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Oxide Inclusions Formed in Steels (Report I)[†]

— Deoxidation Products by Al, Si, Mn, Ti, V —

Nobuya IWAMOTO*

Abstract

Nonmetallic inclusions formed in steels on the refining and the welding have great influences on the physical properties such as corrosion resistance, fatigue and mechanical properties etc. In this review, the structural considerations of non-metallic inclusions formed when various deoxidant was used are given from the viewpoint of undecided problem.

1. Introduction

In the manufacture of steels, nonmetallic inclusions come out from the following reasons such as impurities of the raw materials and fuel used, solution of gas components from the atmosphere and erosion of refractories.

Especially, in the case of welded materials, it has been considered that a plenty of nonmetallic inclusions are formed compared to non-welded steels.

On the other hand, the strengthening effect of homogeneous dispersed oxide in steels, which is of considerable use, is being recently aimed to raise the structure hardness.

However, in general, nonmetallic inclusions in steels bring harmful effects on the corrosion resistance, fatigue and mechanical properties of steels.

In recent years, the requirement for the minimizing of the amounts of nonmetallic inclusions in steels is severe.

In the congress of clean steel in Hungary at 1970,¹⁾ many people discussed many sorts of research topics such as dynamical consideration of deoxidation, the relationship between structure of nonmetallic inclusion and flotation in the molten steel and investigation of complex deoxidants.

In order to obtain good quality of steels, electroslag remelting^{2), 3), 4)} or welding^{5), 6)} has been used very often lately in Japan.

However, there are few reports treating new sorts of fluxes. In the same way, there was only a paper studied nonmetallic inclusions formed in the welded materials.⁷⁾

To study the crystal structure of nonmetallic inclusions formed in steels, furthermore to do state analysis, is one of the countermeasures answering the request for the development of new complex deoxidant.

In the first place, I mention briefly the important items among the development of investigation about nonmetallic inclusions.

For the standpoint of the structure analysis of nonmetallic inclusions, extreme care must be taken to extract them safely without the destruction of their structure from the metallic matrix by proper physical or chemical means.

2. Extraction means

Since 1820, the effort to extract carbide from steels by using various sorts of acid was paid⁸⁾ and the successes of extracting oxide and nitride have been simultaneously reported during these 150 years.⁹⁾

Likewise, iodine, bromine and chlorine were widely used for extraction of nonmetallic inclusions.^{10)~21)} Electrolytic isolation was applied at 1897,^{22), 23)} and zinc sulfate and ferric sulfate aqueous solution were used as an electrolyte. Further, acid-alcoholic solution²⁴⁾ and potassium chloride-ferric sulfate aqueous solution were used for.²⁵⁾ However, it has become necessary to improve the extracting apparatus to prevent the mixing of extracted matters and iron hydroxide precipitates and to use new extracting agent of potassium bromide and sodium citrate aqueous solution.²⁶⁾ Still more, permeable film¹ was established between anode and cathode.²⁷⁾

In **Table 1**, the list of the extracting agents are given.^{27)~33)}

Afterwards, the improvement of extracting vessel was continued, and specimen as cathode of central position was surmounted with circumferential platinum net as anode.³⁴⁾ Furthermore, the quality of the vessel was changed to polystyrol from glass for the use of hydro-fluoric acid as an electrolyte.

To carry on the extraction under constant voltage between specimen and extracting agent, the application

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Table 1. Commonly-used electrolytes.²⁷⁾

Electrolyte	Steels	Isolate	pH	Type of Dissolution	Remarks	Reference
Z—B 5—15% sodium citrate 1.2%KBr 0.6%KI pH adjustable between 6 and 9	Steels with <7%Cr	Carbides Oxides Sulphides Nitrides	9	Ferrous iron active; ferrous iron, partly passive	Polarization increases with increasing chro- mium and carbon contents	28
Z—B+2% ferrous citrate	Ferritic steels with <20%Cr	Carbides Oxides Intermetallic phases	5	Ferrous iron, partly passive with increased active positions	...	29.30
5% sodium citrate + 5% sodium acetate + 1%KCNS + 1% ascorbic acid	High-alloy steels	Carbides Oxides	...	Ferrous iron, active- ferrous iron, partly passive with Cr con- tents of >12%	...	31
5% sodium citrate + % zinc sulphate	Zn—Fe alloys	Iron-zinc compounds	32
3%KBr	Steels with Cr contents <2% and for corro- sion-resistant ferritic steels	Carbides Oxides Intermetallic phases	4—5	Up to 7%Cr ferrous iron, active; above 7% Cr ferrous iron, partly passive	With steels containing <2%Cr, O ₂ must previously be removed completely from the electrolyte	29.30
3%KCl	High-alloy austenitic steels	Carbides Oxides Intermetallic phases	4—5	Ferrous iron, partly passive; ferric iron, active	Applicability to be tested in each indi- vidual case	
3%(NH ₄) ₂ F ₂	Corrosion-resistant steels	At present only for isolation of oxides	...	Ferric iron, active	Double fluorides are formed readily	29.30
1%HCl in alcohol	Alloy steels	Acid-resistant carbides	1—2	Ferrous iron, active	Isolate to be tested for resistance to acid a attack	33

of potentiostat was used for the polarizing characteristics of various specimens were studied. For the first time, the result of cementite was obtained³⁰⁾ and the extraction of intermetallic compounds has become possible.³⁵⁾ Further, 10% hydrochloric acid-90%-ethyl alcohol solution³³⁾ and 10% hydrochloric acid-90%glycol solution³⁶⁾ were applied for the isolation.

