Mechanism of Formation of Non-metallic Inclusions in Aluminium-killed Steels*

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Synopsis

An investigation was undertaken on the deoxidation of molten iron containing varying amounts of manganese by aluminium. Electron microprobe studies confirmed that, in such melts, duplex inclusions such as hercynite ($\text{FeO} \cdot \text{Al}_2\text{O}_3$) or galaxite ($\text{MnO} \cdot \text{Al}_2\text{O}_3$) both enveloped with alumina are formed only when the dissolved oxygen content is well above that normally found in low carbon steels prior to tapping. Since these complex oxides are metastable in presence of aluminium, their reduction to alumina occurs with sufficient holding time. This leads to the conclusion that a possible mechanism for the formation of spinel-type inclusions in steel is associated with reoxidation of steel leading to highly localized regions of oxygen.

I. Introduction

Aluminium is added to steel primarily to control the oxygen level and to obtain grain refinement in steel. Among the common deoxidizers, aluminium has the two-fold advantage in that it is a potential deoxidizer and that, alumina, which is the common deoxidation product with the use of aluminium, can float out of steel much faster compared with other deoxidation products thereby making a clean steel.¹⁻³ However, in addition to the problems encountered in the teeming of aluminium-killed steels,⁴⁻⁷ surface defects in the finished product have also been reported in such steels.

This work was initiated with a view to find a solution for surface defects which were often found in aluminium-killed sheet steels produced by Lackawanna Plant of Bethlehem Steel Corporation (Lackawanna, N.Y., U.S.A.). These steels were rolled into slabs and X-ray study of the non-metallics in several samples taken from these slabs, the non-metallics being isolated by the bromine-methanol extraction procedure by Flinchbaugh and Smerko⁸) and their electron-microprobe study,⁹) revealed the presence of galaxite in majority and hercynite in minority. Further, Luyckx¹⁰) has reported the occurrence of black pencil lines of 2 to 100 inches in length and 0.004 to 0.1 inch in width continuous and homogeneous in aluminium-killed sheet grades and these are due to large inclusions rich in manganese surrounded by a thin film of galaxite. It is considered that incomplete mixing of manganese is the cause of these black lines.

II. Survey of Former Work

The present work is a follow-up of that of Straube *et al.*¹¹) who showed that deoxidation of steel containing manganese and high oxygen ($>0.1\%$) with alumin-

ium results in the formation of 'nest' type inclusions enveloped by alumina, and that reactions during primary ladle deoxidation and secondary precipitation during solidification may result in the formation of spinels when the initial oxygen dissolved in the steel is above a critical level. Their work did not explore the genesis, kinetics of growth, possible reduction of spinels by aluminium or the critical oxygen levels necessary for spinel formation. The present work was directed to examine some of these factors and also postulate a mechanism whereby spinel inclusions are formed in aluminium-killed steels based on the evidences obtained from this work.

III. Experimental

1. Experimental Apparatus

Experimental runs were conducted with 100 lb melts in a magnesia crucible ($8\frac{3}{4}$ " O.D., $7\frac{1}{4}$ " I.D., & $12\frac{3}{4}$ " Ht) placed in a high frequency vacuum induction furnace under argon atmosphere. To facilitate melting of the charge, the crucible was surrounded by a graphite susceptor. This work differs from similar work on deoxidation with silicon and with aluminium in which no inert atmosphere was used.^{12,13}) In this way, in the present investigation it was possible to eliminate the influence of an additional variable, namely, the effect of atmospheric oxidation.

2. Experimental Procedure

The experimental procedure consisted of charging the crucible with 99 lb of electrolytic iron containing 0.015% oxygen along with 0.5 to 1 lb of oxidized electrolytic iron to provide the initial oxygen contents. The electrolytic iron was roasted in a muffle furnace for a few hours and the iron oxide content of the scale was analysed so as to calculate the exact weight of the scale to be mixed with electrolytic iron to have the desired initial oxygen content in the melt. The scale and iron components of the charge were placed in alternate layers to minimise the loss of oxygen due to absorption of iron oxide by the crucible. After melting the charge and attaining a bath temperature of $2910 \pm 10^\circ\text{F}$ as measured by an immersion thermocouple, two samples were taken by means of bucket samplers ($3\frac{3}{4}$ " I.D.). One of the samples was deoxidized with aluminium wire and used for oxygen analysis; the other sample, having no aluminium added, was reserved for metallographic examination.

