Oxide Inclusions Formed in the Steels of Fe-Cr-O System*

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Synopsis

The importance of inclusions in steel has been very much emphasized, and many investigations have been carried out, but in most cases too many variables have been presented to draw any definite conclusion.

In order to obtain a satisfactory solution of the inclusion problem, the authors have pursued from various viewpoints the formation mechanism of inclusions in the steels of Fe-Cr-O system.

They applied new resolving analysis using electron diffraction under higher accelerated voltages and activation analysis based on neutron irradiation.

The results obtained through this investigation are summarized as follows:

(1) It was presumed that the lattice parameters a_0 of the inclusions formed in the steels of Fe-Cr-O system became larger with an increase of the amounts of chromium added. From this phenomenon, it is difficult to accept Hilty, et al.'s description, which reported that distorted spinel and Cr_3O_4 were different matters.

(2) By heat-treatment of the residue extracted from 65% chromium alloy, the appearance of metallic chromium was not recognized, and therefore it became necessary to take consideration on the decomposition equation, $3\text{Cr}_3\text{O}_4 \rightarrow 4\text{Cr}_2\text{O}_3 + \text{Cr}$.

From the inclusion extracted from 18% chromium steel, chromic oxide and normal iron chromite appeared. The distorted iron chromite is regarded to be composed of chromic oxide and normal iron chromite.

(3) When normal iron chromite was added into molten chromium, the distortion degree of the formed iron chromite showed decrement. From this fact, one should admit an important role of iron chromite in the structure of nonmetallic inclusions equilibrated with molten alloy of this system.

I. Introduction

When chromium is added into molten iron, it is important to know the behaviour of chromium in relation to oxygen. Studies on this problem are great helpful for taking off difficulties in identifying the complex inclusions formed when many sorts of deoxidizers are used, as well as for improving the qualities of chromium steels and stainless steels.

Until now, many investigations have been performed about nonmetallic inclusions formed in the steels of Fe-Cr-O system.¹⁾⁻³⁾ Among them, the summarized study by D. C. Hilty, W. D. Forgeng and R. L. Folkman²⁾ has been acknowledged widely, and the phase diagram of this system by M. Hansen is constructed on the basis of this result.

However, the difficulties of finding satisfactory agreements among the results of investigations about nonmetallic inclusions even in this simple system, will be an obstacle to proceed further studies on more complex systems.

The authors are studying the formation mechanism of inclusions in the Fe-Cr-O system from all sides, and making efforts to complete the phase diagrams of this system under the various oxygen potentials. In this paper they summarized the results obtained hitherto as to the following items:

(i) Variation of primary inclusions by changing chromium contents in the steel.

(ii) Behaviours of inclusions submitted to after-heat-treatments.

(iii) Behaviours of inclusions under various solidifying velocities.

(iv) Considerations on the ways of the extraction of inclusions.

(v) Simple experiment about the formation mechanism of inclusions.

While referring to the excellent studies by many former investigators, they applied newly developed ways of investigation such as electron diffraction under higher accelerated voltages, electron probe X-ray microanalyser and activation analysis by neutron irradiation.

II. Experimental Procedures

All the heats were made in the high quality magnesia crucibles using a 15-kVA high frequency furnace at the pressure of 10^{-4} mmHg. After pure iron of about 700 g was melted, a little sample was taken by the method of "Taylor sampler" which is used for the determination of oxygen content in the melt before chromium addition. Ferro-chromium or electrolytic chromium was added to the melt aiming at the chromium contents being 0.7, 1.3, 2, 3, 5, 5.5, 6, 7, 8, 13, 18 and 65%, respectively. The samples were taken so as to determine the oxygen contents in the baths after chromium addition.

Although the experiments were conducted mainly at the temperature of 1 600°C, some of the specimens were melted at 1 650°C in order to know the influence of the molten temperatures on the formation of non-metallic inclusions. Before casting all the heats were held at the temperature of 1 580°C.

