Consideration on the Deoxidation Mechanism of Steel with Metallic Aluminium*

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Synopsis

Although it is important to know the deoxidation process with aluminium as a strong deoxidizer and studies on deoxidation products have been done by many people, the authors could not clarify the process yet. L.S. Sloman and E.L. Evans¹⁾ found some unknown substances formed through aluminium deoxidation. They identified them as silica from the chemical analysis of total isolated residues. C.E. Sims, A. Saller and F.W. Boulger²⁾ reported concerning the deoxidation products with aluminium, that they passed through an intermediate substance like AlO, but the process has remained unknown.

In this paper, the authors discussed how the variation of solidifying and cooling rates influenced the structures of deoxidation products and investigated the effect of after-heat treatments on the transformation of low-temperature type aluminas.

The results obtained are summarized as follows:

(1) Under rapid solidification, the authors could determine the formation of various low-temperature stable modifiers beside corundum. They are chiefly θ -type alumina and supposed to be δ - and κ -types.

(2) From their formation, they could suppose the formation of aluminium hydroxide immediately after the addition of the deoxidizing agent. They must appreciate the role of hydrogen dissolved in molten iron.

(3) For comparison, they used a platelet and a small lump of metallic aluminium. There was difference between their alumina modifications. Especially, in the case of small lump, there appeared γ -type alumina.

(4) Although there are two dehydration paths in alumina modification, they could estimate from this experiment that alumina formed in steels took both processes.

(5) It was difficult, in steel, for each low-temperature form to transform completely to corundum with heat treatment at 1 230°C for two hours, and this result disagreed with the theory that their transformation induced from the dehydration process of aluminium hydrates proceeded easily with heat treatment at 1 200°C for one hour. It seems appropriate to take into consideration the influence of the matrix on the transformation kinetics for these substances.

(6) It was recognized that hercynite ($\text{FeO} \cdot \text{Al}_2\text{O}_3$) was formed when the quenched aluminium-killed steels were heat treated above 1 200°C or slowly solidified from the molten state. This fact is important from the point that the sort of deoxidation products is not dependent on the rate of the weight per cent of aluminium added and the oxygen content dissolved in molten iron.

I. Introduction

Aluminium as strong deoxidizer plays the most important role in metallurgical field, and it is widely used in refining steels. It is customarily accepted that the most stable deoxidation product in steel is corundum, and it is understood from the standpoint of thermodynamics studies.

Experiments about this Fe-Al-O system have been done by many investigators concerning both the de-

oxidation products and their equilibrium studies. H.A. Sloman and E.L. Evans¹⁾, and G.R. Booker, J. Norbury and A.R. Westrope³⁾ pursued the variation of the formation products with increasing of aluminium addition.

H.A. Sloman and E.L. Evans¹⁾ noticed the formation of nonmetallic inclusions which were impossible to be identified, when electric current was cut in a moment after aluminium was added to molten iron. They estimated them to be probably silica from the total chemical analysis of the isolated residues.

In the field of ceramics, there have been determined the transition to corundum via low-temperature aluminas on the dehydration of aluminium hydroxides, but there are now doubtful points about crystal structures and authenticity of existences of some low-temperature types.

The authors tried to determine unknown matters found when rapidly solidified, and as they could certify them, they continued their transformation studies with simple-heat treatments.

II. Experimental Procedures

Practically, all heats were melted in a magnesia crucible of high-grade fitted for the high frequency furnace. All of runs were performed under the pressure of 4×10^{-4} mmHg. The molten bath temperature was measured with a Pt-Rh20%-Pt-Rh5% thermocouple. After pure iron was melted, metallic aluminium, as small lump or platelet, was inserted to the bottom of molten iron to prevent its float.

To measure solidifying and cooling rates the inserted thermocouple was connected to an X-Y recorder (made by Rika Denki, Ltd.).

Many specimens were investigated to study the variation of inclusion formed with altering the ratios of Al/O over wide range from 0.5 to 30, as previous investigators emphasized the importance of the ratio.

As representative case, No. 1 was solidified in the crucible after electric current was continued for four seconds since metallic aluminium was added, and No. 2 was continued for ten seconds. No. 3 was held for ten minutes, but No. 4 was quenched in the copper mould water-cooled. No. 5 was made in the atmosphere of nitrogen to investigate the formation of aluminium nitride for comparison. No. 6 was made to know the effect of small lump of metallic aluminium

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on the formation of aluminous inclusions. These specimens were made with the Al/O ratio of 25.

These solidifying velocities were changed, and cooling velocities were altered as previously described.

