigate how the Ti recovery can be maximized. Special attention is given to inclusion size, and the compositional correlation between inclusion and steel.

2. Experimental

2.1. Experimental Set-up and Procedures

The experiments were performed in a vacuum induction furnace (type VSG 30, 60 kW power supply and 4 kHz frequency). A schematic diagram of the experimental set-up is shown in Fig. 1. A loading chamber, a sampling device and a measurement tool are fitted on the furnace lid to allow Al and Ti additions, sampling, and oxygen and temperature measurements. Information on the O and Ti alloying levels are listed in Table 1. Twenty kilograms of electrolytic iron

(99.98% purity) was melted in a zirconia crucible (inner diameter=150 mm, outer diameter=176 mm, height=275 mm) under Ar atmosphere (99.998% Ar, $O_2 < 5$ ppm, $N_2 < 10$ ppm, 500 mbar). After the iron was fully liquid, the temperature was controlled at around 1 600 to 1 650°C.⁹⁾ Thereafter, the dissolved oxygen content ($a_{[O]}$) and the temperature of the liquid Fe were measured with oxygen probes. Except for Exp. 2, the initial $a_{[O]}$ in the liquid steel ranged from 630 to 870 ppm. Subsequently, a steel sample (conical shape, size: upper diameter= ~ 20 mm, lower diameter= ~ 10 mm, height=16–25 mm) was taken by dipping the spoon sampler in the liquid bath and rapidly withdrawing it. The steel sample cooled down within a few minutes. Depending on the initial $a_{[O]}$ and the desired deoxidation level (Table 1) of the liquid steel, a certain amount of granulated pure Al was added to the liquid steel through the loading chamber. Approximately 2 min later, a sample of the Al-killed steel was taken, instantly followed by a temperature and $a_{[O]}$ measurement. Ti alloying was performed by adding Fe–70wt%Ti alloy to the Al-killed steel through the loading chamber. Except for Exp. 5, the total Ti content was aimed at 525 ppm (Table 1). To investigate the influence of [Ti], the latter was increased to 1 500 ppm in Exp. 5. Ti alloying was immediately followed by one or several samplings and temperature– $a_{[O]}$ measurements. For Exp. 2, 3 and 4, a second Al addition was performed, followed by sampling and temperature– $a_{[O]}$ measurements of the melt. At the end of the experiment, the crucible was tilted and the melt was poured into the mould.

2.2. Characterization of Inclusions

The steel samples taken during the tests were cut in two parts. One half was prepared for microscopical investigation. The specimens were embedded in a low viscosity resin (Epofix) by vacuum impregnation, grinded with diamond plates and polished with diamond paste. Characterization of the inclusions (size, shape and composition) was conducted with a high resolution scanning electron microscope (Philips SEM XL-30 FEG), equipped with an EDAX energy dispersive spectrometer (EDS) detector system with an ultra thin window. The maximum working magnification was set to 5 000 and the effective minimum detectable inclusion size was about $0.5 \mu\text{m}$. For each sample, an area of around 0.15 mm^2 was observed to obtain inclusion size and morphology. At least 25 inclusions were analysed for inclusion chemistry. Inclusion and cluster size were defined by, respectively, the maximum length of the sectioned particle and the diameter of the circle comprising the sectioned cluster.

2.3. Chemical Analysis and Oxygen Determination

The other half of the steel sample was used for chemical analysis with inductively coupled plasma atomic emission spectroscopy (ICP-AES, Varian Liberty series II instrument with an axial plasma configuration). One gram-steel samples were dissolved in a mixture of acid ($H_2O:HCl:HNO_3=10:10:1$) to bring into solution the acid soluble Al and Ti, while the insoluble fraction was recovered on a filtration membrane (not further analysed). The solution was analysed with ICP-AES to obtain [Al] and [Ti]. The standard solutions and blanks were prepared with the same acid

Fig. 1. Schematic diagram of the vacuum induction furnace used in the deoxidation experiments.