3. Mechanical extractions

Electrolytic isolation with observation of micro-structure under optical microscopy³⁷⁾ and mechanical isolation with jack hammer by ultrasonic was applied too. Always, the problem from the mixture of various sorts of nonmetallic inclusions lies on the difficulty of identification of the crystal structures, so chlorination-vacuum method,^{31), 38), 39)} flotation^{40)~42)} and magnetic separations^{27), 40), 41), 43)} were developed for further analysis.

Emission spectroscopy,^{44), 45)} flame-photometry,⁴⁶⁾ fluorescent analysis⁴⁷⁾ and micro-chemical analysis^{48)~54)} were applied too. From the etching of nonmetallic inclusions in the metallic specimen in the following steps, to identify nonmetallic inclusions under unsoltd state has become possible.⁵⁵⁾ The application of XMA⁵⁶⁾ and the investigation of fine precipitates in grain boundary with X-ray means,⁵⁷⁾ and the mineralogical investigation of nonmetallic inclusions in the thinner specimen⁵⁸⁾ have been reported continuously.

4. Problems on the deoxidation products

Aluminium

Aluminium is the most strong deoxidant and widely used for the refining of steels. From the thermodynamical viewpoints, it is known that α -Al₂O₃ (corundum) is formed in steels as stable form.

However, there remains still unknown that the causes of the easiness to form cluster and have difficulty to grow up to larger inclusion of alumina.^{59)~64)}

There are very few reports considered formation mechanism of aluminium deoxidation. Only, Sloman and Evans⁶⁵⁾ have certified unknown inclusion when electric current was cut in a moment after aluminium was added to molten iron. They simply estimated them to be probably silica from the total chemical analysis of the isolated residues.

In the field of mineralogy, there have been determined the transition to corundum via low-temperature aluminas on the dehydration of aluminium hydroxides,⁶⁶⁾ but there are many doubtful points about crystal structures and authenticity of existence 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.⁶⁷⁾

Practically, all heats were melted in a magnesia

crucible of high-grade fitted for the high frequency furnace. All of the runs were performed under the pressure of 4×10^{-4} mmHg. The molten bath temperature was measured with a Pt Rh 20% - Pt Rh 5% 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. As representative case, the specimen was solidified in the crucible after electric current was continued for four seconds since metallic aluminium was added, and the specimen was continued for ten seconds. A specimen was held for ten minutes, but a specimen was made in the atmosphere of nitrogen to investigate the formation of aluminium nitride for comparison. A specimen was made to know the effect of small lump of metallic aluminium on the formation of aluminium inclusions.

Extraction of inclusions from each casts, was carried on with electrolytic means using Koch-Sundermann type isolating vessel. As isolate, the authors used 5% sodium citrate and 1.2% potassium bromide aqueous solution, and they used the electrolytic method with 10% hydrochloric acid-ethanol solution or isolation with iodine-methanol solution too. The extracted residues were fully washed and dried in vacuum and submitted to next various tests. X-ray diffraction patterns of the residues are shown in Fig. 1, and the values of interplanar spacings are given in Table 2.

The following conclusions were derived:

- 1) Under rapid solidification, they could detect the formation of various low-temperature stable modifiers beside corundum. They are chiefly θ and δ types.
- 2) In the case of slow solidification, low-temperature types aluminas transfer to corundum.
- 3) We must wait for the detailed experimental results for solving deoxidation mechanism of metallic aluminium in molten steel.

Afterwards, Miyashita et al have performed the

same experiment and obtained same result with our experiment.⁶⁸⁾ They have derived the following mechanism that the temperature in steel is rapidly raised depending on the heat of reaction when metallic aluminium solved and low temperature aluminas is formed because transformation to α - Al_2O_3 is prevented in the cooling process.

Table 2. Low temperature aluminas formed in aluminium deoxidation.