Metallographic observation on the distribution and size of the inclusion formed in steels were performed with the application of chemical etching mediums.

Extraction from each cast was performed with electrolytic means using a Koch-Sundermann type isolating vessel. As electrolyte, the authors used 5% sodium citrate and 1.2% potassium bromide aqueous solution. For comparison, they used the electrolytic method with 10% hydrochloric acid-ethanol solution or isolation with iodine-methanol solution. The extracted residues were fully washed and dried in vacuum and submitted to next various tests.

X-ray diffraction studies were made with copper or chromium radiation, and electron diffraction was done under high accelerating voltages as 200 kV.

An examination under the polarizing microscope was made and their refractive indices were measured.

Furthermore, they tried to pursue their transformation behaviours with simple heat treatments such as two hour holding above 1 200°C.

III. Experimental Results

Solidifying and cooling curves of the representative specimens from No. 1 to 4 are shown in Fig. 1.

Fig. 1. Solidifying and cooling curves of the representative specimens

1. X-Ray Diffraction Results

X-ray diffraction patterns of the residue isolated from typical specimens are given in Photo 1.

From these results, it will be recognized that low-temperature type aluminas are formed beside corundum (α - Al_2O_3) in the case of rapid solidification. They are reduced to δ - and θ -type aluminas. From the

Photo 1. X-ray diffraction patterns of the residue isolated from typical specimens. (Cu $K\alpha$ fore reflection) ($1/2$)

comparison between No. 1 and 2, the authors could not get any confidence except that the intensities of the diffraction patterns of low-temperature type aluminas become weaker, the more slowly solidified. It was not sufficiently convincing to determine the formation of AlN, which is considered to be a stable compound, in the case of No. 5. The difference between No. 1 and 6, i.e., the influence of the mass of metallic aluminium added is not remarkable, but δ -type alumina is supposed to form in the latter case.

In Table 1 (see p. 26), the measured interplanar spacings and relative intensities of the inclusions isolated from the specimens are shown, and are compared with the standards of various modifiers of alumina in Table 2 (see p. 27).

The formation of hercynite ($\text{FeO} \cdot \text{Al}_2\text{O}_3$) is clarified from the result by chromium radiation.

The appearance of magnetite is supposed in the case of lower ratio of Al/O.

2. Electron Diffraction Results

G.S. Booker, J. Norbury and A.R. Westrope³⁾, as for the shapes of iron containing aluminous inclusions, have developed the investigation in combination with electron diffraction study using the extraction replica technique.

The authors found that the inclusion isolated from their specimens resembled to stringer or dumbbells types, as termed by the above authors. These electron micrographs are shown in Photo 2.

Photo 2.
Electron micrograph of stringer or dumbbells type inclusion ($\times 24\,000$) ($1/2$)

The dendritic inclusions reported by L.v. Bogdandy, et al.¹⁾ was also observed in every specimen. In Photo 3 is the electron micrograph of this type and it was supposed to be κ -type low-temperature alumina from its selected area diffraction analysis.

Photo 3.
Electron micrograph of the dendritic inclusion ($\times 11\,000$) ($1/2$)

Although they found globular type inclusion, it was difficult to identify because it was thick.

Inclusions considered as α - Al_2O_3 was generally difficult to identify. Selected area diffraction patterns of θ -type alumina is shown in Photo 4.

Table 1. Identification of the X-ray diffraction values from the isolated aluminous inclusions (Cu $k\alpha$)

Specimen	No. 1					No. 2					
	I/I_0	d (Å)	α -Al ₂ O ₃	κ -Al ₂ O ₃	θ -Al ₂ O ₃	FeO·Al ₂ O ₃	I/I_0	d (Å)	α -Al ₂ O ₃	κ -Al ₂ O ₃	θ -Al ₂ O ₃
		1.374	(030)				70	1.374	(030)		
20		1.399		1.40	1.40		70	1.388			1.40
		1.405	(124)				70	1.405	(124)	1.40	1.41
50		1.443		1.44		1.43	20	1.443		1.44	
		1.514	(122)				10	1.460		1.46	1.46
5		1.542	(211)	1.55	1.55		20	1.514	(122)	1.50	1.50
		1.547					20	1.547	(211)		1.55
30		1.572				1.56	20	1.572			
		1.605	(116)				100	1.602	(116)		
5		1.672		1.65			10	1.651		1.65	1.63
		1.745	(024)				70	1.745	(024)		
5		1.833		1.84			10	1.799			1.81
		1.968	(202)				10	1.833		1.84	
20		1.992		2.00			10	1.915			1.92
5		2.048			2.03	2.02	20	1.968	(202)	1.96	
		2.096	(113)				40	1.992		2.00	
5		2.150		2.13			50	2.033			2.03
30		2.253			2.26		90	2.096	(113)		
		2.322	(006)				10	2.163		2.13	
70		2.388	(110)				10	2.222			
70		2.466			2.45		10	2.253			2.26
		2.555	(104)				10	2.272			
20		2.726			2.74		50	2.322	(006)	2.34	2.33
20		2.808		2.81			60	2.388	(110)		
50		2.899			2.87	2.87	10	2.455		2.43	2.45
20		3.080		3.06			80	2.555	(104)		
							10	2.726		2.72	2.74
							10	2.807		2.81	
							10	2.899			2.87
							10	3.079		3.06	

