Analysis of Free Magnesium by Spectrometer

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2nd. K.D.Millis World Symposium on Ductile Iron
Hilton Head Island, SC
October 20-22, 1998

ABSTRACT

A new concept which free magnesium might be the key phase on the graphite spheroidization in spheroidal graphite irons would be proposed and verified in this study. The chilled samples contained the different amount of magnesium were prepared and chemically analyzed on the total and inclusive phase using Inductively-coupled Vacuum Plasma Spectrometer. Free magnesium was calculated as the balance of their values. Free magnesium stepwise increased as total magnesium increased. On the other hand, inclusive magnesium was almost equal among the chilled samples. The same series of chilled samples as the above were also analyzed using spectrometer in conjunction with pulse-hight distribution analysis system. The good relationship between the pulse behaviour and the value of free magnesium was obtained, similar to total magnesium in conventional way. The nodularity and the tensile properties of 50mm Y-block showed the good relationship to the value of free magnesium.

INTRODUCTION

In the metallurgical point of view, magnesium is the deoxidizer and desulfurizer element for liquid iron. If magnesium was added the amount over the stoichiometric composition against the free oxygen and sulfer content, magnesium would exceed in liquid iron as both the agents. The excessive amount of magnesium is defined free magnesium in this study. According to the site theory[1)2)] proposed by the author, it is considered that most of free magnesium would have to be gas state and exist as gas bubble in liquid iron because of the low boiling point and less solubility. Gas bubble is considered as an initial site to nucleate and grow spheroidal graphite. The trace of magnesium gas bubble participating in spheroidal graphite have analytically verified. On the other hand, the rest of magnesium would exist as inclusions such

as oxide, sulfide, oxy-sulfide. Many researchers have believed that those inclusions act as the nucleous for the spheroidal graphite formation. However, nobody found the evidence how inclusions affaired spheroidal graphite to grow the final form. The results in this study would show which phase of magnesium affaired the formation of spheroidal graphite.

The elements which have strong tendency to form stable precipitates are rather easy to analyze their metallic phase using spectrometer in conjunction with pulse-hight distribution analysis system[3]. This is because there is big difference between the metallic phase and precipitates on the spectrum intensity in such elements. The spectrum intensity detected at the analyzed spot containing inclusions is much higher than that containing only metallic phase. In the system, each spectrum intensity detected during discharging is exchanged for pulse hight and arranged into the distribution. The pulse-hight distribution would appear two peaks in the case of magnesium. One is for the area with inclusive magnesium and show an unclear peak. Another is for the area with only metallic magnesium and shows a clear peak. The principle for the phase analysis on magnesium using spectrometer with the PDA system is schematically illustrated as shown in Fig.1.

In this paper, the analytical procedure of free magnesium would be introduced, and then, the result would be compared with the nodularity and the tensile properties.

EXPERIMENTAL PROCEDURE

Base iron was smelted in low frequency induction furnace. After chemical composition was adjusted, the liquid iron was once superheated over 1500℃ for about five minutes. Since tap weight was different among heats, tap temperature was changed at the range from 1405℃ to 1480℃. This is because some heats were tapped only for

the experimentation but some others were tapped for practical casting in foundry, too. Nodulization and inoculation were conducted by sandwitch method during tapping. Fe-Si-5.5Mg and Fe-75Si alloys were used for each agent. The chilled samples for analysis were taken from magnesium-treated liquid irons. Metal mold for the sample is shown in Fig.2. The total magnesium content was stepwise adjusted the different content among seven heats adding different amount of Fe-Si-5.5% alloy. The aimed content was rapidly checked with the same spectrometer as used for the free magnesium analysis, but by conventional procedure. To survey the degree of deoxidation in liquid irons with different magnesium levels, free oxygen was measured in each heat after the magnesium treatment using EMF (electro-motive force) probe. 50mm Y-block was cast in furan-bonded sand mold in each heat. It took about three minutes from the finish of the magnesium reaction to the cast.

Total magnesium was analyzed using Inductively-coupled Vacuum Plasma Spectrometer (ICP). Inclusive magnesium was, however, analyzed by complicated method. At first, inclusions such as oxide, sulfide, nitride in the chilled samples were electrolytically extracted using the apparatus shown in Fig.3. The electrolytical extraction was conducted as each sample lost the weight of about 0.5g. The magnesium content in extracted inclusions was then analyzed using ICP. The process of the electrolytical extraction and the analysis is shown in Fig.4. Free magnesium was calculated according to Formula (1);

$$\text{Free Mg} = \text{Total Mg} - \text{Inclusive Mg} \quad \text{---(1)}$$

The other chilled samples in the series of heats were analyzed using spectrometer in conjunction with pulse-hight distribution analysis system[3]. For total magnesium, the middle value in the total frequency distribution is selected and investigated the corelation against the chemically analyzed value. For free magnesium on the other hand, the frequency distribution of metallic magnesium is integrated and the value was investigated the corelation against the analyzed value. Since pre-discharge was

conducted at every analysis, the contamination of the analyzed surface had not to be considered. The sequence for the magnesium phase analysis set in spectrometer is shown in Fig.5. The voltage for discharge and the wave length for detecting the luminous spectrum of magnesium was set at 330V and 280.2nm respectively.