The molten alloy was cast into water-cooled copper mould and the ingots of 15 mm ϕ and 230 mm in length were obtained. The temperature was measured by the immersed Pt-Rh20%-Pt-Rh5% thermocouples. For comparison, pure chromium was melted in a zirconia

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crucible under argon atmosphere and in this case the temperature was measured by optical pyrometer. The chemical analysis of the raw materials used is given in Tables 1, 2 and 3.

The oxygen contents before and after addition of chromium were analysed by vacuum fusion method and the results are shown in Table 4. Each ingot was submitted to chemical and optical analyses, extraction of inclusions and the experiments described afterwards.

To alter the solidifying velocities of steels, they were cast into the (1) graphite mould, (2) CO₂ process sand mould, (3) iron mould with heater or (4) solidified in the crucible. Time—temperature curves for each specimen were measured by immersing thermocouples connected to X-Y recorder²⁾.

Each quenched specimen was heat-treated in the stream of nitrogen according to the following schedules: (1) one-hour holding at 1 000°C and quenched into ice-water, or (2) ten-hour holding at 800° or 1 000°C and quenched or furnace-cooled or (3) 60-hour-holding at 1 000°C and quenched or furnace-cooled.⁹⁾

Using the equipment of Koch-Sundermann type extraction vessel, electrolytic extraction of oxide inclusions was carried out in the electrolyte containing 5% sodium citrate and 1.2% potassium bromide, under

Table 1. Chemical analysis of pure iron (%)

C	Si	Mn	P	S	O
0.008	0.006	0.015	0.004	0.013	0.012

Table 2. Chemical analysis of ferro-chromium (%)

C	Si	Cr	P	S
0.020	0.230	62.00	0.02	0.006

Table 3. Chemical analysis of electrolytic chromium (%)

C	Si	Cr	P	S	Fe	N	O
0.019	0.008	99.39	0.001	0.019	0.11	0.03	0.36

Table 4. Oxygen content of each run molten at 1 600°C before and after ferro-chromium addition (%)

Nominal Cr(%)	3	8	13	18
Before	0.0450	0.0477	0.0470	0.0472
After	0.0435	0.0352	0.0189	0.0266

Table 5. Interplanar spacings of isolated residues

Nominal Cr(%)									
1.3		5		8		18		99.4	
$d(\text{\AA})$	(hkl)	$d(\text{\AA})$	(hkl)	$d(\text{\AA})$	(hkl)	$d(\text{\AA})$	(hkl)	$d(\text{\AA})$	(hkl)
2.972	220	3.024	220	3.052	220	3.072	220	3.098	220
		2.942	202	2.927	202	2.914	202	2.873	202
2.531	311	2.565	311	2.583	311	2.601	311	2.611	311
		2.476	113	2.428	113	2.399	113	2.343	113
2.096	400	2.134	400	2.163	400	2.167	400	2.191	400
		2.017	004	1.986	004	1.936	004	1.897	004
		1.729	422	1.733	422	1.738	422	1.744	422
1.711	422	1.613	333	1.609	333	1.607	333	1.600	333
1.613	333	1.511	440	1.520	440	1.532	440	1.550	440
1.480	440	1.465	404	1.452	404	1.447	404	1.432	404

the experimental conditions having current density of 10 mA/cm², with respect to the steels of below 6% chromium which was produced by adding ferro-chromium. As for the steels produced by adding metallic chromium, 10% hydrochloric acid-alcohol solution was used as electrolyte. To get the results rapidly the authors examined extraction also by bromine-methanol and iodine-methanol solution.

After the extracted residues were cleaned and vacuum-dried, they were submitted to various experiments, i.e., observation of their forms by optical means, measurements of their refractive indices by immersing method⁵⁾, diffraction analyses by electron beam and X-ray (Debye-Scherrer method, Cr $K\alpha$), microanalysis, activation analysis^{6),7)} and after-heat-treatments.

Primary inclusions extracted from the quenched steels were enclosed in the vacuum-sealed quartz or wrapped into platinum foil and heat-treated at 1 000°C in the stream of argon for one hour. Using electron diffraction under the higher accelerating voltages as 200–250 kV, the analysis of thicker inclusions was performed. Activation analysis was conducted to know the amount of chromium and iron in inclusions. Each sample was irradiated with the neutron flux having 4×10^{13} n/cm²/min in the J.R.R. No. 1 reactor for 20 minutes and having 6×10^{13} n/cm²/min in the J.R.R. No. 2 reactor for 100 hours at Japan Atomic Energy Research Institute.