Table 1. Oxygen activities (ppm) prior and after Al-deoxidation (measured with Celox probes) and total Ti alloying level (ppm). Values with * are corrected for reoxidation of the steel.

Exp.	Initial $a_{[O]}$	$a_{[O]}$ after first Al deoxidation	$a_{[O]}$ after second Al deoxidation	Amount of Ti addition
1	817	1.5	-	525
2	1265	224*	16	
3	661	138*	11	
4	868	277*	7.4	
5	631	2.8	2.5	1500

concentrations as those of the sample solutions. $a_{[O]}$ and temperature of the liquid steel were on-line measured by the intermittent immersion of single-use oxygen probes (Celox type B, provided by Heraeus Electro-Nite). The data were collected by a Multi-Lab III Celox instrument (v3.01). At 1600°C, the lowest analytical limit and the accuracy of O probe measurements are, respectively, about 10^{-5} ppm and 0.04 ppm.

3. Results and Discussion

The sampling moment, [Al], [Ti], $a_{[O]}$ and the corresponding Al and Ti contents of the Ti–Al–O inclusions in the samples are summarized in **Table 2**. The symbols ()_c and ()_s refer to, respectively, the concentrations in clusters and in single particles.

3.1. Compositional Evolution of Metal and Inclusions during Al/Ti and Al/Ti/Al Deoxidation

3.1.1. Al/Ti Deoxidation

Changes in [Al], [Ti] and $a_{[O]}$ during Al–Ti deoxidation as a function of time after Al deoxidation for Exp. 1 are shown in **Fig. 2**. With Al addition, the liquid steel was rapidly deoxidized from an initial $a_{[O]}$ level of 817 to 1.5 ppm. Thereafter, $a_{[O]}$ remained constant at this low level until the completion of the experiment. There was no decrease in $a_{[O]}$ after Ti addition. With Ti alloying (aimed at 525 ppm), the [Ti] reached a level of approximately 505 ppm. Thereafter, it remained almost constant (see Table 2). Only 45 ppm [Ti] was lost after holding the melt for 60 min in the crucible without top slag coverage. This confirms that Ti can be efficiently alloyed into the liquid steel after a strong Al deoxidation. On the other hand, the [Al] gradually decreased with time, as a result of [Al] oxidation through reaction with the residual oxygen in the Ar gas flow. Considering the metal composition changes with time for every test, the reoxidation rate of the melt is evaluated at approximately 20 ppm/min. Only pure Al₂O₃ inclusions were observed in the metal samples taken after Ti alloying (**Table 3**).

3.1.2. Al/Ti/Al Deoxidation

Figure 3 shows the evolutions of [Al], [Ti], $a_{[O]}$ and the (Ti)_s/(Al)_s ratio in the Ti–Al–O inclusions as a function of time after the first Al addition for Exp. 2. The purpose of this test was to perform a partial deoxidation of the steel with the first Al addition, followed by Ti alloying and a second Al addition. As seen in the upper diagram of Fig. 3, $a_{[O]}$ was controlled at 64 ppm by the first Al addition. $a_{[O]}$ at the moment of the Ti addition was corrected to 224 ppm to take into account steel reoxidation during the 8 min between the oxygen measurement and the Ti addition. It was further reduced to 22 and 16 ppm with, respectively, Ti alloying (aimed at 525 ppm) and a second Al addition. The former suggests that part of the added Ti was consumed through Ti deoxidation. This is confirmed by analyses of the inclusion composition. The ratio (Ti)_s/(Al)_s in the small randomly dispersed inclusions drastically increased after Ti addition (lower diagram of Fig. 3), while only 78 ppm [Ti] was obtained in the bulk metal immediately after Ti addition, indicating the occurrence of Ti deoxidation. After the

Table 2. Chemical composition of liquid steel and that of inclusions. t_{Al1} , t_{Ti} and t_{Al2} represent, respectively, the time after first Al addition, Ti addition and second Al addition. $a_{[O]}$ was measured with Celox probes. * indicates modified $a_{[O]}$ values considering the reoxidation rate of the steel. [Al] and [Ti] were obtained with ICP-AES. The inclusion composition was determined by EDS analysis. ()_c and ()_s refer to the content in clusters and in single particles.