I/I_0	$d(\text{\AA})$	α - Al_2O_3	κ - Al_2O_3	θ - Al_2O_3	FeAl_2O_4
	1.374	(030)			
20	1.399		1.40	1.40	
	1.405	(124)			
50	1.443		1.44		1.43
	1.514	(122)			
5	1.542	(211)	1.55	1.55	
	1.547				
30	1.572				1.56
	1.605	(116)			
5	1.672		1.65		
	1.745	(024)			
5	1.833		1.84		
	1.968	(202)			
20	1.992		2.00		
5	2.048			2.03	2.02
	2.096	(113)			
5	2.150		2.13		
30	2.253			2.26	
	2.322	(006)			
70	2.388	(110)			
70	2.466			2.45	
	2.555	(104)			
20	2.726			2.74	
20	2.808		2.81		
50	2.899			2.87	2 2.87
20	3.080		3.06		

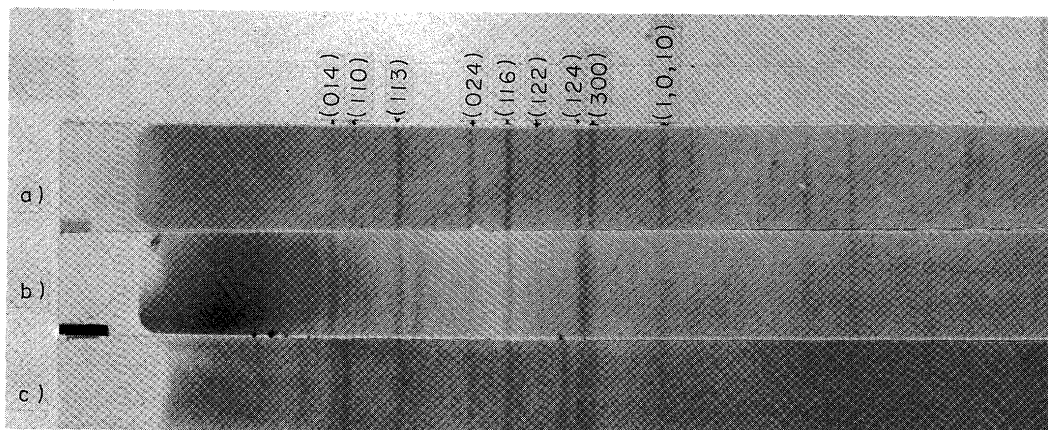


Fig. 1. Low temperature aluminas formed in steel.

a) α - Al_2O_3 (as standard) b) deoxidized in nitrogen atmosphere c) rapidly solidified after added aluminium lump.

Koyama et al have studied the complex deoxidations of aluminum accompanying Mn, Si, Ca or rare earth metals.⁶⁹⁾ Likewise, the mixture of aluminium with CaO, BaO, NaCl, and CaF₂ and fluorite was studied. It was certified that the difference of alumina shape depending on the sorts of complex deoxidants. They concluded from the experiments above described that it should be considered of the effect of the process of nucleus formation of the deoxidants added.

However, the strange behaviour of aluminium deoxidation in steel should be pursued with appropriate means in future.

Silicon

Silicon as strong deoxidizer plays most important role in metallurgical field and it is widely used in refining steels.

An important problem in steelmaking, whether oxide inclusions formed in practical steels come from deoxidant products or from the destruction fragment of refractory used should be pursued. Especially, silicon is appropriate to study above problem because silica has various isomorphs such as quartz, cristobalite and amorphous silica.

According to Fenner's study⁷⁰⁾ concerning silica transformation, quartz should appear as a most stable form in molten alloys. Until now, many investigators have studied the oxide inclusions formed in Si-containing steels. Sloman and Evans have reported the formation of α -tridymite, fayalite and another one which were impossible to identify.⁷¹⁾ Ao determined quartz and cristobalite in practical steels and he concluded that they are originated from deoxidant.⁷²⁾ On the other hand, he thought that glassy material is based on deoxidant as well as refractory destruction. Takeuchi, Fukazawa and Oda have determined quartz and cristobalite and indicated that the effect of high pressure in molten steels should be considered.⁷³⁾ Adachi and Iwamoto have emphasized the impurity effect on the transformation of silica and have recognized all the isomorphs of silica can be formed under experimental conditions such as variation of solidifying velocity on the formation of silica and the dissolution of dilute hydrofluoric acid aqueous solution and the application of infra-red absorption technique to identify isomorphs of silica were tried.⁷⁴⁾

Amorphous silica always appear in every specimens of rapidly or slowly solidified. A plenty of amorphous silica forms when specimen was solidified in crucible.

Especially, in the case of 3%Si containing slowly solidified specimen, extraordinary plenty of amorphous silica appear and they surmounted the specimen

during extraction. It was certified that these gellike matters change to jellylike one when washed fully and their X-ray result showed amorphous patterns. After few monthes, their structure change gradually and it was determined that the peaks of $d=2.211\text{\AA}$ and $d=2.549\text{\AA}$ appear after 3 years passage. These values agree with the results of low quartz ($I/I_0=60$), but the disappearance of $d=1.85\text{\AA}$ ($I/I_0=90$) is unclear. The variation of the X-ray diffraction pattern is shown in Fig. 2. Furthermore, when specimen lapsed for 3 years, a scanty of amorphous materials was observed when compared to the extraction behaviour of specimen immediately manufactured. From these results, it was anticipated that the transformation from amorphous to crystalline materials with the passage of time should be hold in mind to pursue the deoxidation mechanism of silicon in steel.

Because the amorphous materials give the difficulty of determining various sorts of silica polymorphs, the treatment of hydrofluoric acid aqueous solution to dissolve the amorphous materials was tried. The results made clear by this means are given in Table 3.