Photo 4. Electron micrograph and the selected area electron diffraction (200 kV) patterns. (After heat-treated) (θ -type Al₂O₃) ($\times 12\,700$) ($1/2$)

3. Metallographic Observation Results

Segregated corundum appears when electric current is continued to apply for from eight to ten minutes after metallic aluminium was added. On the other hand,

this tendency was not observed from the specimens rapidly solidified. Likely, the authors could detect corundum inclusions under the reflected polarized ray because they exhibited sufficient crystal growth when slowly solidified. Segregated corundum is shown in Photo 5.

Hercynite is not detectable as elongated particles as described by G.R. Booker, et al.³⁾ and the identification is not possible from the behaviour under the polarized ray if they are hercynite or low-temperature type alumina. This aspect is shown in Photo. 6 (a) and (b).

When the ratio of Al/O was lower, wustite was observed as shown in Photo 7.

Formation of magnetite seems apposite as described by G.R. Booker, et al.³⁾ but it is necessary to pursue for the confidence of its appearance.

Table 2. X-ray diffraction data for oxides of aluminium⁽¹¹⁾⁻⁽¹⁴⁾

α -Alumina			γ -Alumina			δ -Alumina		η -Alumina			θ -Alumina		ι -Alumina		κ -Alumina		χ -Alumina	
(hkl)	d (Å)	I/I_0	(hkl)	d (Å)	I/I_0	d (Å)	I/I_0	(hkl)	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0
012	3.493	77	111	4.56	40	5.05	20	111	4.6	20	5.25	20	5.45	100	6.2	20	4.8	100
104	2.553	82	220	2.80	20	4.58	20	220	2.8	5	4.55	60	3.47	100	4.52	10	2.4	50
110	2.380	41	311	2.39	80	4.10	10	311	2.4	60	3.56	10	2.92	20	4.2	5	2.29	10
006	2.317	3	222	2.28	50	3.55	?	222	2.29	10	2.87	80	2.72	80	3.06	40	2.13	200
113	2.090	100	400	1.977	100	3.05	?	400	1.99	80	2.74	80	2.59	80	2.81	60	2.00	100
202	1.964	1	511	1.520	30	2.89	40	333	1.53	5	2.58	20	2.46	5	2.72	10	1.54	5
024	1.742	48	440	1.395	100	2.75	80	440	1.41	100	2.45	80	2.34	80	2.59	80	1.40	100
116	1.602	80	444	1.140	20	2.60	20	533	1.21	?	2.33	60	2.24	80	2.43	20		
211	1.548	3	731	1.027	10	2.45	60	444	1.15	5	2.26	60	2.15	40	2.34	40		
122	1.514	9	800	0.989	10	2.30	40	553	1.04	?	2.17	?	1.99	5	2.28	5		
124	1.405	37	840	0.884	10	2.18	?	800	0.995	?	2.13	5	1.88	20	2.18	5		
300	1.375	58	844	0.806	20	2.01	80				2.03	80	1.73	40	2.13	80		
125	1.337	1				1.96	20				1.92	40	1.61	20	2.07	20		
2 0 8	1.276	3				1.92	10				1.81	20	1.55	60	2.00	40		
10 10	1.240	13				1.86	?				1.75	5	1.492	10	1.96	10		
1 1 9	1.235	9				1.81	10				1.63	10	1.461	10	1.88	60		
220	1.191	8				1.63	?				1.55	60	1.41	5	1.84	20		
						1.55	40				1.50	40	1.346	10	1.76	10		
						1.52	20				1.46	40	1.288	60	1.65	60		
						1.50	10				1.44	5			1.55	5		
						1.46	20				1.41	60			1.50	20		
						1.41	40				1.40	100			1.46	20		
						1.40	100				1.35	5			1.44	30		
						1.30	30								1.40	100		
															1.35	20		

Photo 5.
Segregated corundum
($\times 1\,380$) ($1/2$)

Photo 7.
Optical micrograph of
wustite. (1% nital-etched)
($\times 1\,380$) ($1/2$)

Photo 6(a) and (b). Optical micrographs of the aluminous inclusions (under crossed nicols) ($\times 1\,380$) ($1/2$)

4. Observation under Polarized Microscopy and the Measure-

ment of Refractive Index

In Photo 8, the residues isolated from the specimens are indicated, and it is seen that the formation of dendritic inclusions occurs in every case.