Sample	Time (min)			Steel composition (ppm)			Inclusion composition (at %)			
	t_{Al1}	t_{Ti}	t_{Al2}	$a_{[O]}$	[Al]	[Ti]	(Ti) _c	(Al) _c	(Ti) _s	(Al) _s
1A	3	-	-	1.5	2000	-	-	86.4	-	-
1B	6	2	-	1.5	1912	505	-	72.7	-	-
1C	-	14	-	1.3	1649	488	-	90.7	-	-
1D	-	19	-	1.3	1495	453	-	85.8	-	-
1E	-	57	-	2.8	949	460	-	-	-	-
2A0	1	-	-	17	420	0	-	-	-	-
2A	22	-	-	224*	2	0	0	82.8	0	15.8
2B	28	1	-	22	1	78	1.15	90.4	58.0	9.93
2C	-	12	-	20	32	67	16.2	69.9	43.0	5.23
2D	-	14	1	16	537	304	0.53	75.3	22.0	21.6
2E	-	-	11	17	283	347	-	-	22.7	21.3
3A	2	-	-	138*	23	0	0	67.5	0	9.00
3B	8	3	-	23	18	255	7.8	73.3	18.7	8.70
3C	-	11	-	39	16	54	18.6	59.3	32.4	8.20
3D	-	20	-	79	4	7	-	-	4.60	1.51
3E	-	81	3	10.8	634	118	0.28	52.8	2.04	22.7
3F	-	-	17	11.1	367	153	-	-	7.80	24.3
4A	4	-	-	277*	21	0	0.22	72.6	0.28	10.4
4B	30	1	-	45	1	52	12.8	69.6	51.3	9.1
4C	-	20	2	7.4	623	184	0.51	78.9	3.1	9.0
4D	-	-	10	10.6	468	254	0.43	78.0	6.1	22.0
4E	-	-	18	13	346	294	0.88	80.9	8.6	27.5
5A	2	-	-	2.8	1894	0	0	92.7	0	71.8
5B	9	1	-	2.5	1803	828	0	78.3	4.10	29.8
5C	-	23	-	2.5	1266	808	0	78.4	14.2	28.3
5D	-	29	3	2.5	1808	866	0	69.8	4.41	13.5
5E	-	-	20	2.1	1733	900	-	-	5.54	17.1

Fig. 2. Evolution of [Al], [Ti] and $a_{[O]}$ in liquid steel after Al–Ti deoxidation (Exp. 1).

second Al addition, $a_{[O]}$ is still relatively high (upper diagram of Fig. 3, $a_{[O]} = 16$ ppm), substantiating the findings by Kunisada *et al.*⁵⁾ that Ti/Al deoxidation was less efficient than single Al deoxidation. With the second Al addition, [Ti] rose abruptly. Afterwards, it increased moderately with time. Meanwhile [Al] decreases. Apparently, Ti containing oxides formed during Ti alloying were reduced after the second Al addition, the reduction proceeding fast at the be-

Table 3. Inclusion type and dimensions (in μm) in the samples. t_{Al1} , t_{Ti} and t_{Al2} represent, respectively, the time after first Al addition, Ti addition and second Al addition. d_{mean} , d_{max} and d_{min} are respectively the mean, maximum and minimum diameters of the inclusions.