Previously, the effectiveness of infra-red identification to determine the isomorphs of silica has been said in three papers.^{75)~77)} From the studies, it was said that quartz and α -cristobalite in natural were identified. In Fig. 3, infra-red absorption results of Si deoxidation products extracted from steels were compared with the one of synthesized materials. shown in Fig. 4. As extracted residue, we can always find the formation of fayalite. However, agreement of the results between synthesized ones, tridymite and cristobalite, and the extracted residues was not recognized.

As conclusion, it was determined that it is impossible to discuss the existence of isomorphs of silica from infra-red absorption study.

Likewise, an attempt to try differential thermal analysis for quantitative analysis of the isomorphs of

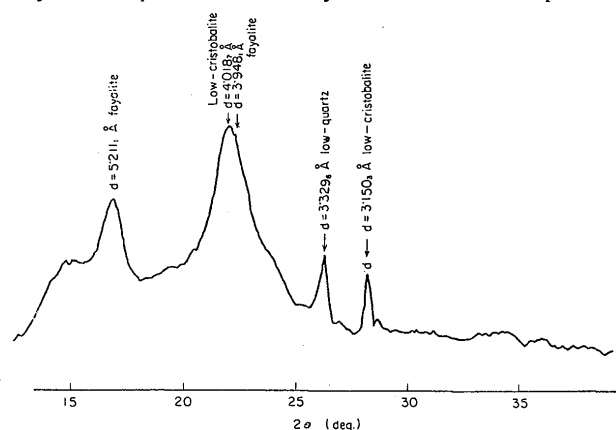


Fig. 2. X-ray diffraction profile of the non-metallic inclusions extracted from 3%Si containing alloy which are left 3 years after manufactured.

Table 3. X-ray diffraction results of non-metallic inclusions extracted from silicon deoxidized alloys.

Si%	Solidifying Velocity	Inclusions determined
0.5	crucible-solidified	high-cristobalite, low-tridymite, fayalite, low-quartz, amorphous silica
0.5	cast to Cu-mould	high-cristobalite, high-quartz, amorphous silica
1.0	crucible-solidified	low-cristobalite, fayalite, amorphous silica
1.0	cast to Cu-mould	high-cristobalite, high-tridymite, fayalite, high-quartz, amorphous silica
3.0	crucible-solidified	high-cristobalite, low-tridymite, amorphous silica
3.0	cast to Cu-mould	high-cristobalite, high-tridymite, fayalite
4.0	crucible-solidified	amorphous silica
4.0	cast to Cu-mould	high-cristobalite, high-tridymite, fayalite, high-quartz, amorphous silica

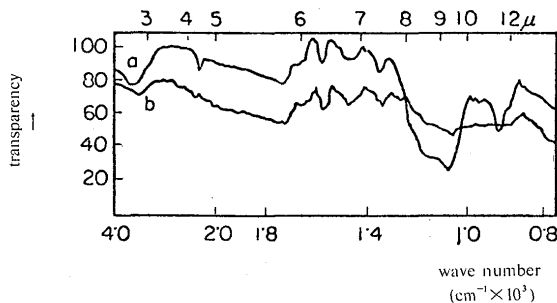
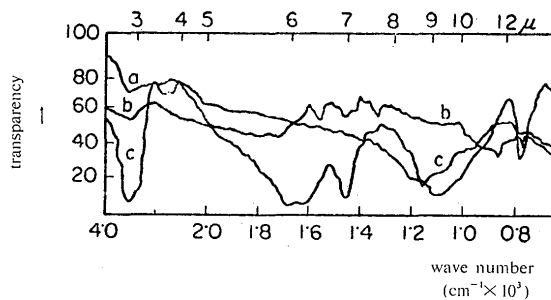


Fig. 3. Infra-red absorption results of non-metallic inclusions from a) 4%Si containing alloy rapidly solidified and b) same specimen but slowly solidified.

Fig. 4. Infra-red absorption results of various specimens synthesized a) low cristobalite, b) fayalite, c) amorphous SiO₂.

silica formed in steels have been done.^{78)~80)} Previously, it was reported that two absorption peaks of 130 and 175°C in the case of tridymite and a peak of 580°C of quartz and absorption near 260°C of cristobalite appear. Our experimental results will be shown in Fig. 5. Good confidence of absorption near 260°C from high temperature heat-treated amorphous silica synthesized with the result from cristobalite was found. Fayalite gave sharp absorption peak near 380°C, and it was recognized that it probably due to the oxidation behaviour of iron. In the case of the extracted residues from 3%Si containing alloy, they did not show sharp absorption peak. But sharp absorption peak near 175°C appeared in the case of same specimen treated with hydrofluoric acid aqueous solution.

