Electron Probe Microanalysis of Titanium and Zirconium Carbonitride Inclusions in Steel*

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Synopsis

Titanium and zirconium inclusions in various steels are analysed by means of an electron probe microanalyser and an optical microscope.

As results, the titanium nitride and the solid solution of carbide and nitride are observed, and also those having the core structure are recognized. In a Cr-Mo steel, titanium carbides contain molybdenum.

Furthermore, it is found that the titanium nitride and carbide can be distinguished from their colour under an optical microscope.

In steels, behaviour of zirconium is similar to that of titanium, and angular zirconium inclusions are observed. These zirconium inclusions in a low carbon steel are also studied and the similar inclusions, ZrC, ZrN, and ZrC+ZrN, are identified.

I. Introduction

In steels containing titanium, angular non-metallic inclusions which formed in molten steel are observed with an optical microscope. They have been called titanium nitride (TiN) or titanium carbide (TiC) and sometimes called carbonitride because it is suggested that they are uniform solid solutions of nitride and carbide.¹⁾⁻⁴⁾

In the present work, these inclusions in various types of steel are investigated by means of an electron probe microanalyser (EPMA) and an optical microscope.

As results, the titanium nitride and the solid solution of carbide and nitride are observed, and also inclusions of the core structure are recognized.

Besides them, TiC which contains molybdenum is found in a Cr-Mo cast steel.

Furthermore, it is found that the TiN and TiC can be distinguished from their colour under an optical microscope.

In steels, behaviour of zirconium is similar to that of titanium, and angular zirconium inclusions which are

considered to be carbide, nitride or carbonitride are observed.⁵⁾ Zirconium carbide (ZrC) and zirconium nitride (ZrN) in a low carbon steel are studied and the similar results as titanium inclusions are obtained.

II. Experiment

1. Samples

Carbon steels containing titanium from 0.07 to 0.12%, 18-8 stainless steel and 20-30 heat resisting steel containing 0.42 and 0.38%Ti, respectively, were mainly examined. The compositions of the steels are listed in Table 1.

2. Electron Probe Microanalysis

An ARL-Shimadzu type electron probe microanalyser was used. The experimental conditions are shown in Table 2.

In X-ray spectroanalysis of nitrogen in TiN, the TiL α line overlaps on NK α lines. In Fig. 1 the spectra of NK α from boron nitride and TiL α from titanium metal are shown, and it is obvious that some amount of TiL α is included in measured results if we detect nitrogen at the wavelength of peak of NK α . In the present work, the NK α is detected at the shorter-wavelength shown by an arrow in Fig. 1, where the intensity of TiL α line is negligible.⁶⁾

III. Results

1. Titanium Nitride (TiN)

The titanium inclusion observed in the low alloy steel (Sample No. 1) is found to be nearly pure TiN. The optical micrograph of the inclusion is shown in

Table 1. Compositions of samples (wt%)

No.	Type of steel	C	Si	Mn	P	S	Cu	Cr	Ni	Ti	Mo	Zr
1	Low alloy steel	0.10	0.50	0.50	—	—	—	0.74	0.29	0.08	—	—
2	Medium carbon steel	0.38	0.27	0.72	0.010	0.010	0.05	0.05	—	0.10	—	—
3	High carbon steel	0.68	0.28	0.86	0.019	0.020	—	—	—	0.07	—	—
4	Cr-Mo cast steel	1.99	1.49	0.69	0.021	0.007	0.12	0.87	—	0.12	0.27	—
5	18-8 stainless steel	0.06	0.48	1.60	0.021	0.008	0.07	17.65	12.23	0.42	0.06	—
6	20-30 heat resisting steel	0.08	0.55	1.23	0.022	0.007	0.11	20.50	32.50	0.38	0.10	—
7	Low carbon steel	0.17	0.41	1.34	0.022	0.022	—	—	—	—	—	0.07

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Table 2. Analysing condition of electron probe microanalyser

Analysing crystal	Rowland circle radius (inch)	Line
Pb-stearate	4	CK α (I) NK α (I)
ADP	4	ZrL α (I) MoL α (I)
LiF	4	TiK α (I) CrK α (I) FeK α (I)
SiO ₂	11	FeK α (I)
LiF	11	ZrK α (I) MoK α (I)

Accelerating voltage: 15 to 30 kV

Sample current: 0.05 to 0.15 μ AProbe size: 0.3 to 0.5 μ

Photo. 1(a) and its colour is orange yellow. The results of line analysis across the inclusion is shown in Fig. 2(a).