Tensile properties of 50mm Y-block in each magnesium level was examined at the position shown in Fig.6. The microstructure was examined at the holder of every tensile test piece.

RESULTS

(1) Sampling

The chemical composition of chilled samples and the free oxygen content in magnesium treated liquid irons are shown in Table 1. The residual magnesium content could be controlled for every heat as approximately aimed. The decrease of sulfer and free oxygen content was observed in every heat after liquid treatment. For example, the chemical composition including free oxygen of base iron for heat No.5 is shown in Table 1.

The microstructure of analyzed surface is shown in Fig.7. Although magnesium treated liquid irons were poured into metal mold, sphere graphite precipitated at the analyzed surface and the diameter was 3-5μm. Most of inclusion was the size of 0.5-5 μm. Big inclusion about 20μm was rarely observed. Besides sphere graphite and inclusion, the similar size of void were observed. The number of sphere graphite at the center area was greater than that at the periphery area.

(2) ICP analysis

The result of ICP analysis on total and inclusive magnesium are shown in Table 2. The calculated value of free magnesium is also shown in Table 2. The total magnesium content was quite a close to the result of conventional emission spectrum analysis as

shown in Table 1. There was no big difference on the inclusive magnesium content among the chilled samples although the total magnesium content was stepwise different. In other words, the deoxidation degree was considered to be nearly equal among the series of magnesium treated liquid irons, as shown in the result of the free oxygen measurement. The similar condition was forecast on the desulfurization.

(3) Emission spectrum analysis

An example of the pulse profile on magnesium in sample No.6 is shown in Fig.8. The intensity from free magnesium was about half of the maximum value in this case. On the other hand, the intensity from inclusive magnesium was over about seventy per cent of maximum value. The plots of chemical analysis value to spectrum intensity on both total and free magnesium are shown in Fig.9. There were good relationships between them in both phases of magnesium. In other words, good calibration curve was obtained for both. In the case of total magnesium curve, the data obtained in this study were additionally plotted on conventional one.

The analysis mark was observed using SEM. The SEM photograph is shown in Fig.10. As the result, many spots with crater-like hollow were observed. The hollows were formed by vaporizing the sample surface during discharging. The analytical information was get from there. It is said that the diameter and the depth are about the same and are 5-20μm. However, there were so many hollows which the size was out of this range

(4) Micro and mechanical properties in test samples

The microstructure of 50mm Y-block in each magnesium level is shown in Fig.11. Spheroidal ratio increased with increasing the free magnesium content. There was no relation to the content of inclusive magnesium on that ratio. It seemed that spheroidal ratio almost saturated when the content of free magnesium exceeded about 0.030 mass% against the sulfur range of 0.012-0.015 mass%. This was also true of the tensile properties as shown in Table 3. All properties changed with the content of

free magnesium.

CONSIDERATION

Although ledeburite cementite was also extracted with oxide, sulfide and nitride when magnesium in inclusion was analyzed, this would not influence the above experimental results. There is the fundamental reason why ledeburite cementite would not contain magnesium. Magnesium atom had little possiblity to form the substitutional and interstitial type solid solution in ledeburite cementite because of the atomic size. The diameter of magnesium atom (3.20Å[5]) is much bigger than that of iron atom (2.48Å[5]) and carbon atom (1.54Å[5]). The results of emission spectrum analysis support that magnesium had almost no solubility into cementite lattice showing good corelation to chemical analysis. If magnesium could resolve into ledeburite cementite, magnesium might evenly distribute in cementite and the content of inclusive magnesium would be much higher than this study. Magnesium also had almost no solubility into austenite because of the same reason as ledeburite cementite. It is considered that free magnesium could distribute at the interfacial site between ledeburite cementite and austenite. Most of free magnesium would exist as gas bubble, as mentioned in introduction. If it was true, the distribution of free magnesium would be dotted with spots as a trace of gas bubble. For example, many voids were actually observed in this study. The precipitation of magnesium carbide might have no chance in chilled sample because it was unstable over about 660℃[6].

According to the detail observation recently reported by T.Skaland[7], the size of magnesium contained inclusion in ϕ30mm sample was mentioned as 0.4-2.0μm. Y.Igarashi[8] also reported it was about 1.0μm. In this study, inclusion was 0.5-20μm. These figures are all the result of 2-dimensional (2-D) observation. The measured 2-D

diameters (dA) can be converted into 3-D values (dv) through formula[9](2);

$$dv = da \cdot \pi/2 \quad ---(2)$$

The actual size must be surely bigger than the pore of nucleopore filter (0.2μm). Magnesium contained inclusion in chilled samples would be all extracted and chemically analyzed exactly.