Even if standard cristobalite has given as absorption peak near 260°C, it is unknown matter whether cristobalite formed in every specimen having different history show absorption peak at same temperature or not. There exists same problem related to tridymite whether it shows two absorption peaks or not. According to our result, there appears only one peak. It should be emphasized that the effects of the possi-

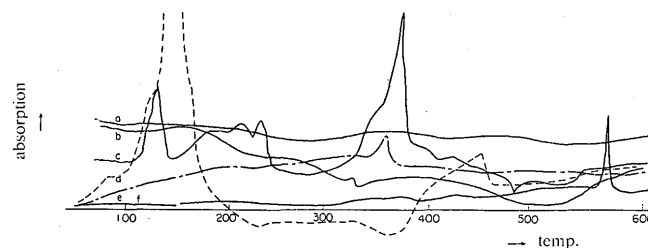


Fig. 5. Differential thermal analysis results.

a) fayalite, b) inclusions extracted from 3%Si containing alloy slowly solidified, c) amorphous SiO₂ synthesized, d) specimen (b) HF treated, e) low cristobalite, f) brazilian quartz.

bility of solid solubility of another element as well as the difference on degree of crystallization must be considered on the analysis of experimental results.

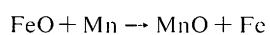
When same circumstances such as abnormal haviour on the X-ray diffraction intensities and disappearance of some interplanar spacing values occur, the influences above described should be considered as well as the effect of lattice defect as stacking disorder.

Furthermore, there are another problems that it is difficult to obtain standard tridymite and cristobalite because transformation velocity is sluggish in some case and it is necessary to add some mineralizer to promote transformation. Consequently, it is understood that these impurifying effect give great differences on the various experimental results.

Manganese

Manganese is the deoxidant usually used with aluminium and silicon in metallurgy.

As deoxidation reaction,



is given.

According to the systematic study concerning manganese deoxidation by Sloman and Evans,⁸¹⁾ they concluded that the solid solubility between manganese oxide and ferrous oxide is recognized though there exists the difference of composition depending on the manganese content added. With the increase of manganese content, the content of manganese oxide in the inclusions increases, and it becomes nearly pure MnO when manganese above 0.7% was added. In addition to this result, they have concluded that iodine-alcoholic solution has harmful action to dissolve manganese oxide especially having higher content of MnO from the comparison of the chemical content of the extracted inclusions with the X-ray diffraction values of them, from which Jay and Andrews⁸²⁾ have given the content of manganese oxide in inclusions.

The author have summarized the following problems about the manganese deoxidation:

- 1) Whether manganese oxide and ferrous oxide can make complete solid solution or not. Depending on the manganese content added, whether the formation of secondary phase is possible or not.
- 2) Are there good extracting technique to isolate safely manganese oxide and ferrous oxide?

Although Jay and Andrews have confirmed inter solid solubility between FeO and MnO, there exist another theories that there are two phases region between 30~60% or 45~80%MnO respectively.^{83), 84)}

In Fig. 6, the lattice parameter variation depend-

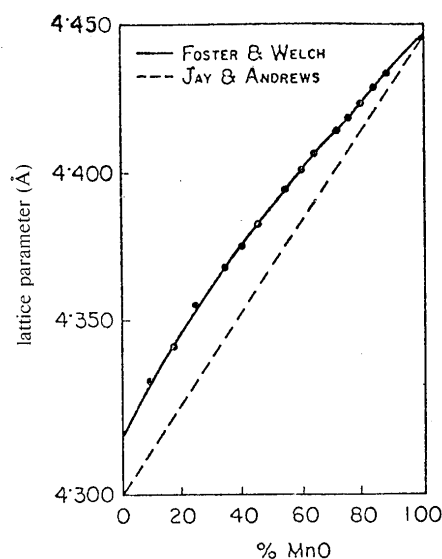


Fig. 6. Lattice parameter of (Fe·Mn)O.

ing on the content of MnO is given.^{82), 85), 86).} It must be remembered that these experiments were carried on under argon atmosphere. Reinvestigation of this experiment will be necessary in future.

From the studies about defect structure of manganese oxide and ferrous oxide,^{87), 88), 89)} their defect behaviours are different under same equilibrating partial oxygen pressure and they show different transformation of crystal structure due to the experimental temperature.

Segawa et al have said that the amount of inclusions decreases with the increase of manganese content added, and the contents of SiO₂ and Al₂O₃ increase on the other hand.⁹⁰⁾ They concluded that the content of manganese added has important effect on the inclusion formation. From these results, it is difficult to accept the substitutional equation between ferrous oxide and manganese oxide.

Many investigators have studied the extracting means about free cutting steels,⁹¹⁾ ferrous oxide⁹²⁾ and practical steels in market.⁹³⁾ As conclusion, it was verified that the effect of temperature of extracting agent is the most important about the stability of manganese oxide.