Fig. 1. Spectra of NK α and TiLl

Fig. 2. Line analysis of titanium inclusions

- (a) Low alloy steel (Sample No. 1)
 (b) Medium carbon steel (Sample No. 2)
 (c) High carbon steel (Sample No. 3)
 (d) Cr-Mo cast steel (Sample No. 4)

Experimental condition:

15 kV, 0.11 μ A	TiK α	10 000 cps full scale
	FeK α	2 000 cps full scale
	CK α	2 500 cps full scale
	NK α	500 cps full scale

2. Titanium Carbonitride [Ti(C, N)] Which Is a Solid Solution of Carbide and Nitride

Both inclusions observed in the medium carbon steel (Sample No. 2) and the high carbon steel (Sample No. 3) are solid solution of TiC and TiN which are usually called titanium carbonitride, Ti(C, N). The line analysis of the inclusion in Sample No. 2 is given in Fig. 2(b) and its colour is similar to TiN.

The ratio of TiC to TiN in Ti(C, N) in the high carbon steel (Sample No. 3) is higher than that of medium carbon steel (Sample No. 2), and the line analysis is shown in Fig. 2(c).

3. Titanium Molybdenum Carbide [(Ti, Mo)C]

In the examined steels, pure TiC inclusion was not found but TiC containing molybdenum was found in Cr-Mo cast steel (Sample No. 4).

The colour is bluish white as shown in Photo. 1(b).

Figure 2(d) shows the line analysis across the above inclusion, where NK α is scarcely detected. This also means that the separation of TiL α from NK α is successful.

In Fig. 2(d), the intensity of TiK α is weaker than those of Figs. 2(b) and (c), because this inclusion is a solid solution of TiC and Mo₂C.

4. Core Structure: [(Ti, Mo)C+TiN] and [TiC+TiN]

In Cr-Mo cast steel (Sample No. 4), 18-8 stainless steel (Sample No. 5), and 20-30 heat resisting steel (Sample No. 6), non-metallic inclusions having core structure which consists of carbide and nitride were found. In these cases, the nitride always concentrated in the center of the inclusion is surrounded by the carbide.^{6),7)}

In the Cr-Mo cast steel, the surrounding carbide contains molybdenum, and in the stainless steel and the heat resisting steel, the carbide is TiC only.

Photograph 1(b) is an optical micrograph of the core structure type inclusion found in the Cr-Mo cast steel. The core and the surroundings can be distinguished by their colour. Figure 3(a) shows the result of line analysis which has been presented in our previous paper,⁷⁾ where the NK α was not completely separated from TiL α and the magnitude of the overlapping is shown by the broken curve. At that time, the reason why TiK α intensity decreases in the surrounding carbide was not understood. As shown by line analysis of molybdenum in Fig. 3(b), the reason is the coexistence of molybdenum in the carbide.

The electron beam scanning images (EBS) of the core structure inclusion are shown in Photo. 2.

In the 18-8 stainless steel and the 20-30 heat resisting steel, almost all inclusions have the core structure, TiC+TiN, and EBS images of the inclusion in the 18-8 steel are shown in Photo. 3.

Figures 4(a) and (b) are the line analysis results of the inclusions in the 18-8 stainless steel and the 20-30, heat resisting steel, respectively, and they show that molybdenum does not exist in carbide, although a small quantity of molybdenum exists in matrix. The

Fig. 3. Line analysis of the core structure type inclusion in Cr-Mo cast steel

(a) 20 kV, 0.15 μ A	TiK α	20 000 cps full scale
	CK α	2 000 cps full scale
	NK α	1 000 cps full scale
(b) 30 kV, 0.05 μ A	TiK α	10 000 cps full scale
	MoK α	200 cps full scale
	CK α	500 cps full scale

boundary between TiC and TiN is not clear compared to that of the Cr-Mo cast steel, and a gradual change of carbide and nitride ratio is observed. Carbon content in the core nitride and nitrogen content in the surrounding carbide are not clear, because the resolving power of EPMA is essentially about 1 μ .

5. Zirconium Carbide (ZrC), Zirconium Nitride (ZrN), and Core Structure (ZrC+ZrN)

In the low carbon steel containing zirconium (Sample No. 7), ZrC, ZrN, and the core structure (ZrC+ZrN) were observed. In the core structure

Photo. 1.
Optical micrographs of titanium inclusions
(a) In low alloy steel (Sample No. 1)
(b) In Cr-Mo cast steel (Sample No. 4)
10 μ

Photo. 2.
Images of the core structure type inclusion in the
Cr-Mo cast steel (corresponding to Photo. 1(a)).
Experimental condition :
30 kV, 0.05 μ A (MoL α , FeK α , CrK α , TiK α ,
NK α , and CK α)
S.C. : sample current
B.S.E. : back-scattered electron

inclusion, ZrN exists in the core and ZrC surrounds the nitride.

As shown in Photo. 4, the colour of the ZrC is orange and that of ZrN is yellowish white, and the core structure inclusion shows the colours corresponding to their constituents.