The analysis result of free magnesium correlated with the nodularity and mechanical properties but that of inclusive magnesium did not. This means that the content of free magnesium is an indispensable factor for the graphite spheroidization but that of inclusive magnesium is not. The precise quality control of spheroidal graphite cast iron should be discussed and conducted with the content of free magnesium.

Magnesium is the best element for the graphite spheroidization in liquid state because of the vaporization and solubility behaviour at the temperature range from the magnesium treatment to the solidification finish.

CONCLUSIONS

1) Free magnesium as metallic phase in chilled sample could be analyzed with high accuracy using spectrometer in conjunction with pulse-hight distribution analysis system.
2) When total magnesium increased, free magnesium also increased but inclusive magnesium had almost no change.
3) When free magnesium increased, the nodularity and tensile properties also increased.

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ACKNOWLEDGEMENT

I wish to express appreciation to Mr.Makoto Fujino for his operation of spectrometer and to Miss Chiaki Takano for her kind support.

LIST OF FIGURE CAPTIONS

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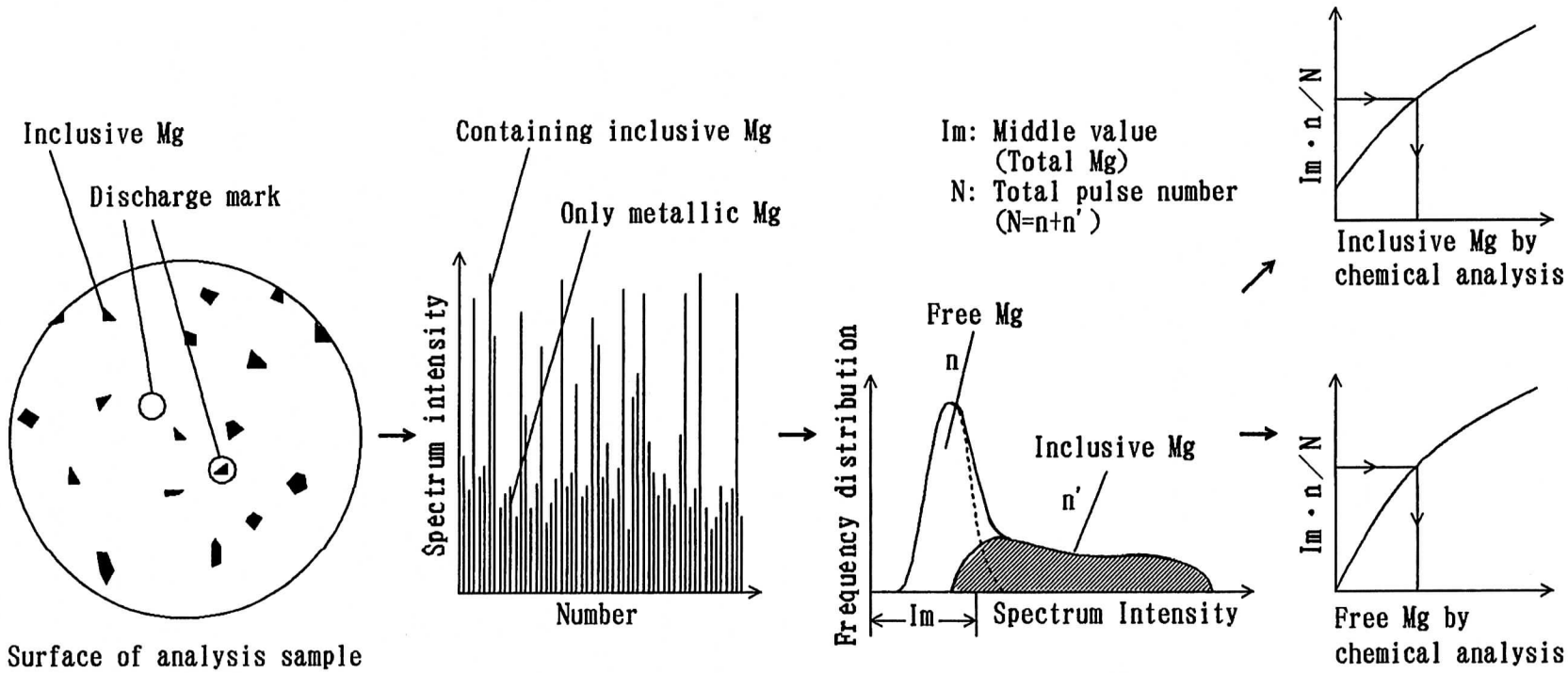


Fig.1 Principle of phase analysis for magnesium in chilled sample of spheroidal graphite iron. Illustration for aluminium analysis in reference[3] was arranged for magnesium.