Generally, as shown in Fig. 7, it is believed that complete solid solution between manganese oxide and ferrous oxide are formed in an extensive limit of manganese content, although it's composition depends upon manganese content added.⁹⁴⁾ The authors have tried extraction of inclusions formed in 1.38% Mn containing steel with acetylaceton-carbon tetrachloride-perchloric acid solution as well as 10% hydrochloric acid-90%ethyl alcoholic solution.⁹⁵⁾ From this experiment, distinguishable X-ray diffraction patterns in addition to manganese oxide were obtained. It is necessary to study whether these patterns are

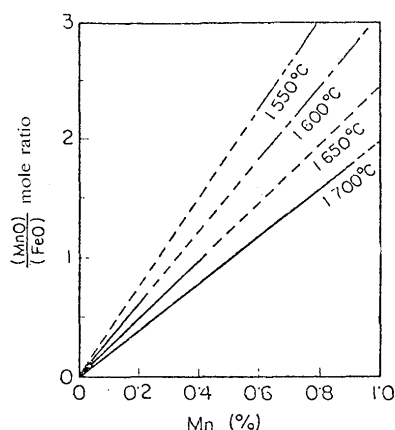


Fig. 7. Relationship between manganese content in molten steel and composition of the non-metallic inclusion.⁹⁴⁾

originated from the secondary phase or not.

Titan

Titan has deoxidizing and denitrizing powers correspond to aluminium or zircon.

Until now, many investigators have studied oxide inclusions formed in titan containing steels. Wentrup and Heber⁹⁶⁾ and Pickering⁹⁷⁾ have confirmed the mineralogical study of Fe-Ti alloys under optical microscopy. Evans and Sloman have performed X-ray diffraction study of the extracted residus.⁹⁸⁾ Hadley and Derge have accomplished Ti-O phase diagram.⁹⁹⁾ Chipman¹⁰⁰⁾ and Segawa et al¹⁰¹⁾ have carried on the equilibrium study. Suzuki et al have done X-ray diffraction study of oxides formed at surface of the molten alloys when equilibrium was hold.¹⁰²⁾

According to previous studies, oxide inclusions formed in steels of Fe-Ti-O system are as follows:

Wentrup and Heber: FeO, FeO·TiO₂, and Ti₂O₃ are formed in order with the increase of titan added.

Pickering: "X" which is impossible to identify, Fe₃O₄, titanian magnetite spinel, and FeO·TiO₂ and TiO₂ and Ti₃O₅ and α-Ti₂O₃ and TiO are formed.

Evans and Sloman: Ti₂O₃ and TiO are formed when titan content is above 0.2%.

Below the value, Ti₃O₅ (anosovite) and TiO₂ are formed.

When oxygen content has become excess, FeO·TiO₂ (titanium magnetite), spinel and Fe₃O₄ are formed.

Hadley and Derge: below 0.5% Ti, FeO·TiO₂ melt 0.5~1.0% Ti, solid TiO₂ reduced and containing FeO

1.0~5.0% Ti, Ti₂O₃

above 5.0% Ti, TiO

Segawa et al: below 0.2% Ti, Ti₃O₅

until 2.0% Ti, α-Ti₂O₃

above 5% Ti, TiO

Suzuki et al: below 0.31% Ti, Ti₃O₅

0.5~5% Ti, Ti₂O₃

1.69% Ti-Ti₂O₃ and low temperature type Ti₃O₅

5~9% Ti, TiO

It will be anticipated that experimental results above described do not agree well.

The following subjects have been unsolved until now.

1) In the case of low titan containing steel, oxide inclusions formed is unclear as well as niobium deoxidation.

2) Although Chipman et al have certified rutile (TiO₂), their X-ray diffraction values do not agree with the standard values of ASTM X-ray card.

3) Pseudobrookite which is seen in Fe-Ti-O phase diagram can not find in every results.

From the reasons, the authors have thought to certify the equilibrium relation between metallic phase containing titan and various sorts of oxide inclusions. The authors have applied "in vacuo quenching" method.

From these experiments, the following results were obtained and shown in Fig. 8.¹⁰³⁾

1) In either case, TiO phase can equilibrate with intermetallic compound Fe₂Ti and metallic phase containing titan above 27%.

2) Ti₂O₃ phase are formed in wider regions of titan added.

3) It was verified that Ti₃O₅, named as anosovite up to this time, is not simple Ti₃O₅-FeO·2TiO₂ solid solution but contains a plenty of Al₂O₃ as impurity.

Interplanar spacing values of Ti₃O₅ of our result was compared with one by Segawa et al in Table 4.¹⁰⁴⁾ Zudanov and Rusakov obtained anosovite from slag.¹⁰⁴⁾ For such a reason, it has been said that pseudobrookite can not form in steels, and the disagreement of X-ray diffraction value between anosovite extracted from steels and the synthesized one. was caused from impurities. Suzuki et al have noticed the effect of Al₂O₃ on the composition of anosovite, although they did not study of mutual reaction. They compared the X-ray diffraction value with α-Al₂O₃, and determined coexistence of Ti₃O₅ with Al₂O₃ as oxide inclusions from Fe-Ti alloys containing titan below 0.26%.