Figure 5 shows the line analyses of ZrC, ZrN, and the core structure (ZrC+ZrN). The intensities of CK α and NK α are weaker than those of titanium inclusions due to the larger absorption coefficient of zirconium. The background levels of CK α and NK α shown in Fig. 5 increase in zirconium inclusion than

Photo. 3. EBS images of the core structure type inclusion in the 18-8 stainless steel.
Experimental condition : 20 kV, 0.15 μ A (TiK α , NK α , and CK α)

Photo. 4. Optical micrographs of zirconium inclusions

Fig. 4.
Line analysis of the core structure type inclusions
(a) 18-8 stainless steel (Sample No. 5)
(b) 20-30 heat resisting steel (Sample No. 6)
30 kV, 0.05 μ A TiK α 10 000 cps full scale
 MoK α 200 cps full scale
 CK α 500 cps full scale
 NK α 100 cps full scale

Fig. 5. Line analysis of zirconium inclusions in low carbon steel (Sample No. 7)

- (a) ZrC
(b) ZrN
(c) ZrC+ZrN

Experimental condition :

15 kV, 0.11 μ A	FeK α	2 500 cps full scale
	ZrL α	9 000 cps full scale
	CK α	100 cps full scale (40 cps base line)
	NK α	80 cps full scale (40 cps base line)

that of matrix because the continuous X-rays increase.

6. Quantitative Analysis

Results of the quantitative analysis of metallic elements in inclusions are given in Table 3. The atomic number corrections given by Poole and Thomas⁸⁾ and the modified Philibert's absorption correction^{9),10)} were applied, where the mass absorption

coefficients were quoted from the Birks' table.¹¹⁾ Corrected results agree well with the stoichiometric value.

Quantitative analysis of carbon and nitrogen constituent in the inclusion cannot be completed because the mass absorption coefficients of titanium or zirconium for CK α and NK α are not decided. The quantitative analyses of carbon and nitrogen in the titanium inclusions will be given using the experimental results shown in the present paper in the near future.

IV. Conclusion

The angular titanium inclusions in steels, which have not been precisely identified hitherto, were analysed by an electron probe microanalyser, and it was found that their structures depend on the composition of matrix steel.

In conclusion, the results are listed in Table 4.

In solid solution type inclusion, the carbide concentration increases with an increase of carbon content in the matrix.

The appearance of the core structure inclusion means that the temperature of precipitation is different for nitride and carbide, and nitride precipitates at an early stage in cooling and solidification of molten steel.

But the reason why the core structures are observed in the Cr-Mo cast steel and the high alloy steels cannot be interpreted, and it is necessary to investigate the effect of alloying elements on the precipitation.

In the Cr-Mo cast steel, molybdenum was detected in TiC. This inclusion is suggested to be a solid solution of Mo₂C and TiC which has been reported by Elemenko *et al.*¹²⁾

The colour of TiC is bluish white and TiN is orange yellow, and they are distinguished by the optical microscopic observation.

The similar combination of carbide and nitride were observed in zirconium inclusion in the low carbon steel.

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Table 3. Quantitative analysis of metallic elements in inclusions

Precipitate	Matrix	I_A^{AB}/I_A^{A1}			Corrected (Weight fraction)			Total ²⁾ (Weight fraction)
		TiK α	MoL α	ZrL α	Ti	Mo	Zr	
TiC	Synthetic	0.734	—	—	0.798	—	—	0.998
(Ti, Mo) C	Cr-Mo cast steel	0.490	0.166	—	0.583	0.247	—	0.729+0.278=1.007 ³⁾ 0.729+0.262=0.991 ⁴⁾
TiN	Low alloy steel	0.703	—	—	0.765	—	—	0.988
ZrC	Low carbon steel	—	—	0.854	—	—	0.885	1.001
ZrN	Low carbon steel	—	—	0.856	—	—	0.894	1.032

1) Acc. volt. 30 kV 2) As stoichiometric compound 3) TiC+MoC 4) TiC+Mo₂C

Table 4. Titanium inclusions in steels

No.	Type of steel	Composition of steel				Structure of inclusion
		C	Cr	Mo	Ti	
1	Low alloy steel	0.10	0.14	—	0.08	TiN
2	Medium carbon steel	0.38	0.05	—	0.60	Ti (C, N)
3	High carbon steel	0.68	—	—	0.07	Ti (C, N)
4	Cr-Mo cast steel	1.99	0.87	0.27	0.12	TiN+(Ti, Mo) C
5	18-8 stainless steel	0.06	17.65	0.06	0.42	TiN+TiC
6	20-30 heat resisting steel	0.08	20.80	0.10	0.33	TiN+TiC

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