Sample	Time (min)			Cluster			Single particle within clusters			Random distributed single particles			Type of inclusions
	t_{Al1}	t_{Ti}	t_{Al2}	d_{mean}	d_{max}	d_{min}	d_{mean}	d_{max}	d_{min}	d_{mean}	d_{max}	d_{min}	
1A	3	-	-	-	-	-	3.81	6.96	1.39	-	-	-	Al ₂ O ₃ cluster
1B	6	2	-	891	1580	487	4.26	16.9	1.22	-	-	-	Al ₂ O ₃ cluster
1C	14	-	-	836	1060	515	2.67	8.71	1.13	0.78	0.94	0.52	Al ₂ O ₃ cluster
1D	19	-	-	921	1580	414	2.57	6.79	1.04	1.16	1.23	1.08	Al ₂ O ₃ cluster
1E	57	-	-	-	-	-	-	-	-	-	-	-	Al ₂ O ₃ cluster
2A	22	-	-	977	2160	109	3.52	7.66	1.22	1.80	2.51	1.18	Al ₂ O ₃ cluster + small spherical Al ₂ O ₃
2B	28	1	-	1060	3500	195	3.36	10.1	0.70	2.53	3.66	1.60	Al ₂ (Ti)O ₃ cluster + small Ti-Al oxides
2C	12	-	-	1155	2980	403	3.44	8.79	1.57	1.47	2.40	0.61	Al ₂ (Ti)O ₃ cluster + small Ti-Al oxides
2D	14	1	-	2158	8000	230	4.39	11.5	1.39	2.11	3.45	0.91	large Al ₂ O ₃ cluster + few small Ti-Al oxides
2E	11	-	-	-	-	-	-	-	-	-	-	-	Al ₂ O ₃ cluster
3A	2	-	-	52	174	20	2.56	4.35	0.87	1.83	4.09	0.78	Al ₂ O ₃ cluster
3B	8	3	-	426	670	181	-	-	-	1.33	3.13	0.70	Al ₂ (Ti)O ₃ cluster + small Ti-Al oxides
3C	11	-	-	1562	3250	635	3.10	10.3	1.22	1.20	2.70	0.44	large Al ₂ O ₃ clusters + small Ti-Al oxides
3D	20	-	-	-	-	-	-	-	-	0.97	1.92	0.45	large Al ₂ O ₃ clusters + small Ti-Al oxides
3E	81	3	-	360	1120	68	2.77	7.40	1.04	1.48	2.12	0.61	Al ₂ O ₃ cluster
3F	17	-	-	-	-	-	-	-	-	-	-	-	-
4A	4	-	-	652	1890	237	2.21	5.40	0.70	1.66	3.22	0.78	Al ₂ O ₃ cluster + small Al-Si oxides
4B	30	1	-	1100	1950	433	4.03	15.1	1.04	2.08	9.40	0.96	Al ₂ (Ti)O ₃ cluster + small Ti-Al oxides
4C	20	2	-	486	1320	240	2.34	4.44	0.96	1.49	2.96	0.31	Al ₂ O ₃ cluster + small Ti-Al oxides
4D	10	-	-	414	795	127	2.55	5.48	0.52	1.89	3.31	1.13	Al ₂ O ₃ cluster + few small Ti-Al oxides
4E	18	-	-	-	-	-	3.31	6.27	1.22	1.77	3.57	0.63	few Al ₂ O ₃ cluster + few small Ti-Al oxides
5A	2	-	-	776	2810	20	2.52	4.79	0.87	1.31	3.57	0.44	Al ₂ O ₃ cluster + small spherical Al ₂ O ₃
5B	9	1	-	1232	4060	162	2.64	11.1	0.87	1.06	1.46	0.73	Al ₂ O ₃ cluster + few small spherical Ti-Al oxides
5C	23	-	-	1528	2860	411	3.69	11.30	1.31	1.27	2.86	0.80	Al ₂ O ₃ cluster + few small spherical Ti-Al oxides
5D	29	3	-	3475	3560	3390	3.53	7.49	1.74	0.95	2.33	0.49	Al ₂ O ₃ cluster + few small spherical Ti-Al oxides with TiN overgrowth -
5E	20	-	-	-	-	-	-	-	-	0.74	1.08	0.21	Al ₂ O ₃ cluster + small spherical Al ₂ O ₃

ginning. The $(\text{Ti})_s/(\text{Al})_s$ ratio in the Ti–Al–O inclusions dropped rapidly from around 8 to 1 within 1 min after the second Al addition, and remained constant at $(\text{Ti})_s/(\text{Al})_s = 1$ (lower diagram of Fig. 3). A fraction of Ti was inevitably lost during the alloying process since Ti containing oxides could not be completely reduced with the second Al addition under the present test conditions.