The characteristic values of physical properties of the various modifiers of alumina are illustrated in Table 3. Compared with it, the authors can understand the usefulness of the measurement of their refractive indices.

The presence of low-temperature aluminas was confirmed. But it was difficult to measure the small globular inclusion considered as corundum, because they exhibited highly illuminated aspect.

a: No. 1, b: No. 3, c: No. 5, d: No. 6

Photo 8. Optical micrographs of the isolated inclusions ($\times 920$) ($1/2$)

5. Results of After-Heat Treatment

The authors gave heat treatments at 800° or 1 200°C from five minutes to two hours to the specimens having low-temperature aluminas. For example, the transition diagram of α -trihydrate by heating is shown in Fig. 2. From this, they can understand that alumina polymorphs transform easily into corundum on heating at 1 200°C for one hour.

But, the transition of low-temperature aluminas to corundum is not perfect with the treatments described above. Only the reflected intensities of low-temperature aluminas became weaker, and those of κ -type alumina diminished and those of θ -type alumina became stronger with those of δ -type alumina diminished. The transition seems to occur gradually with these treatments.

IV. Discussion

It was clarified that various low-temperature alumi-

Fig. 2. Transformation by heating α -type trihydrate¹³⁾

nas beside corundum were formed as deoxidation products in rapidly solidified steel. From the results obtained that δ -, κ - and θ -type aluminas were formed in a moment after metallic aluminium was added and when rapidly solidified, the authors could estimate that the both dehydration paths, viz. the transformations into corundum via κ - and χ -type from gibbsite or via γ -, δ - and θ -type from bayarite, occur in the deoxidation process with aluminium in steel. Transition sequences of alumina from the different aluminium-hydrates are given in Fig. 3.

It seems appropriate to make consideration on the formation of hercynite and wustite beside corundum and other aluminas in the deoxidizing experiment with Al/O ratio of 25.

Fig. 3. Transition sequences of alumina from the different hydrates¹²⁾

Although things have been progressively distinctive at the present time, there exist many questionable points about the structures and the formation processes of low-temperature aluminas. M. Plummer⁵⁾ found rather δ - or θ -type aluminas than corundum when he tried to make corundum by passing γ -type alumina

Table 3. Crystallographic properties of various alumina modifications^{15),16)}

Compn.	α	θ	κ	δ	γ	η	χ	ρ
	Al ₂ O ₃	(Nearly as Al ₂ O ₃ having a little H ₂ O)						
Cryst. struct.	Hexagonal	Monoclinic	Hexagonal	Tetragonal	Tetragonal	Cubic	Hexagonal	?
Space group	D _{3d} ⁶	C _{2h} ³				O _h ⁷		
Lattice spacing (Å)	a	4.76	11.8	9.71	7.94	8.01	7.92	5.56
	b	12.99	2.92					
	c		5.64	17.86	23.5	7.73		13.44
	$\alpha = 55^\circ 17'$	$\beta = 104^\circ$						
Sp. gravity	3.98	3.4—3.9	3.1—3.3	≤ 3.2	≤ 3.2	2.5—3.6	≤ 3.0	
Refractive index	$n \approx 1.760$ $\omega \approx 1.768$	1.66—1.67	1.67—1.69			1.59—1.65	1.63—1.65	

through an oxy-hydrogen flame in 1958. For the reason of this, he gave the following suppositions, that is, he expected some thermal transformation into δ - or θ -type alumina either in the unmelted core or in particles after solidified, or applied the idea introduced by G. Ervin Jr.⁶⁾ based on the configuration of aluminium and oxygen in the crystal lattice during transformation.

In this study, the authors could not appreciate any evidence of the difference in temperature, as indicated by him, in the metallic addition, from the fact that the diffraction patterns of low-temperature aluminas beside corundum were observed when a thin sheet was employed as well as when a small lump of aluminium was used.

G. Ervin Jr.⁶⁾ thought that the structure of the low-temperature aluminas was composed of the same oxygen network as high-temperature aluminas but with a lower degree of order in the aluminium atom arrangement. But, it must be indispensable to solve this problem. Before discussing this, it will be instructive to consider first the difference of the configuration of oxygen between corundum and γ -type alumina. Corundum is characterized by oxygen atoms in hexagonal close-packing in contrast of cubic close-packing of γ -type alumina.