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Following the initial sampling, electrolytic manganese was added by plunging a container of electrolytic manganese to the bottom of the melt with a rod inserted through a sampling valve. After dissolution of the manganese and stabilization of the bath temperature at $2910^{\circ}\pm 10^{\circ}\text{F}$, two additional samples were taken and these were treated similarly. The bath was then deoxidized by plunging aluminium (0.1 to 0.2 lb) in the form of a cone attached to a steel rod. Simultaneously, a stop watch was started and sample 1 was taken at zero time. Additional samples 2 to 8 were taken at intervals of 7 sec. Samples 9, 10 and 11 were taken at 5 min, 15 min and half hour intervals, respectively.

All samples were air-cooled. Although some preliminary samples were quenched in water, heat transfer calculations indicated that the time for $\frac{3}{4}$ " samples to solidify in air was only 5 to 6 sec. Water quenching was, therefore, felt unnecessary and discarded. Following sampling of the melt, the temperature was recorded and the power shut off allowing the melt to solidify in the crucible.

A few experimental melts were made to study the effect of manganese on the genesis of non-metallics in iron deoxidized with aluminium. Fifteen samples were obtained during each run as explained above. Oxygen analyses by vacuum fusion and spectrographic analyses for aluminium and manganese were conducted on all samples in duplicate. The majority of samples were examined metallographically with selected samples studied by electron microprobe. Several samples were submitted for particle size distribution analysis by Coulter counter following inclusion extraction.

3. Experimental Difficulties

The major experimental difficulty was the variable oxygen recovery from the scale due to possible decomposition of the scale under argon atmosphere, heterogeneity and crucible absorption of the scale. In later runs, the time from the power on to the melt down was maintained constant and this provided some improvement in the control of the initial oxygen.

IV. Results and Discussion

The experimental results obtained are divided into two groups:

- 1) Aluminium deoxidation in the absence of manganese
- 2) Aluminium deoxidation in the presence of manganese

1. Aluminium Deoxidation in the Absence of Manganese

The experimental results are shown in Table 1 which demonstrate the influence of the initial oxygen dissolved in the melt prior to the addition of aluminium on inclusion formation. Table 1 also gives the aluminium content of the samples. No evidence of the formation of hercynite was observed in the first three runs. However, with an initial oxygen content of 0.155%, hercynite was found in the sample taken 10 sec after aluminium addition. This is shown in Photo. 1, inclusion 1, where the X-ray line scan of aluminium has two peaks on either side of the scan which correspond to low scan of iron. The point counts of aluminium and iron of inclusion 1 show that the inclusion has the hercynite composition at the centre surrounded by an envelope of alumina. There are two inclusions in region 2, Photo. 1, one of which is alumina and the other hercynite surrounded by alumina as evidenced by point counts of iron and aluminium. As seen in Photo. 2, the metastable hercynite was fully reduced to alumina in sample 10 taken 16 min after aluminium addition. However, a trace of FeO remains along with alumina in sample 9 taken 5 min after aluminium addition.

2. Aluminium Deoxidation in the Presence of Manganese

Referring to Table 2 it can be seen that, with manganese present and initial oxygen content of 0.021%, no spinel inclusions were detected. When the initial oxygen levels exceed the manganese-oxygen equilibrium, primary Mn(Fe)O inclusions were found in samples taken prior to aluminium deoxidation. Following the aluminium addition, a reaction occurred which resulted in Mn(Fe)O inclusions fusing with alumina to form galaxite which is subsequently enveloped with alumina. Initiation of this reaction was indeed rapid with spinel observed in samples taken immediately or a few seconds after aluminium addition. This reaction proceeded with time and after seven and half minutes the stable alumina phase remained.