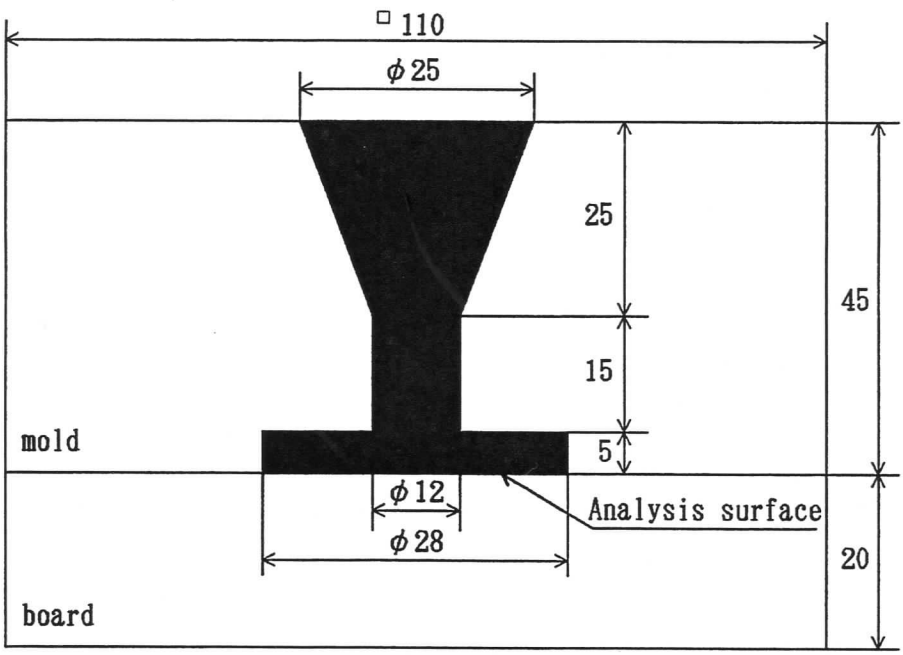


Fig.2 Steel mold and board for sampling.

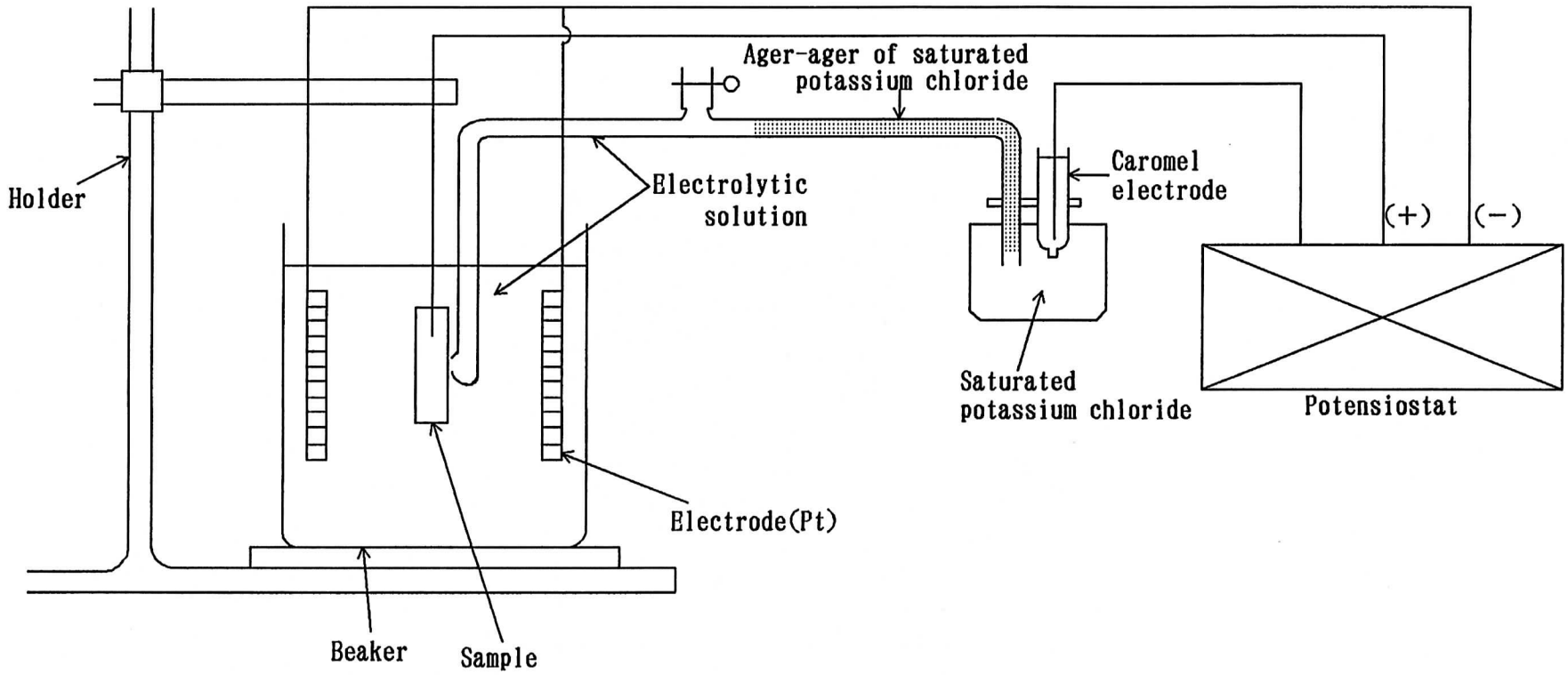


Fig.3 Apparatus for electrolytic extraction.