III. Experimental Results and Consideration

(1) In Table 5, X-ray diffraction values of the residues extracted from the quenched specimens are given. From the lattice parameters reflected by (400) plane, it is understood that the more increase the chromium contents of residues, the greater become the lattice parameters a_0 .

The calculated values by (400) plane were decided to use because it was difficult to determine the accurate lattice parameters from each diffraction value by Nelson-Riley's method due to weak reflection from the planes of higher order as shown in Table 6.

The distortion degree indicated by c/a axial ratio changes from unity to 0.97 in the case of 1.7–3%Cr, to 0.95 at 5%Cr, 0.92 at 8%Cr, and 0.89 at 13–18%Cr and becomes to 0.86 at 65–99.4%. From Table 6, it became clear to reach 8.76Å in the case of the residues extracted from pure chromium.

Table 6. Reflected values from (400) planes

Nominal Cr(%)	1.3	5	6	7	8	18	65	99.4
<i>d</i>	2.096	2.134	2.147	2.152	2.163	2.167	2.186	2.191
<i>a</i> (400)	8.384	8.536	8.588	8.608	8.652	8.668	8.744	8.764

Fig. 1. The lattice parameters a_0 and c_0 of the inclusions extracted in comparison with chromium contents added to the specimens

In Fig. 1, the lattice parameters a_0 and c_0 of the inclusions extracted from chromium steels, high chromium alloy and molten chromium are compared with chromium contents of various specimens.

The variation of the diffraction patterns of the inclusion extracted from the steels of various chromium contents are shown in Photo 1.

The summarized results by D. C. Hilty, W. J. Forgeng and R. L. Folkman²⁾, which are often referred as the most acceptable ones, are as follows:

- (i) Low chromium, up to about 3%Cr: $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, which is solid solution with Fe_3O_4 and $a_0=8.23\text{--}8.30\text{\AA}$.
- (ii) Medium chromium, 3–9%Cr: distorted spinel and $c/a=0.98\text{--}0.95$, $a_0=8.39\text{--}8.48\text{\AA}$.
- (iii) High chromium: Cr_3O_4 and $c/a=0.88\text{--}0.86$, $a_0=8.64\text{--}8.72\text{\AA}$.

It is an important point in their study that the distorted spinel is a different matter from Cr_3O_4 and it is probably intermediate one between $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ and Cr_3O_4 .

Comparing the above results with the authors' ones, there is a discordance in the distortion degree: the latter gives $c/a=0.92$ in the case of 8% chromium steel. But it is agreeable that the diffraction values show a continuous increase in accordance with an increase in chromium addition. It can be supposed that there might be mutual solid solubility between $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ and other end members, and therefore this point is to be discussed in the following.

Attention should be paid to the difference in the results obtained from the steels produced with the addition of ferro-chromium and metallic chromium¹⁰⁾. The influence of the difference of the melting point and co-existing impurity, especially silicon, must be considered.

From this fact, it is necessary to discuss whether the

Photo 1. X-ray diffraction patterns of the residue extracted from various chromium steels, 65% chromium alloy and electrolytic chromium compared with normal iron chromite and chromic oxide (Cr K_α)

description in the short note by J. Chipman¹¹⁾, that chromite and Cr_3O_4 precipitate in chromium steel as the result of the incomplete mixing of the deoxidizer in steel, is apposite. When electrolytic chromium is added, Cr_2O_3 certainly appears as the inclusion and $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ appears with distorted iron chromite.

As for the formation of $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, the authors agree with J. Chipman's opinion. But there is a question about the formation of Cr_2O_3 . If Cr_3O_4 exists as actual substance as Hilty, et al. say, the decomposition behaviour of it must be considered. It seems appropriate to think that Cr_2O_3 is formed in

the chromium rich regions because Cr_2O_3 always appears in despite of chromium contents in the quenched specimens. This supposition agrees with the authors' results.