The progress of the reaction starting with Mn(Fe)O

Table 1. Effect of initial oxygen levels on inclusion formation in aluminium-deoxidized iron melts containing no manganese

Run No.	Initial oxygen (%)	%Al at the time of sampling	Time after Al addition (sec)	Primary inclusions before Al addition	Inclusions identified in the sample by electron microprobe
704X025	0.048	0.14	13	none	Al_2O_3
704X035	0.083	N.D.	14	none	Al_2O_3
704X037	0.062	0.31	9	none	Al_2O_3
704Y001	0.155	0.58	10	none	$\text{FeO}\cdot\text{Al}_2\text{O}_3$ enveloped by Al_2O_3 ; Al_2O_3
		0.60	300		Al_2O_3 ; trace of FeO
		0.80	960		Al_2O_3

N.D.=Not Determined

Photo. 1. Photomicrograph and microprobe analysis of sample #2, Heat 704Y001, with 0%Mn

and terminating with Al_2O_3 , is illustrated in Photo. 3, samples being taken at different time intervals after aluminium addition. As shown in Photo. 4, sample D taken immediately after manganese addition contains Mn(Fe)O inclusions. Sample 1 taken immediately after aluminium addition contains both Mn(Fe)O inclusions (Region B, Photo. 5 in p. 596) as

Photo. 2. Photomicrograph and microprobe analysis of samples #9 and #10, Heat 704Y001, with 0%Mn

well as $\text{Mn(Fe)O} \cdot \text{Al}_2\text{O}_3$ (Region A, Photo 5). Sample 2 taken 13 sec after aluminium addition shows the presence of $\text{Mn(Fe)O} \cdot \text{Al}_2\text{O}_3$ and also Al_2O_3 (Photo. 4). Sample 9 taken 310 sec after aluminium addition shows the presence of galaxite enveloped by alumina and sample 10 taken 30 min after aluminium addition shows the presence of alumina only and no galaxite as seen from Photo. 6 (see p. 597). Photograph 3 also reveals the duplex inclusion, namely, galaxite (lighter shade) enveloped by a layer of alumina (darker shade).

An interesting feature observed during the course of the present investigation is the occurrence of an alumina inclusion adjacent to a hercynite or galaxite

Table 2. Effect of initial oxygen levels on inclusion formation in aluminium deoxidised iron melts containing manganese

Run No.	Initial oxygen (%)	After manganese addition			Time after Al addition (sec)	Primary inclusions before Al addition	Inclusions identified in the sample by electron microprobe
		%Mn	%Al	%O			
704X036	0.021	0.25	0.13	0.016	11	none	Al ₂ O ₃
704X038	0.091	0.36	0.07	0.093	0	Mn(Fe)O	Mn(Fe)O
		0.34	0.28	0.056	8		Mn(Fe)O·Al ₂ O ₃
		0.28	0.35	0.027	51		Mn(Fe)O·Al ₂ O ₃ with Al ₂ O ₃ envelope
		0.28	0.05	0.020	300		Mn(Fe)O·Al ₂ O ₃ with Al ₂ O ₃ envelope; Al ₂ O ₃
704X024	0.093	0.53	0.01	0.083	0	Mn(Fe)O	Mn(Fe)O; Mn(Fe)O·Al ₂ O ₃
		0.43	0.14	0.033	13		Mn(Fe)O·Al ₂ O ₃ ; Al ₂ O ₃
		0.44	0.56	0.135	310		Mn(Fe)O·Al ₂ O ₃ with Al ₂ O ₃ envelope; Al ₂ O ₃
		0.42	0.07	0.039	1800		Al ₂ O ₃
704X011	0.180	0.29	0.47	0.061	0	Mn(Fe)O	Mn(Fe)O·Al ₂ O ₃ with Al ₂ O ₃ envelope; Al ₂ O ₃
		0.28	0.28	0.074	28		Mn(Fe)O·Al ₂ O ₃ with Al ₂ O ₃ envelope; Al ₂ O ₃
		0.33	0.89	0.033	270		Mn(Fe)O·Al ₂ O ₃ with Al ₂ O ₃ envelope; Al ₂ O ₃
		0.32	0.38	0.081	433		Al ₂ O ₃ ; trace of Mn(Fe)O·Al ₂ O ₃