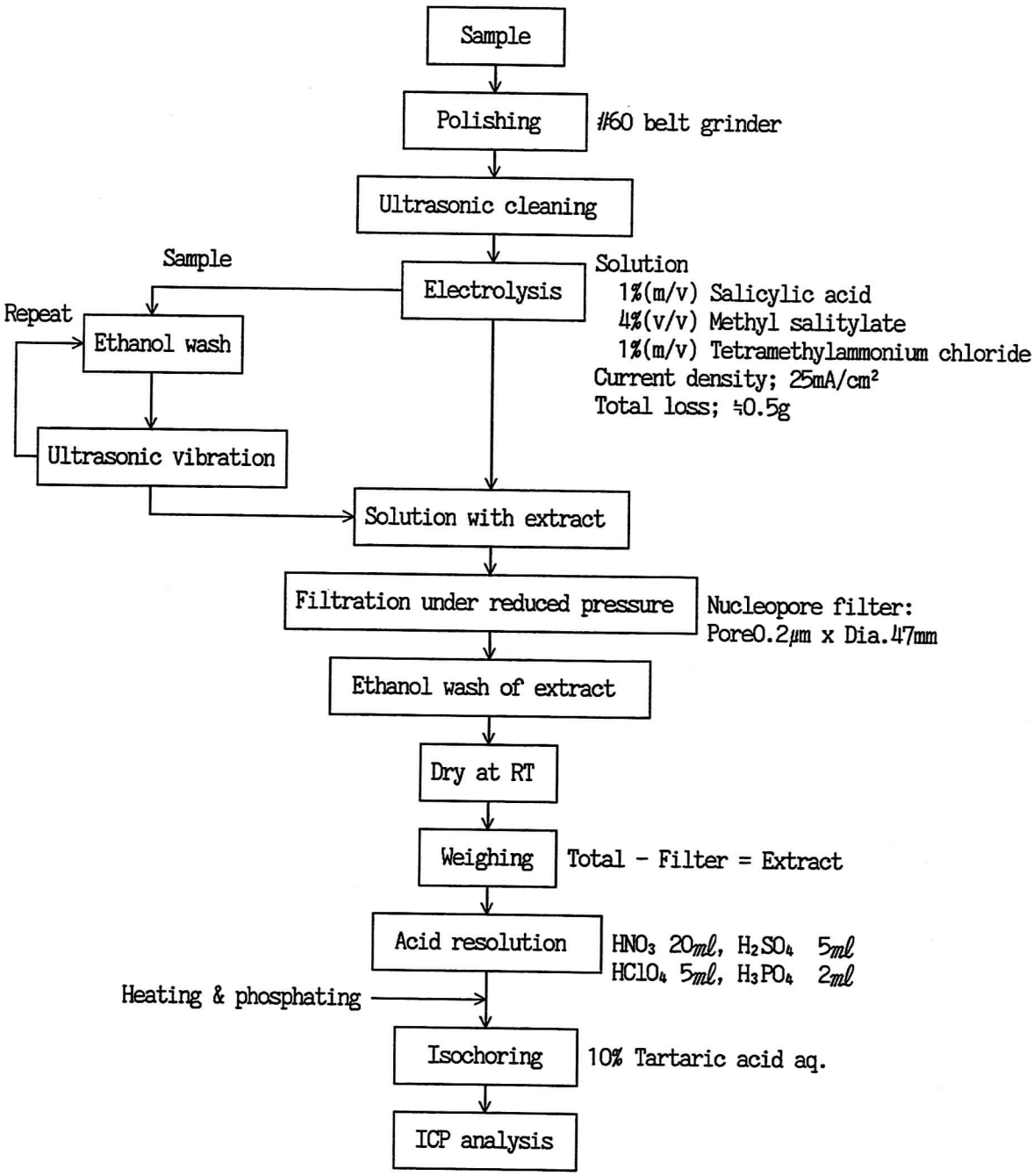


Fig.4 Flow chart of electrolytical extraction and determination for inclusive magnesium.