When ferro-chromium is added, the diffraction patterns of the extracted inclusions show diffuseness more and less. On the cause of this fact the authors have discussed in the previous papers^{6),7)}. It is sure that impure elements have some influence on the formed inclusions.

Then, a consideration has been given to the influence of the simple after-heat-treatments and various solidifying velocities on the inclusions formed in various chromium steels.

(2) In Table 7, the results of the analysis on the effect of after-heat-treatments are given. In the case of 18% chromium steel, the change of the distortion degree from 0.89 to 0.92 was observed after

simple one-hour keeping at 1 000°C. This signifies the continuity of the distortion degree of iron chromite. It is difficult to distinguish $\text{FeO}\cdot\text{Cr}_2\text{O}_3$ from $c/a=0.97$ type iron chromite, especially when the latter has the nearer lattice parameter to $\text{FeO}\cdot\text{Cr}_2\text{O}_3$. It seems apposite to consider the co-existence of $\text{FeO}\cdot\text{Cr}_2\text{O}_3$ and $c/a=0.97$ type iron chromite in the region of the lower chromium content. This fact is proved by the disappearance of the diffuseness of the diffraction patterns of the residues extracted from 2% chromium steel by bromine-methanol method. It is important that $\text{FeO}\cdot\text{Cr}_2\text{O}_3$ and Cr_2O_3 appear as ultimate products with the increment of the holding time at 1 000°C, and these substances are supposed to be composing members of primary inclusions. In Table 8, the representative X-ray diffraction values of the residues extracted from various specimens are shown. In Photo 2, the variation of the diffraction patterns of

Table 7. Variation of inclusions based upon after-heat-treatments

Nominal Cr(%)	5	18
Primary	$c/a=0.95$ type iron chromite	$c/a=0.89$ type iron chromite
1 000°C×1 hr→Q.	$c/a=0.95$, Cr_2O_3	$c/a=0.92$, Cr_2O_3 , $\text{FeO}\cdot\text{Cr}_2\text{O}_3^*$
800°C×10 hrs→F.C.	$c/a=0.95(20)$, Cr_2O_3 , $\text{FeO}\cdot\text{Cr}_2\text{O}_3$	Cr_2O_3 , $\text{FeO}\cdot\text{Cr}_2\text{O}_3^*$
1 000°C×10 hrs→F.C.	$c/a=0.95(20)$, Cr_2O_3 , $\text{FeO}\cdot\text{Cr}_2\text{O}_3$	Cr_2O_3 , $\text{FeO}\cdot\text{Cr}_2\text{O}_3^*$
1 000°C×60 hrs→F.C.	$\text{FeO}\cdot\text{Cr}_2\text{O}_3$, Cr_2O_3 , $c/a=0.95$ (Negligible)	Cr_2O_3 , $\text{FeO}\cdot\text{Cr}_2\text{O}_3^*$

Parentthesized value expresses relative intensities.
* Illustrates probably to contain $c/a=0.97$ type iron chromite.

Table 8. X-ray diffraction values of the isolated residues from the specimens after heat-treated for 60 hours at 1 000°C

Nominal Cr(%)				FeO·Cr ₂ O ₃	Cr ₂ O ₃	0.95 type iron chromite
5		18				
<i>I</i> / <i>I</i> ₀	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₀	<i>d</i> (Å)			
20	3.652	20	3.659		(012)	
20	2.955	50	2.976	(220)		
50	2.652	30	2.669		(104)	
5	2.555					(311)
50	2.529	80	2.534	(311)		
50	2.486	30	2.483		(110)	
10	2.405	30	2.401*			
		40	2.237*			
30	2.180	30	2.179		(113)	
		100	2.114*			
40	2.077			(400)		
20	1.816	20	1.817		(024)	
		20	1.718	(422)		
70	1.674	40	1.673		(116)	
		30	1.634*			
20	1.614	40	1.613	(511)		
30	1.484	50	1.484	(400)		
50	1.466	20	1.465		(214)	

* Illustrates diffraction patterns by Cr_2N .

the residues extracted from heat-treated chromium steel produced with the addition of metallic chromium is given because they show sharpness. From these results, it can not be concluded whether $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ and Cr_2O_3 were induced from the secondary precipitates or the product decomposed from primary inclusions.