Sampling times after aluminium addition are given in parentheses.
Photo. 3. Photomicrographs of samples from Heat 704X024, with 0.4%Mn

inclusion enveloped by alumina as can be seen from Tables 1 and 2. Also region 2, Photo. 1 and sample 2, Photo. 4 reveal similar features. This may be the result of polishing the sample when some inclusions get cut along the outer rim of alumina while others along the centre.

It was shown by McLean¹²⁾ that galaxite spinels are thermodynamically stable only at very low aluminium activities (less than 10⁻³). Since aluminium normally present in aluminium-deoxidized steels far exceeds the minimum necessary to provide alumina as the stable phase, the presence of spinel inclusions would not be expected in such steels. The present work confirms that alumina is the stable deoxidation product with the use of aluminium. In the case of runs conducted without manganese, hercynite was

Photo. 4. Microprobe analysis of samples #D and #2, with 0.4%Mn, Heat 704X024

rapidly reduced to alumina in about 5 min. The retention of galaxite inclusions in the runs conducted with manganese was possible only when primary Mn(Fe)O inclusions were present prior to aluminium deoxidation. This required an initial oxygen content of about 0.091%. Reduction of Mn(Fe)O through galaxite phase to alumina was completed in about $7\frac{1}{2}$ min.

Some information on the size of inclusions was obtained by particle size distribution work using the Coulter counter and correlating this information with the phases present in the inclusions as revealed by electron microprobe. From Fig. 1 (see p. 598), it can be seen that the average particle size of inclusions in heat 704X024 shows a tendency to increase slightly from 7μ in sample 2 to 10μ in sample 8. This may be attributed to the development of the alumina envelope in sample 8 over the galaxite inclusion present in

sample 2. The average sizes of inclusions in samples 9 and 10 were beyond the sensitivity range of the instrument to be measured. Also, there is considerable increase in the number of particles of size less than 10μ in sample 9 as compared with sample 8. Further, there is considerable decrease in the number of particles of the same size in sample 10 as compared with sample 9. This is taken to interpret that there is breakdown of larger particles in sample 8 to smaller ones in sample 9 in about 5 min and that there is also some float out of particles in sample 10 as compared with sample 9. The complete reduction of

The Aluminium content of inclusion A is very low; the aluminium X-ray Line Scan show a high peak because of the use of sensitive count rate.

Photo. 5. Microprobe analysis of sample #1, Heat 704X024, with 0.4% Mn

spinel by aluminium could be explained on the basis that the inclusions break down exposing the inner unreduced spinel to the action of aluminium as can be discerned from samples 8 and 9 (Fig. 1).

It is opportune to review briefly the findings of others and also the evidences obtained from this work on the reduction of spinel inclusions by aluminium dissolved in the iron melt. Straube *et al.*¹¹⁾ explain the formation of small round alumina particles as being due to the possible reduction of spinels by aluminium. However, no proof by way of electron microprobe studies is given. Also, Luyckx *et al.*¹⁵⁾ explain the formation of spinels in molten steel as metastable phases which continue to exist in steel in view of the shortage of time available for the reduction of spinels with aluminium to reach completion. Straube *et al.* have found that during the early stage of this reduction reaction, galaxite crystals become coated with