4) In previous studies, the formation of TiO in alloys containing high titan was reported. Matsushita et al have indicated the possibility of TiN in place of TiO.¹⁰⁵⁾ As a matter of fact, Suzuki et al have described the colour of this material as bronze and goldlike. From the tone of colour, we can recognize the matter as TiN. When considered the difference of X-ray diffraction values between TiO and TiN, it should be

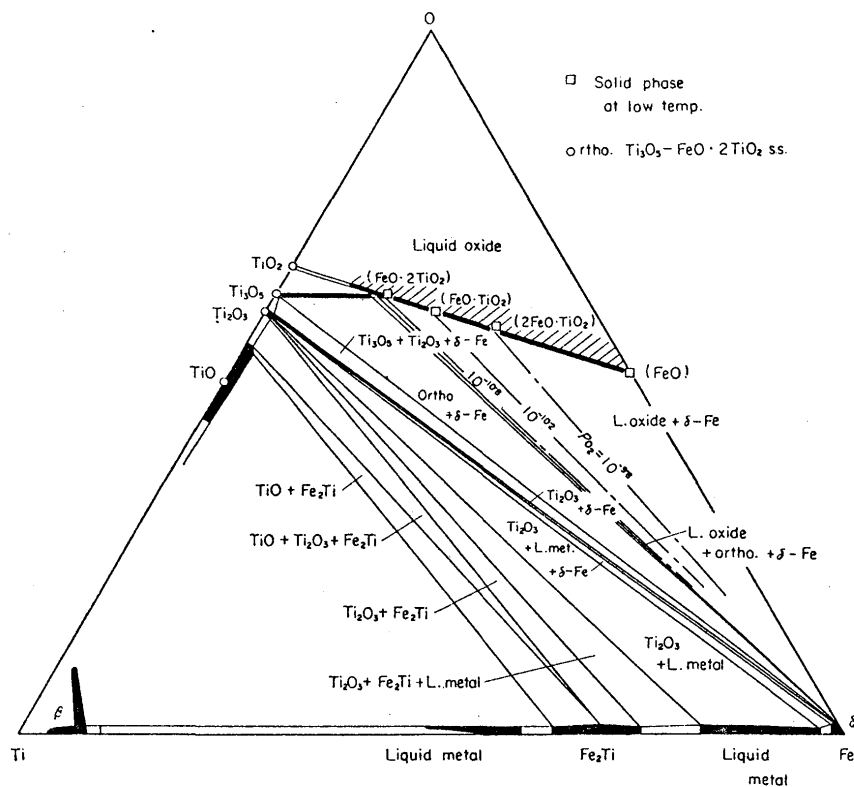


Fig. 8. Iso-thermal phase diagram of Fe-Ti-O system at 1500 C.

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Table 5. Solid solubility between anosovite (A) and pseudobrookite (PB).

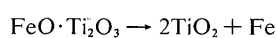
No	Mixing ratio (mole)	Exp. Condns.	Products	Lattice parameter (Å)		
1	Fe ₂ O ₃ : TiO ₂ = 1 : 4	CO ₂ = 1/4, 1200°C Vac. Quench (1500°C)	FeO·2TiO ₂	a = 9.84	b = 3.74 ₅	c = 10.06 ₅
2	PB : A = 3 : 1		(Fe _{0.75} Ti _{2.25}) O ₅	a = 9.85	b = 3.80	c = 10.06 ₅
3	PB : A = 1 : 1		(Fe _{0.5} Ti _{2.5}) O ₅	a = 9.85 ₅	b = 3.78	c = 10.03
4	PB : A = 1 : 3		(Fe _{0.25} Ti _{2.75}) O ₅	a = 9.89 ₅	b = 3.79 ₅	c = 9.99
5	PB : A = 1 : 4		(Fe _{0.2} Ti _{2.8}) O ₅	a = 9.90 ₅	b = 3.79	c = 9.99
6	PB : A = 0.09 : 0.91		(Fe _{0.09} Ti _{2.91}) O ₅	a = 3.78	b = 3.78	c = 9.99 ₅
7	Ti : TiO ₂ = 1 : 5		Ti ₃ O ₅ (High Temp.)	a = 9.80 ₅	b = 3.79	c = 9.98 ₅

emphasized the similarity of $a_0 = 4.240\text{Å}$ of TiN and $a_0 = 4.235\text{Å}$ of TiO.

The crystal structure of Ti₃O₅ were given by Anderson and Magnelli,¹⁰⁶⁾ Åsbrink and Magnelli,¹⁰⁷⁾ and Zhadanov and Rosakov¹⁰⁴⁾ (ASTM X-ray card), but there remains disagreement. Anderson et al. have given values of $a = 9.757\text{Å}$, $b = 3.802\text{Å}$, $c = 9.452\text{Å}$ and $\beta = 93.11^\circ$ as monoclinic structure. Åsbrink et al. have said that high temperature Ti₃O₅ (anosovite) above transformation temperature of about 120°C takes structure of monoclinic slightly distorted from rhombohedral and having the values of $a = 9.82\text{Å}$, $b = 3.78\text{Å}$, $c = 9.97\text{Å}$ and $\beta = 91.0^\circ$. At higher temperature, it changes to rhombohedral structure turning to $\beta = 90^\circ$ continuously and it becomes as stable forms in room temperature from the substitution of few iron atom to titan atom in lattice. Further increase of the substitution to be (Ti_{0.92}Fe_{0.08})₃O₅, they say it takes $\beta = 90^\circ$. As shown in **Table 5**, Ti₃O₅ made at 1500°C is resemble to the one by Åsbrink et al. From these consideration, it has become clear that the data by Anderson corresponds to low temperature Ti₃O₅ and ASTM X-ray card is from impured Ti₃O₅.