G. Ervin Jr.⁶⁾ considered that in the dehydration process of aluminium hydroxide, the oxygen network forms readily but aluminium ions have to reach their stable positions by diffusion through the oxygen network.

The authors should be reflected from the standpoint based upon the present knowledge⁷⁾ which clarified the structure of θ -type alumina that the low-temperature forms may be regarded as disordered modifications of γ -type alumina.

In the field of ceramics, it has been reported that the formation temperature of corundum is above 1200°C. From the experimental evidence that the low-temperature aluminas were detected in the aluminium-killed steel held at 1600°C for a moment after killing, there should be a considerable effect of the molten iron surrounding the inclusions formed on the transformation. Likewise, the effect of impure elements must be also taken into account.

Hence, they are unable to deny the possibility of the formation of low-temperature alumina even when they could not find the evidence of their existence. This consideration is supported from the result that the low-temperature aluminas remained after the simple heat treatment for longer time in spite of the easiness of alumina transformation.

For these facts, it should be interpreted from other reasons.

Although there exists a question whether low-temperature aluminas precipitate from the matrix on the solidifying period, it was disapproved from the fact that the appearance of such low-temperature aluminas are limited only when the specimen was rapidly solidified.

Some unknown substances, which are formed in an

aluminium-killed steel, informed by H.A. Sloman and E.L. Evans¹⁾ will be supposed as low-temperature alumina identified by the authors.

About the deoxidation behaviours of metallic aluminium in steel, it is necessary to consider the influence of hydrogen dissolved in molten iron.

Many investigators⁸⁾ have pursued the effect of hydrogen from the standpoint of hydrogen embrittlement, although it was difficult to measure its solubility and to know the existing state in steel.

Iwase and Fukushima⁹⁾ stated that when iron contained carbon or oxygen or sulphur or silicon or titanium or vanadium they would become hydride by combining with hydrogen, and Shimokawa¹⁰⁾ said that the reason for higher hydrogen contents than the calculated value from the equilibrium studies was probably the slow diffusion velocity of hydrogen in steel and the existence of molecular hydrogen, and it was important to suppose the existence of hydride formed through the combination with impurities.

Usually, alumina is used as an active dehydration agent for the use of gas-washer, and the adsorbing behaviour of water is significant. The authors should like to consider that hydrogen dissolved in molten steel plays an important role in the case of aluminium deoxidation from the facts that all sorts of aluminas contain some water, and its removal is difficult by means of heating at high temperatures and it is noticed from the study of N.M.R.

Although it was not possible to detect the formation of intermittent products as AlO reported by C.E. Sims, et al.²⁾, it is necessary to promote the studies of the deoxidation processes of various deoxidizers from reaction kinetics.

And it was not approved that the ratio of Al/O could be accepted as an indication for the determination of inclusions formed in steel. This fact agrees with the observation by L.v. Bogdandy, et al.⁴⁾ that there was a tendency that various inclusions such as alumina and wustite took various positions in steel, and there is a possibility to get an erroneous information depending on the choice of extracting and analytical means.

V. Conclusions

The authors studied deoxidation products in steels deoxidized with aluminium and investigated the effect of solidifying and cooling rates on the formation behaviours with various after-heat treatments.

The results summarized are as follows:

(1) Under rapid solidification, they could detect the formation of various low-temperature stable modifiers beside corundum. They were chiefly θ -type alumina, and supposed to be σ - and κ -types.

(2) From their formation, they could suppose the formation of aluminium hydroxide in a moment after addition of deoxidizing agent. They must appreciate the role of hydrogen in molten steel.

(3) For comparison, they used a platelet or a small lump of metallic aluminium. There was a difference between their alumina modifications. Especially, in

the case of small lump, there appeared γ -type alumina.

(4) Although there were two dehydration processes in alumina modification, they could estimate from this experiment that alumina formed in steels took the both paths.

(5) It was difficult for such low-temperature forms to transform perfectly to corundum in steel with heat treatment at 1 230°C for two hours, and this result disagreed with the theory that the transformation of the aluminas formed from the dehydration processes of aluminium hydrates proceeds easily with heat treatment at 1 200°C for one hour. It seems appropriate to take into consideration the influence of the matrix on the transformation kinetics of these substances.

(6) From the fact that the intensity of X-ray diffraction pattern of hercynite increased when the quenched specimens were heat-treated, the substance was considered to be a substantial secondary precipitate.

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