a solid alumina layer which hinders further reaction between the dissolved aluminium and the spinel. On the contrary, the results of the present work indicate that the spinels would be completely reduced to alumina provided the steel is held for sufficient time in the ladle after aluminium deoxidation before it is teemed. Evidences have been obtained from this work for spinel reduction by aluminium from electron microprobe studies. For example, in heat 704Y001, inclusions in sample taken 10 sec after aluminium addition showed hercynite enveloped by alumina, sample taken 300 sec after aluminium addition showed that the inclusions are nearly all alumina with a trace of FeO, while the sample taken 960 sec after aluminium addition showed that the inclusions are all alumina. Again in heat 704X011, the sample taken 433 sec after aluminium addition showed alumina with a trace of galaxite spinel. These would prove that there is progressive reduction of spinels by aluminium. It is well known that, for rapid separation of inclusions, they must have high interfacial tension with liquid steel.¹⁶⁾ Since the interfacial tension between molten iron and a solid oxide is always decreased when the solid phase contains iron oxide¹⁴⁾ or MnO,¹⁶⁾ this would mean that aluminates float out slower as

Photo. 6.
Microprobe analysis of samples
#9 and #10, Heat 704X024,
with 0.4%Mn

compared with pure alumina. It is also established that spinel inclusions are metastable in the presence of excess aluminium dissolved in steel. Therefore the contention that spinel inclusions were enveloped by alumina floating out of steel without reduction appears to be less probable.

V. Mechanism of Spinel Formation

It is possible to suggest a mechanism whereby spinel inclusions may be found in aluminium-killed steels. During tapping, reoxidation of the liquid steel from exposure to air and inadequate mixing of the deoxidizer causes the formation of highly localized regions of oxygen and the formation of Mn(Fe)O which would eventually lead to the formation of spinels. For example, Farrell *et al.*¹⁷⁾ have emphasized the elimi-

nation of reoxidation of molten steel as a major step in improving steel cleanliness. According to Chipman,¹⁸⁾ incomplete mixing of the deoxidizer causes concentration gradients in liquid steel and a considerable period of time must elapse before mixing can take place through the process of shear and elimination of concentration gradients by diffusion. In a critical review, Bell¹⁹⁾ thinks that the discrepancies between the aluminium deoxidation constants obtained by various workers may be due to a tendency for hercynite rather than alumina to be formed, even under conditions where alumina would be the more stable phase. This is supported by the statement of Forward and Elliott²⁰⁾ that a phase other than the equilibrium phase may in fact form with supersaturation. Iyengar²¹⁾ has discussed extensively its thermo-

Fig. 1. Oxide inclusion size distribution of samples from Heat 704X024 with 0.4% Mn

dynamic significance. With sufficient time allowed in the ladle, the spinels are reduced to alumina particles by the excess aluminium present in steel and the alumina particles have the opportunity to float out of steel. For example, Luyckx¹⁰⁾ has found that the black pencil line frequency in aluminium-killed sheet steels is reduced more than half with a ladle holding time of 8 min. Further, reoxidation while teeming and segregation during solidification may initiate the formation of spinels which have less opportunity to get reduced to alumina or to float out of liquid steel with increasing viscosity of steel on cooling down and therefore are retained in the solidified ingot. Moreover, the conditions for spinel formation become more favourable as the temperature decreases since aluminates can form at lower and lower oxygen levels. In addition, there is the effect that the ratio of oxygen to deoxidizer is continuously increasing during the solidification process.¹⁴⁾ Based on this analysis the ladle holding time before teeming and the extent of exposure of liquid steel to air during tapping and teeming would influence the presence of spinels in the

solidified steels.

The proposed reaction mechanisms and illustrations are shown in Fig. 2. It is assumed that no 'sub-oxides' or 'clusters' exist between aluminium and oxygen atoms, although the Sub-oxide concept^{22,23)} and the Cluster theory²⁴⁾ have been postulated. First the Mn(Fe)O nucleus forms with sufficient oxygen present in a steel containing manganese. This is very rapidly converted into galaxite by collision with aluminium atoms. Photograph 5, region A, shows a spherical galaxite inclusion which acts as nucleus for the formation of galaxite enveloped by alumina by collision of aluminium and oxygen atoms. Alternately, it can be envisaged that the galaxite inclusion is getting reduced by the dissolved aluminium in the melt resulting in the formation of galaxite enveloped by alumina. Straube *et al.*¹¹⁾ have pointed out that the interface reaction between the spinel and aluminium dissolved in steel may be hindered by the formation of a solid alumina layer on the spinel inclusion. In order to explain the complete reducibility of spinel by aluminium, it is proposed that the alumina coating over the spinel is not pervious but discontinuous. Wherever there is discontinuity, the spinel gets exposed and then reduced by aluminium dissolved in steel. Coulter counter data (Fig. 1) appear to support this view.