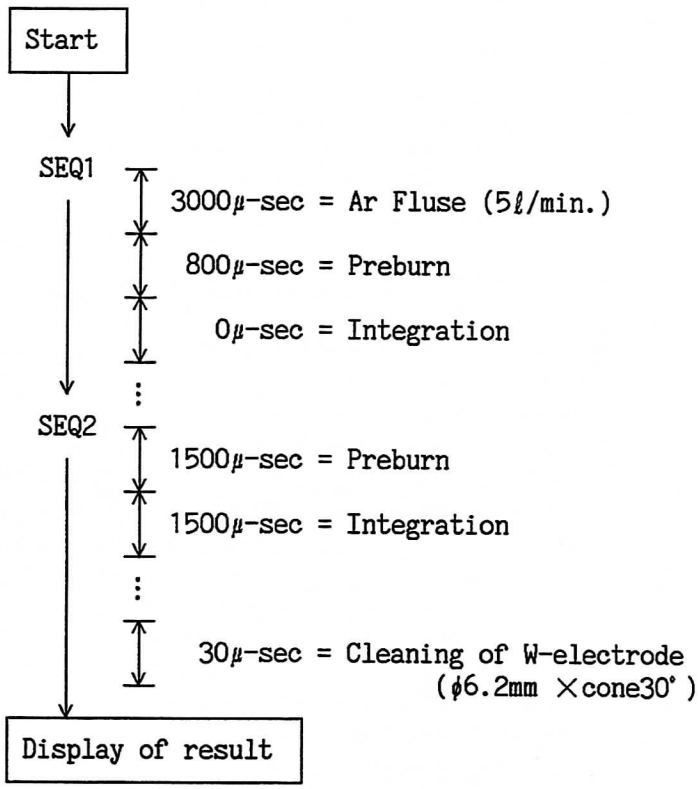


Fig.5 Sequence set in spectrometer for magnesium phase analysis.

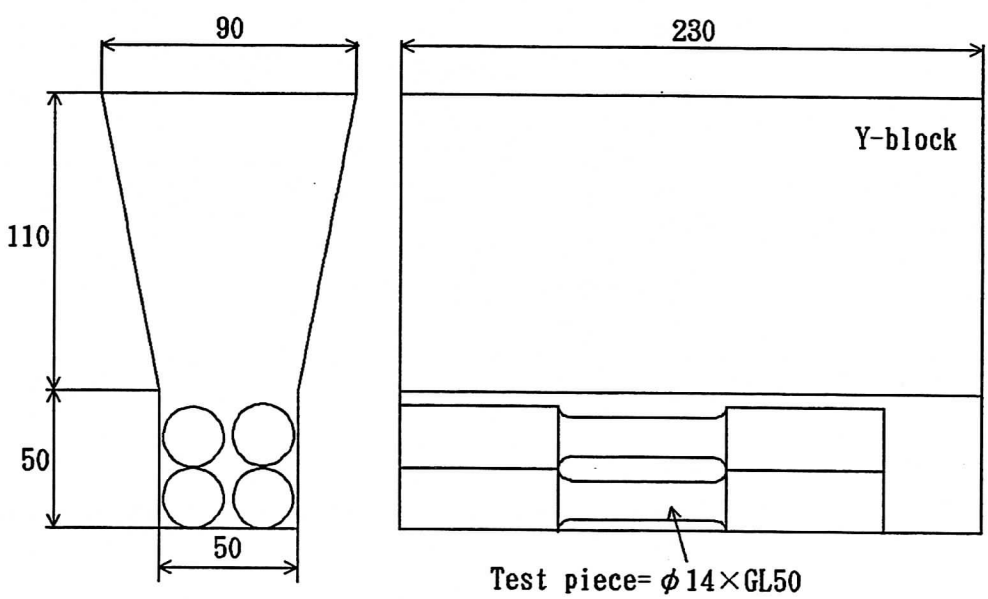
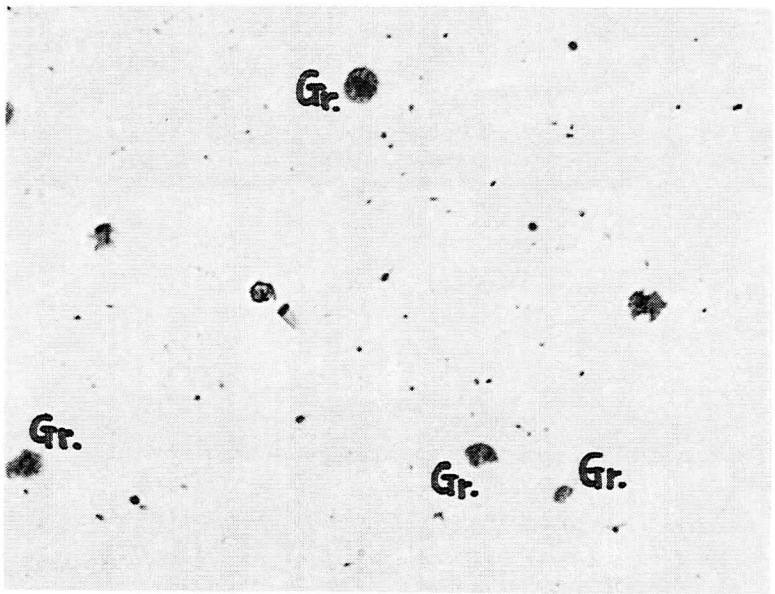
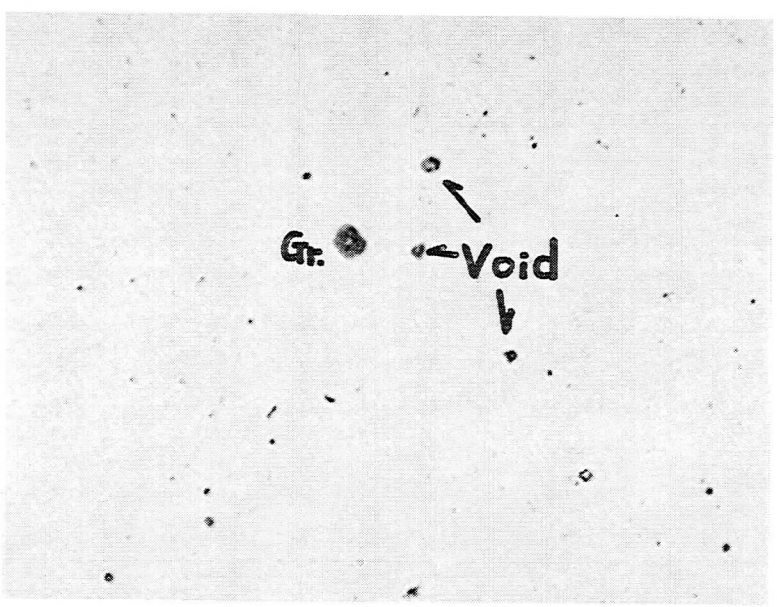