3.2. Characteristics of Al/Ti and Al/Ti/Al Deoxidation Products

3.2.1. Overview of Inclusions Formed during Deoxidation

Per sample the following information is provided in Table 3: (1) sampling moment (t_{Al1} , t_{Ti} and t_{Al2} are respectively the holding times after first Al addition, Ti addition and second Al addition), (2) inclusion size (d_{mean} , d_{max} and d_{min} are respectively the mean, maximum and minimum diameters for complete cluster, single particle within a cluster, and single particles randomly distributed in the steel matrix) and (3) type of inclusions. Prior to Ti alloying, only Al₂O₃ inclusions, mainly present as clusters, were found.

After the Ti addition, the inclusions can be roughly categorized into two types: large Al₂O₃ clusters (Fig. 4(a)) and small Ti–Al oxide particles (Fig. 4(b)). The latter are randomly distributed in the steel matrix. These small particles consist of a Ti–Al–O core with Al₂O₃ overgrowth (Fig. 4(b)). In some samples taken immediately after Ti alloying (2B, 3B and 4B), several Ti oxide particles were detected in the Al₂O₃ clusters (Fig. 4(c)). After the second Al addition, only Al₂O₃ clusters and a limited amount of small Al–Ti–O inclusions were found in the samples, owing to the reduction of Al–Ti–O inclusions by Al addition. Few cubic TiN particles with Al–Ti oxide core, formed through reaction with residual N₂ in the Ar gas flow, were observed below the sample surface in Exp. 5 in which Ti alloying level was raised to 1 500 ppm (Fig. 4(d)). Based on Thermo-Calc predictions, Van der Eijk *et al.*¹⁰⁾ pointed out that the TiN formation probably occurs through an exchange reaction with Ti₂O₃ (or Ti₃O₅) in the solid state. No evidence indicating the existence of a liquid Al–Ti–O phase was found during the SEM observations. An extremely fast quenching of the

sample may be required to be assured about the liquid or solid state of the Al–Ti–O inclusions at steelmaking temperature.

3.2.2. Inclusion Size

The average size of single Ti–Al–O inclusions varies from 0.75 to 2.5 μm , while single Al_2O_3 particles within the clusters ranged from 2.2 to 4.4 μm (Table 3). No correlation was found between particle size and time after first Al deoxidation and/or Ti alloying. Nevertheless, Table 3 shows that the average size of the single Ti–Al–O inclusions is about 2 μm smaller than that of the single Al_2O_3 particles within clusters. This might be explained by the different levels of supersaturation with respect to the [Al]–[O]–

Al_2O_3 (s) and [Ti]–[O]– TiO_x (s) equilibria. For a given [O], [Al] has a much higher supersaturation level with respect to [Ti],¹⁾ resulting in a larger driving force for precipitation and growth of Al_2O_3 inclusions compared with TiO_x inclusions. The size of the Al_2O_3 clusters ranged from 50 μm to 1.5 mm. As shown in Fig. 5, the diameter of the cluster increased with time between the first and second Al addition, due to coalescence of Al_2O_3 particles. Collision-coagulation mechanisms, and especially turbulent and Stokes collisions, seem to be the major contributor to inclusion growth under the present conditions.