For fear of piling up of secondary inclusion in the case of after-heat-treatment of the quenched specimen, and to avoid the possibility of dissolving the precipitated α -Cr in the extraction process, if exists as Hilty, et al. say, extracted residues were heat-treated.

It was found that the primary inclusion from 18% chromium decomposed into iron chromite and chromic oxide whereas inclusion from 65% chromium steel into chromic oxide only. This fact suggests that the primary inclusions extracted from various chromium steels are composed of iron chromite and chromic oxide accompanied with other factors. Furthermore, it was found through the experiment that the appearance of metallic chromium was difficult to confirm. This is shown in Photo 3.

(3) To know the influence of the solidifying velocities on the structures of inclusions, the authors studied the variation of inclusions formed in steels solidified under various velocities. The variation of the for-

med inclusions are shown in Table 9. The time-temperature curves of every specimen studied are shown in Fig. 2.

From these results, it is clear that 0.95 type iron chromite is difficult to decompose compared with 0.89 type. The amount of Cr_2O_3 increases in the case of crucible-solidified steel, and the distortion degree decreases from 0.89 to 0.95 in case of 18% chromium steel. The appearance of Cr_2O_3 is considered to be caused by the secondary precipitation at low chromium contents, but it is not clear whether $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ appeared as a result of the decomposition from primary inclusion or precipitation at high chromium contents. The representative X-ray diffraction values of the ex-

Photo 2. Variation of the diffraction patterns of inclusions extracted from 5 and 18% chromium heat-treated

Photo. 3. X-ray diffraction patterns extracted residue, heat-treated at 1000°C and 1 hour held, in comparison with standard $\text{FeO} \cdot \text{Cr}_2\text{O}_3$

Fig. 2. Solidification curves of various specimens

Table 9. Variation of inclusions based upon solidification velocities

Nominal Cr(%)	5	18
Primary	$c/a=0.95$ type iron chromite	$c/a=0.89$ type iron chromite
Cast into graphite mould	$c/a=0.95$, $\text{Cr}_2\text{O}_3(10)$	$c/a=0.89(30)$, $c/a=0.95$, $\text{Cr}_2\text{O}_3(30)$, $\text{FeO}\cdot\text{Cr}_2\text{O}_3$
Cast into sand mould	Reacted	Reacted
Crucible-solidified	$c/a=0.95$, $\text{Cr}_2\text{O}_3(40)$, $\text{FeO}\cdot\text{Cr}_2\text{O}_3$	$c/a=0.95$, $\text{Cr}_2\text{O}_3(80)$, $\text{FeO}\cdot\text{Cr}_2\text{O}_3$

Note: parenthesized value expresses relative intensities.

Table 10. X-ray diffraction values of the isolated inclusions from crucible-solidified chromium containing steels (CrK α)

Nominal Cr(%)						c/a=0.95 type iron chromite	FeO·Cr ₂ O ₃	Cr ₂ O ₃
5		8		18				
I/I ₀	d(Å)	I/I ₀	d(Å)	I/I ₀	d(Å)			
30	3.017					(220)		
50	2.942	30	2.976	20	2.945	(202)		
40	2.656	50	2.668	80	2.668			(104)
90	2.555	70	2.561	30	2.550	(311)		
30	2.520	55	2.527	30	2.519		(311)	
70	2.470	40	2.477	60	2.470	(113)		(110)
		40	2.419			(222)		
		30	2.179	50	2.177			(113)
40	2.127	30	2.131	10	2.123	(400)		
60	2.075	100	2.076	20	2.077	?	(400)	
40	2.026	20	2.032	10	2.029	(004)		
20	1.814	20	1.814	50	1.815			(024)
50	1.722	10	1.727			(242)		
40	1.673	45	1.673	100	1.672			(116)
70	1.636	25	1.635	25	1.635	(511)		
50	1.612	25	1.614			(333)		
		25	1.600	25	1.598			(122)
				20	1.577	(115)		
40	1.521							
30	1.506					(440)		
100	1.467	60	1.474	60	1.472	(404)	(440)	(214)

tracted residues are given in Table 10.