Fig.6 Schematic illustration of Y-block and tensile test pieces (mm).



a. Center



b. Periphery 10μm

Fig.7 Microstructure of analyzed surface in chilled sample No.6 (2% Nital etch).

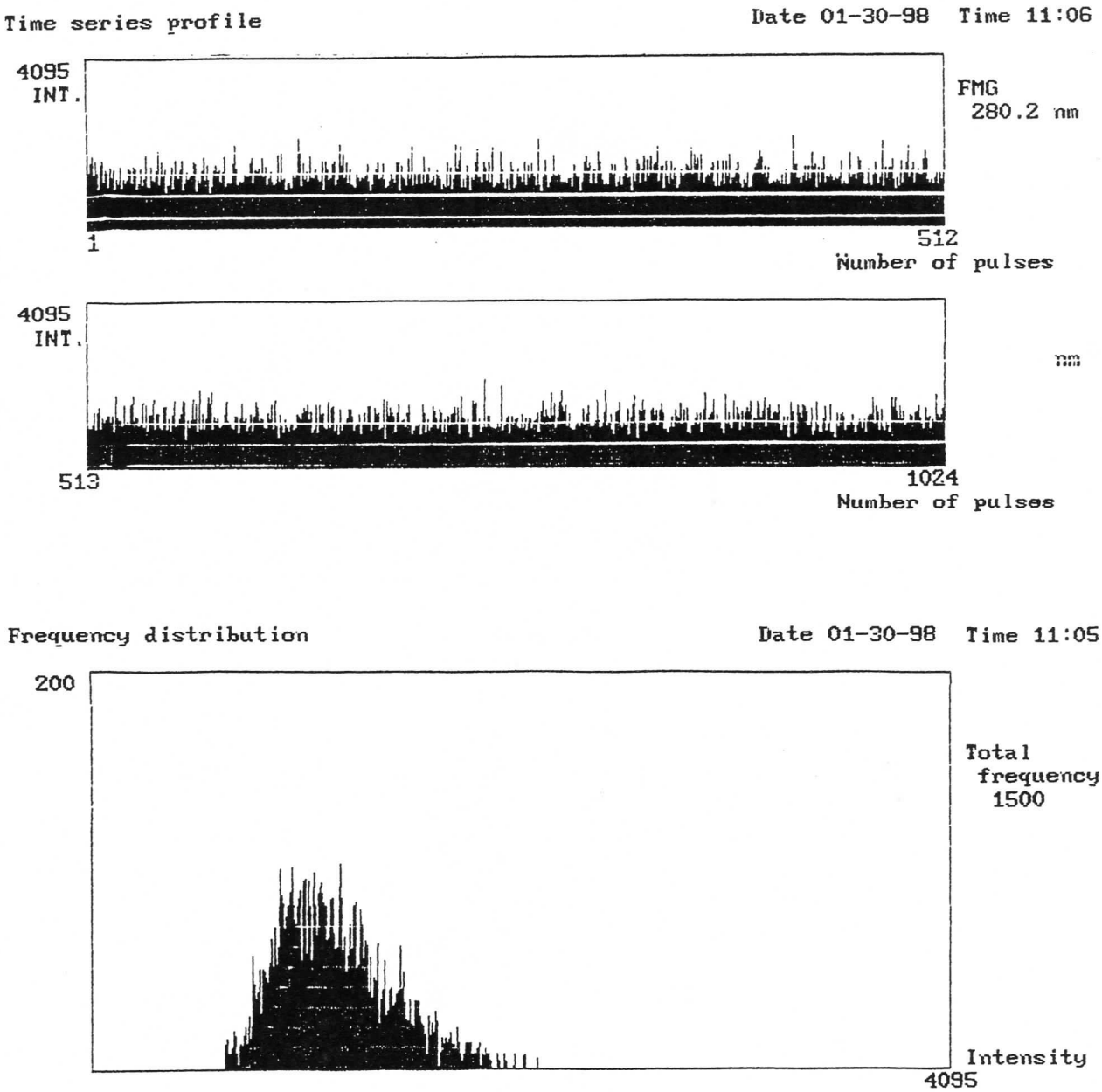
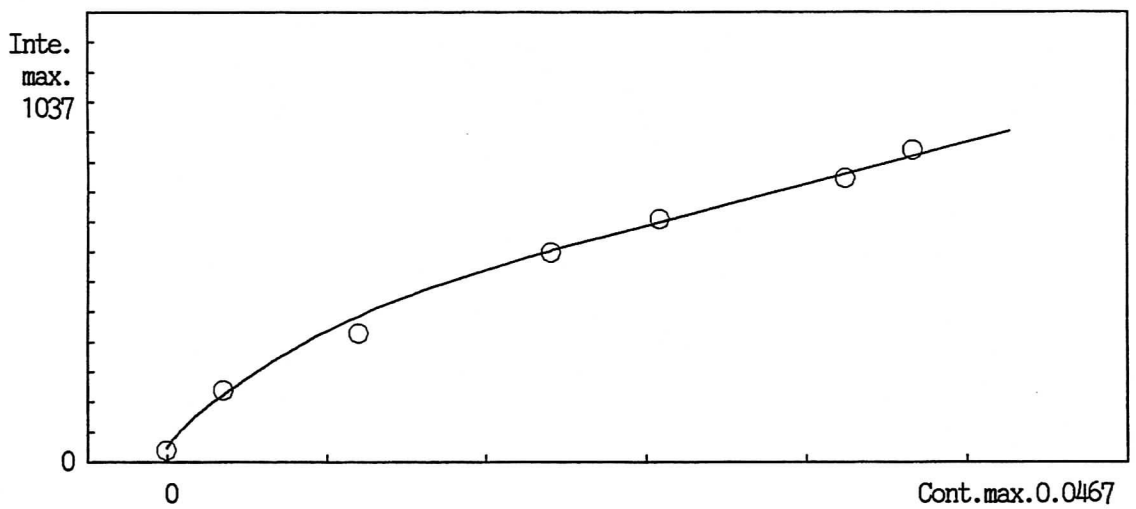