3.2.3. Inclusion Composition

Figure 6 shows the influence of [Al] on the $(\text{Ti})_s/(\text{Al})_s$ ratio of the inclusions. The Ti content in the Ti–Al–O inclusions rapidly decreases with increasing [Al]. It can be concluded from these experimental data that more than 300 ppm [Al] is required to prevent the formation of Ti-oxides during Ti alloying, as a result of low $a_{[\text{O}]}$ in the liquid steel. It is therefore essential to ensure a sufficiently high [Al] value and homogeneity throughout the ladle prior to Ti addition, to avoid locally low [Al], high $a_{[\text{O}]}$ and high [Ti],

Fig. 3. Changes in [Al], [Ti] and $a_{[\text{O}]}$ in liquid steel, and changes in $(\text{Ti})_s/(\text{Al})_s$ ratio in inclusions with time during Al–Ti–Al deoxidation (Exp. 2).

Fig. 5. Evolution of the average cluster size with time after first Al addition.

Fig. 4. Types of inclusions observed after Ti alloying: (a) Al_2O_3 cluster (3B, 3 min after Ti addition); (b) small Ti–Al–O particles with Al_2O_3 overgrowth (3B, 3 min after Ti addition); (c) Al–Ti–O cluster (2C, 12 min after Ti addition); and (d) cubic TiN (5D, 3 min after second Al addition).

Fig. 6. Correlation between [Al] and the $(\text{Ti})_s/(\text{Al})_s$ ratio in the Ti–Al–O inclusions.

causing the formation of Al–Ti–O inclusions.

3.3. Ti Deoxidation during Ti Alloying and Reduction of Ti Containing Inclusions by a Strong Second Al Deoxidation

3.3.1. Oxidation of Ti during Ti Alloying

The influence of $a_{[\text{O}]}$ prior to Ti addition on the oxidation of Ti was investigated by varying $a_{[\text{O}]}$ before Ti alloying. Figure 7 depicts the evolution of [Ti] and [O] in the steel before and after Ti addition for Exp. 1 to 4. [O] prior to Ti addition were adjusted to take into account the reoxidation of the melt occurring between the oxygen measurement and the Ti addition. In the ideal case, when Ti_3O_5 –[Ti]–[O] equilibrium would be reached without reoxidation of the melt, the melt composition after Ti addition would correspond to the open markers in Fig. 7. The observed steel composition evolutions during Ti addition for Exp. 1 to 4 are indicated by the arrows and grey markers. The steel composition after Ti addition tends to the corresponding equilibrium value. However, higher [O] and lower [Ti] are attained compared to the equilibrium composition, suggesting that equilibrium is not reached and/or reoxidation of the melt occurs (1 to 2 min elapsed between Ti addition and the next sampling and oxygen measurement). As seen in Fig. 7, the extent of Ti oxidation strongly depends on $a_{[\text{O}]}$ prior to Ti addition. Low $a_{[\text{O}]}$ prior to Ti alloying prevents Ti oxidation during Ti alloying to 525 ppm (Exp. 1), while Ti loss by oxidation increases significantly with $a_{[\text{O}]}$ prior to Ti alloying (Exp. 2, 3 and 4).

With Exp. 5, the Ti alloying level was raised to 1 500 ppm after that low $a_{[\text{O}]}$ was achieved through Al deoxidation, in order to assess whether [Ti] oxidation may be achieved by combining high [Ti] and low $a_{[\text{O}]}$. Although Ti-containing inclusions were found near the sample surface (samples 5B, C and D in Table 3), they have a low Ti content. The Ti to Al ratio of the inclusions ranged between 0.1 and 0.5 (Table 2). Raising the Ti alloying level to 1 500 ppm had no significant effect on [Ti] oxidation when low $a_{[\text{O}]}$ was maintained.

3.3.2. Reduction of Ti Containing Inclusions by a Strong Second Al Deoxidation

Figure 8 shows the changes in [Al] and [Ti] as a function of time after the second Al addition. The reduction of Ti oxides took place efficiently in the beginning of the second

Fig. 7. Relation between [Ti] and $a_{[\text{O}]}$ before and after Ti addition for Exp. 1 to 4. Solid black and solid grey markers correspond to, respectively, the observed melt composition before and after Ti addition. The solid line shows the $\text{Ti}_3\text{O}_5(\text{s})$ –[Ti]–[O] equilibrium relation at 1 620 °C. Open markers indicate the calculated melt compositions after Ti addition, considering the stoichiometry of the Ti oxidation reaction and assuming that equilibrium is reached.