In the next place, the phase relation between anosovite and pseudobrookite as end member, respectively, was studied. The results obtained are shown in **Table 5**. It was verified that both can form pseudo-binary and can solid soluble each other in a wider regions.

According to Halla, the existence of spinel phase (FeO·Ti₂O₃) containing lattice parameter of $a_0 = 8.47\text{Å}$ was reported.¹⁰⁸⁾ Evans and Sloman have considered the reaction of



in the solidifying process in steels, it was impossible to accept this material by our experiment.

From our study concerning equilibrium between metallic iron and FeO-TiO₂ pseudo-binary liquidus oxide, ulvospinel (2FeO·TiO₂), ilmenite (FeO·TiO₂)

and pseudobrookite (FeO·2TiO₂) has appeared as solidified phase in order with the decrease of the equilibrating oxygen partial pressure. It was verified from the gravimetric experiment that ulvospinel has excess oxygen content than the stoichiometric composition and pseudobrookite has composition of titan rich.

From the aforementioned results, it was considered that FeO-TiO₂ oxide melt (2FeO·TiO₂ and FeO·TiO₂ as solidified phases) is formed in case of low titan containing alloy, and Ti₂O₃ and oxide of rhombohedral structure (which contains considerable impure oxides in Ti₃O₅-FeO·2TiO₂ solid solution) are formed in alloy containing titan below 30%.

Vanadium

Vanadium has strong combining affinities with oxygen, nitrogen and carbon as well as titan. Vanadium is an element calling our attention from the prominent property in alloys. The deoxidizing power is intermediate between silicon and manganese. In regard to the reaction with oxygen in steels, studies of Chipman and Dastur,¹⁰⁹⁾ Samarin¹¹⁰⁾ and Narita¹¹¹⁾ were published. However, all the papers are based on the equilibrium study, and there are no problem about deoxidation products, that is to say, FeV₂O₄, V₂O₃ and VO are formed with the increase of vanadium content added in turn.

Our results obtained are shown in **Table 6**.

Table 6. Deoxidation products of vanadium.

wt % V Nominal	Chem. Analyzed wt % V	Products
0.05	0.02	FeO·V ₂ O ₃ ($a_0 = 8.45\text{Å}$)
0.1	0.03	FeO·V ₂ O ₃ ($a_0 = 8.45\text{Å}$), wV ₂ O ₃
0.5	0.23	FeO·V ₂ O ₃ ($a_0 = 8.45\text{Å}$), mV ₂ O ₃
1.0		V ₂ O ₃ , wFeO·V ₂ O ₃ ($a_0 = 8.455\text{Å}$)
5.0	4.88	VO ($a = 4.132\text{Å}$), mV ₂ O ₃
10.0		VO ($a = 4.136\text{Å}$), mV ₂ O ₃

W ... Weak
m ... medium X ray intensity

Generally, agreement will be seen with previous studies except detailed points.

As study of Fe-Ti-O phase diagram, oxidation at high temperature, solid solubility with other oxides and variation of crystal structure were carried on by Jager, Rahmel and Korn.¹¹²⁾ However, there are no studies treated ternary system.

Until now, solid solubility of spinel phase ranging from $\text{FeO} \cdot \text{V}_2\text{O}_3$ to $2\text{FeO} \cdot \text{V}_2\text{O}_3$ is reported.¹¹³⁾ Concerned with the change of lattice parameter, there are two opinions. With the increase of solid solubility of wüstite, one says gradual decrease of the lattice parameter and other says the value is independent. Some says that there exists another spinel of $2\text{FeO} \cdot \text{VO}_2$.

As described above, the structure of spinel formed in steels containing low vanadium is still unclear. Therefore, the authors have tried to accomplish phase diagram of Fe-V spinel which contains gas phase as one variable. It has become clear that no solid solubility of V_2O_3 to spinel is recognized, and independents to oxygen partial pressure equilibrated although the solid solubility of wüstite depends on the oxygen partial pressure and the amount of solid solubility decreases with the decrease of the partial pressure and the variation of the lattice parameter is small not to accept the result of Jäger et al.

On the other hand, it has become obvious that oxide inclusion formed in steel containing high vanadium corresponds to $\text{VO}_{1.20}$.

5. Summary

In this review, the structural considerations of nonmetallic inclusions formed when various deoxidant such as aluminium, silicon, manganese, and titan and vanadium was used are given from the viewpoint of undecided problem. In the next issue, the deoxidation product by niobium, chromium zirconium and complex deoxidants will be considered.

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