From the experimental results above described, it can be said that the decomposition of *c/a*=0.95 type iron chromite needs longer holding time at high temperature or slower solidifying velocities. It is also understood that the formation of FeO·Cr₂O₃ requires some holding time at high temperature from the fact that the amount of FeO·Cr₂O₃ increases in case of the specimen which is cast into iron mould and held one hour at 800°C.

It seems adequate to think that their results may have been obtained by rapid solidification of the samples because Cr₃O₄ appears in all the samples containing higher chromium.

Hilty, et al.'s results are as follows :

	Low chromium	Medium chromium	High chromium	Very high chromium
Ingot sample	Chromite	Distorted spinel Cr ₃ O ₄ Chromite Cr ₂ O ₃	Cr ₇ O ₄ Cr ₂ O ₃ Chromite	Cr ₃ O ₄ Cr ₂ O ₃ Chromite

(4) In extraction of nonmetallic inclusions formed in steels it is important not to destroy their original structure. In this study, the authors applied the electrochemical isolating method and the solvent is-

olating one. In Photo 4, the diffraction patterns from the residues extracted by both bromine—and iodine methanol isolating methods are compared. From this, the occurrence of destruction of normal iron chromite is understandable.

(5) To know the cause of the formation of iron chromite with tetragonal structure, the authors performed a simple experiment adding synthesized normal iron chromite to molten pure iron. As a result, it was found that iron chromite played an important role in the formation of the distorted iron chromite in steels. When normal iron chromite is added into molten electrolytic chromium—in this case inclusion formed

Photo 4. Comparison of the diffraction patterns of inclusions extracted from 18% chromium steel with bromine- and iodine-methanol isolation (Cr K α)

is iron chromite having distortion degree of $c/a=0.86$ —the distortion degree of iron chromite increases to 0.89¹⁴⁾. Iron chromite is one of the end members of the formed inclusion which is in equilibrium with molten alloy, but it is not still clear what the other end members are. Cr_3O_4 , if exists, may be regarded as the other end member judging from the crystal structure, but the authors can not agree with the equation, $3\text{Cr}_3\text{O}_4 \rightarrow 4\text{Cr}_2\text{O}_3 + \text{Cr}$, which is presented by Hilty, et al.²⁾, because appearance of such metallic chromium is not recognized.

There were no papers reporting on the variation of the elements which compose inclusions under various experimental conditions. It is not easy to get the accurate chemical composition of the inclusions, because the amounts of the extracted residues are limited to the order of mg, and liable to be contaminated during extraction.

W. Koch, J. Bruch and H. Rohde have reported some interesting results— $c/a=0.97$ – 0.98 type iron chromite appears when the quenched specimens having only $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ as primary inclusions are annealed³⁾. Reason of this will be clarified afterwards if the authors could get the information about the variation of the elements composing inclusions.

R.E. Hook and A.M. Adair¹³⁾ suggested that through emission spectroscopy the inclusion extracted from ultra-pure chromium was found to contain about 10% of iron and this is in agreement with the result of Hilty, et al.²⁾ Indeed, iron plays an important role for the formation of inclusions in the Fe-Cr-O system.

In order to suppress the difficulty of analysis and to get information about the behaviour of iron, the authors conducted the activation analysis of the extracted residues by neutron irradiation. Through this analysis it was recognized that the percentage of chromium was increased in the inclusion extracted from lower chromium steel and decreased in those from

higher chromium steel on account of after-heat-treatment. In the case of the analysis of primary inclusion, chromium as the composing element was clarified from this experiment. These results obtained was able to explain from the variation of oxygen potential equilibrated with molten alloy of this system.¹⁵⁾