Fig. 8. Changes in [Al] and [Ti] with time after second Al deoxidation.

Al addition, but the complete recovery of Ti from Ti–Al–O inclusions took time. The combination of higher Ti addition (1 500 ppm) and higher [Al] (Exp. 5) results in a higher [Ti].

The comparison of the results in Fig. 8 with respect to Exp. 2, 3 and 4 indicates that, with identical Ti alloying levels (525 ppm Ti) and similar [Al], distinct [Ti] were achieved after similar second Al additions. The time between Ti addition and second Al addition influences Ti recovery. As shown in Fig. 9, with longer time between Ti addition and second Al addition, lower [Ti] were achieved after the second Al deoxidation. The rise and removal of Ti–Al–O inclusions to the liquid steel surface hinder Ti recovery at longer times. Less Ti–Al–O inclusions were available in the bulk steel to react with [Al] when late second Al addition was performed. Hence, to improve Ti recovery, Al addition should be made shortly after Ti alloying.

Fig. 9. Relation between the amount of Ti recovered after the second Al addition and the time between Ti alloying and the second Al addition.

3.4. Thermodynamic Considerations

3.4.1. Inclusion Phase Stability

Ti forms many types of oxide and some of them have large solid solubility.¹¹⁾ When [Ti] and [Al] simultaneously exist in the liquid steel at a given $a_{[O]}$, equilibrium in the Fe(l)–Al₂O₃–TiO_x–AlTiO_x system can be expressed by the reactions,

selecting Ti₂O₃ and Ti₃O₅ as stable Ti oxides in the investigated range of [Ti], [Al] and $a_{[O]}$. The standard reaction Gibbs free energy changes ΔG° are expressed in cal·mol⁻¹.

Using the interaction coefficients of **Table 4** and the standard reaction Gibbs free energy changes of reactions (1) to (7), the equilibrium diagram of the Fe–Al–Ti–O system can be drawn at 1620°C (**Fig. 10**). It gives the type of oxides formed at equilibrium as a function of [Al], [Ti] and [O]. Thick lines mark the phase boundaries of the deoxidation products, whereas thin lines delimit the liquid Fe stable region at a given $a_{[O]}$. The compositions of the steel samples taken after Ti addition are superimposed on the diagram. The samples containing predominantly Al₂O₃ inclusions (solid square markers) are located in the Al₂O₃ stable region, while those containing Ti–Al–O complex inclusions (solid dot markers) are close to the calculated line or within the Ti oxide stable region. To prevent [Ti] oxidation during

Table 4. Interaction coefficients used in the present work.

<i>i</i>	<i>j</i>	<i>e_i^j</i>	Ref.
O	Al	-0.83	16)
	Ti	-0.6	17)
	O	-0.2	17)
Al	Al	0.045	17)
	Ti	0.004	18)
	O	-1.4	16)
Ti	Al	0.0037	18)
	Ti	0.013	17)
	O	-1.8	17)

Fig. 10. Equilibrium diagram for the system Fe–Al–Ti–O at 1620°C and various $a_{[O]}$ (10 to 200 ppm). Square markers indicate the metal composition of the samples in which Al₂O₃ inclusions were found, while round markers correspond to the metal composition of the samples containing Al–Ti–O inclusions.

alloying, it is essential to control [Al] to a sufficiently high value. This required [Al] is determined by the line delimiting the Al₂O₃ stable region. According to the calculations and considering that [Ti] is aimed at 525 ppm, approximately 200 ppm [Al] is required prior to Ti addition to prevent [Ti] oxidation. This calculated value is consistent with the experimental results depicted in Fig. 10. This is also in a good agreement with the compositional analyses of the inclusions shown in Fig. 6.