According to the work of McLean,¹⁴⁾ in a melt containing no manganese at 1 600°C, $\underline{O}$ in Eq. (1) reacts directly with $\underline{Al}$ in Eq. (2) to form pure alumina if the $\underline{O}$ is less than 0.058%. At the same temperature, in a melt containing 0.3% Mn, the two elements react to form alumina if the $\underline{O}$ is less than 0.021%. In excess of these oxygen levels (critical point oxygen), spinels would be formed. According to the same work, in the plot of $[a_O]$ vs. $[a_{Al}]$, for a melt containing no manganese, $[a_{Al}] = 9 \times 10^{-6}$ and $[a_O] = 5.8 \times 10^{-2}$ at 1 600°C. That is $[a_{Al}] \times [a_O] = 5.22 \times 10^{-7}$. If the product of the activities of aluminium and oxygen exceeds this value, hercynite would precipitate out. Again, $[a_{Al}] = 5.2 \times 10^{-5}$ and $[a_O] = 2.1 \times 10^{-2}$ for a melt containing 0.3% Mn at 1 600°C. That is $[a_{Al}] \times [a_O] = 10.92 \times 10^{-7}$. If the product of the activities of aluminium and oxygen exceeds this value, precipitation of galaxite would occur.

The practical aspects of this work are two fold. Firstly, it has been seen that holding time has profound effect on the elimination of spinel inclusions if formed in aluminium-killed steels. Secondly, the formation and retention of spinels in molten steel could be decreased if agitation is maintained in the ladle after the tapping operation, for example, by argon purging through porous plugs at the ladle bottom. Besides eliminating the temperature gradients in steel, argon purging enhances the floatation of non-metallics with the result oxygen removal is excellent. Further there is also some removal of hydrogen and nitrogen dissolved in steel. The influence of argon purging on steel cleanness has been discussed by various authors.^{25,26)}

Reactions

Illustration

Legend

Fig. 2. Mechanism of formation and reduction of spinel inclusions in aluminium-killed steels

VI. Conclusions

(1) In aluminium-killed steels, alumina is the stable deoxidation product; spinel inclusions like hercynite ($\text{FeO} \cdot \text{Al}_2\text{O}_3$) or galaxite ($\text{MnO} \cdot \text{Al}_2\text{O}_3$) are formed only when the dissolved oxygen in steel is well above that normally obtained for low carbon steels. The observation supports the earlier work of Straube *et al.*¹¹⁾

(2) Spinel formation in aluminium-killed steels is associated with reoxidation of steel during tapping and teeming, incomplete mixing of the deoxidizer and/or segregation during solidification.

(3) Hercynite and galaxite which are metastable in the presence of excess aluminium in steel are reduced to alumina particles in 5 to 7½ min after aluminium deoxidation. This is contrary to the findings of Straube *et al.*¹¹⁾ who stated that once the alumina envelope forms around the spinel, further reaction between the spinel and aluminium dissolved in the melt is prevented.

(4) Allowing a ladle holding time of about 8 min or argon purging of molten steel in the ladle after aluminium deoxidation would make aluminium-killed steels free of spinels. This conclusion leads to a better understanding of the statistical study made by Luyckx.¹⁰⁾

(5) The mechanism of formation of spinels de-

pends upon the availability of Mn(Fe)O nucleus which is converted to galaxite instantaneously. An alumina envelope forms around galaxite either by the reduction of galaxite by dissolved aluminium or the interaction between the dissolved aluminium and oxygen on the inclusion surface.

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