G.W. Healy and J.C. Schottmiller¹⁶⁾ informed that Cr^{2+} is stable at high temperature in the form of Cr_2SiO_4 co-existing with SiO_2 . However, as for the existence of CrO , G.W. Healy and J.C. Schottmiller¹⁶⁾, and W. J. Kramers and J.R. Smith¹⁷⁾ reported that there was no evidence of its formation. From these facts the formation of $\text{Cr}_3\text{O}_4 (\text{Cr}^{2+}\text{O} \cdot \text{Cr}_2\text{O}_3)$ at high temperature is not obvious. R.E. Hook and A.M. Adair¹³⁾ have reported that no evidence was found to support Hilty, et al.'s equation²⁾. The authors agree with this opinion, but their expression is contradictory when compared with the authors' experimental results obtained through the heat-treatment of the extracted residues.

Recently, A. Hoffmann¹⁸⁾ reported about equilibrium in the system $\text{FeO}-\text{Cr}_2\text{O}_3$. He has described the success in obtaining $c/a=0.87$ type iron chromite from 10%FeO and 90% Cr_2O_3 at the temperature of 1700°–1800°C in an arc furnace with tungsten electrode. But it is necessary to consider the possible effect of ionization under this experimental condition. The authors believe that in their experiment¹⁹⁾ $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ was formed at first at low temperature and it reacted with residual Cr_2O_3 , but it was not clear that they reacted mutually without other factors such as lattice disorder introduced under experimental conditions.

The authors succeeded to obtain iron chromite having axial ratio $c/a=0.95$ by dealing $\text{Fe}_2\text{O}_3-\text{Cr}_2\text{O}_3$ sesquioxide solid solution in the hydrogen-carbon-dioxide atmosphere at 1550°–1650°C.²⁰⁾

And also a phase diagram about $\text{FeO} \cdot \text{Cr}_2\text{O}_3-\text{Cr}_2\text{O}_3-\text{Fe}_2\text{O}_3$ was given.²¹⁾

P.V. Riboud and A. Muan²²⁾ have published the phase diagram of $\text{FeO}-\text{Cr}_2\text{O}_3$, but it is different from A. Hoffmann's. Considerable parts of the diagram have been brought to completion but the most important region is still obscure. The published diagrams are given in Fig. 3. The existence of Cr_3O_4 must be investigated from various viewpoints so that a complete solution may be obtained on the distorted iron chromite formed in this system. The characteristic shapes of the

(a) After Riboud and Muan²²⁾*

* Phase relations in an atmosphere consisting of a CO_2-H_2 mixture in ratio 1:1.

(b) After Hoffman¹⁸⁾

Fig. 3. $\text{FeO}-\text{Cr}_2\text{O}_3$ phase diagrams

Photo 5. Characteristic shapes of inclusions and limited electron diffraction patterns ($1/2$)

extracted residues and the limited electron diffraction patterns are given in Photo 5.

IV. Conclusions

The authors investigated the primary inclusions formed in the steels of Fe-Cr-O system when the chromium addition was changed from 0.7 to 99.4%, and studied also on their decomposing behaviours and secondary precipitates when the quenched specimens were heat-treated or when the specimens were solidified under various velocities. The results obtained are as follows:

(1) It was presumed that the lattice parameters a_0 of the inclusions formed in the steels of Fe-Cr-O system became larger with an increase of the amounts of chromium added. Conversely, the lattice parameters c_0 became smaller. From this phenomenon, it is difficult to accept Hilty, et. al's. description²⁾ saying that spinel and Cr_3O_4 are different matters.

(2) By heat-treatment of the residue extracted from 65% chromium steel, the appearance of metal-

lic chromium was not recognized, and therefore it became necessary to take consideration on the decomposition equation, $3\text{Cr}_3\text{O}_4 \rightarrow 4\text{Cr}_2\text{O}_3 + \text{Cr}$.

From the inclusion extracted from 18% chromium steel, chromic oxide and normal iron chromite appeared. The distorted iron chromite is regarded to be composed of chromic oxide and normal iron chromite.

(3) When normal iron chromite was added into molten chromium, the distortion degree of the formed iron chromite showed decrement. From this fact, one should admit an important role of iron chromite in the structure of nonmetallic inclusion equilibrated with molten alloy of this system.

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