3.4.2. Reaction Mechanism during Al/Ti/Al Deoxidation

Figure 11 shows, for Exp. 3, the evolution of the liquid steel composition superimposed on the inclusion phase diagram. As indicated by the open circle (point A), the [Ti] and [Al] at the moment of Ti addition fell within the Ti₃O₅ stable region. This was intentionally controlled by partial Al deoxidation and Ti addition. Just after the addition, [Ti] reacted with oxygen in steel to form Ti oxides, resulting in a decrease of $a_{[O]}$ and [Ti] (from point A to point B). The steel was gradually reoxidized by the residual oxygen in the Ar flow, causing an increase in $a_{[O]}$ and a decrease of [Ti], while [Al] remained constant (from point B to point C). This is consistent with the fact that the steel composition evolved in the Ti₃O₅ stable region, where only Ti oxidation is predicted. The steel composition reached the Ti₃O₅/Al₂O₃·TiO₂ phase boundary at point C. By steel reoxidation, both [Ti] and [Al] decrease through reaction with oxygen, as entering the Al₂O₃·TiO₂ stable region where both Al and Ti oxidation is possible (from point C to point D).

Fig. 11. Evolution of [Ti] and [Al] during Exp. 3, plotted on the computed equilibrium diagram of the Fe–Al–Ti–O system at 1620°C. $a_{[O]}$ is given next to each point.

Meanwhile, $a_{[O]}$ increased. [Ti] and [Al] proceeded through the Al_2TiO_5 stable region and approached the $Al_2O_3 \cdot TiO_2 / Al_2O_3$ phase boundary (point D), where $Fe(l) \cdot Al_2O_3 \cdot TiO_2(s) \cdot Al_2O_3(s)$ equilibrium is established. Twenty minutes elapsed between Ti addition (point A) and point D. The second Al addition was then performed. Steel deoxidation and Ti recovery from Ti–Al–O inclusions simultaneously took place, resulting in a decrease of $a_{[O]}$ and a considerable increase of [Ti]. Hence, the steel composition moved to the point E, where Al_2O_3 is stable. The reduction reaction proceeded with time by consuming [Al] and increasing [Ti] up to point F. This reduction process was also observed during Exp. 2 and 4 (Fig. 8). In the case of strong second Al deoxidation (implying high [Al]), [Ti] and [Al] changed with time, attempting to maximize Ti recovery by consuming [Al] until the Ti_3O_5 / Al_2O_3 phase boundary is reached.

4. Conclusions

(1) Only Al_2O_3 inclusions were observed when strong Al deoxidation prior to Ti alloying was performed. On the other hand, with partially deoxidized steel prior to Ti addition ($a_{[O]} = 140\text{--}280$ ppm), Ti deoxidation took place. In that case, large Al_2O_3 clusters and small Ti–Al oxide particles randomly distributed in the steel were found. After the second Al addition, only Al_2O_3 clusters and few small Ti–Al–O inclusions remained due to the reduction of Ti oxides by [Al].

(2) The extent of [Ti] oxidation increased with $a_{[O]}$ prior to Ti alloying. No Ti deoxidation occurred with low

$a_{[O]}$ prior to Ti alloying. On the other hand, increasing the Ti addition to 1500 ppm had no significant effect on Ti deoxidation.

(3) The reduction of Ti oxides through the second Al addition was confirmed by inclusion observations and compositional analysis of the samples. Ti recovery from Ti–Al–O inclusions occurred rapidly after the second Al addition and was enhanced by performing the latter shortly after Ti alloying.

(4) The combination of experimental and calculated results shows that, in order to prevent Ti oxidation, it is essential to maintain [Al] to a sufficiently high value. Approximately 200 ppm [Al] is necessary prior to Ti addition to minimize Ti loss during the alloying process.

(5) The mechanisms of Ti–Al deoxidation reactions involving inclusion formation at various stages of the experiments were elucidated based on the calculated Fe–Al–Ti–O phase diagram.

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