Fig.8 Example of pulse profile detected by discharging (Sample No.6).



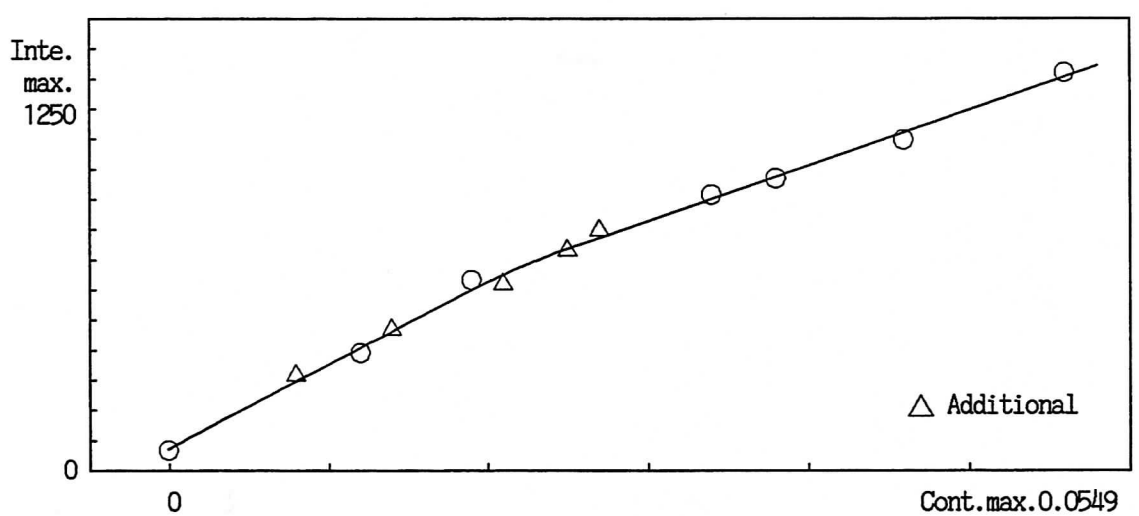
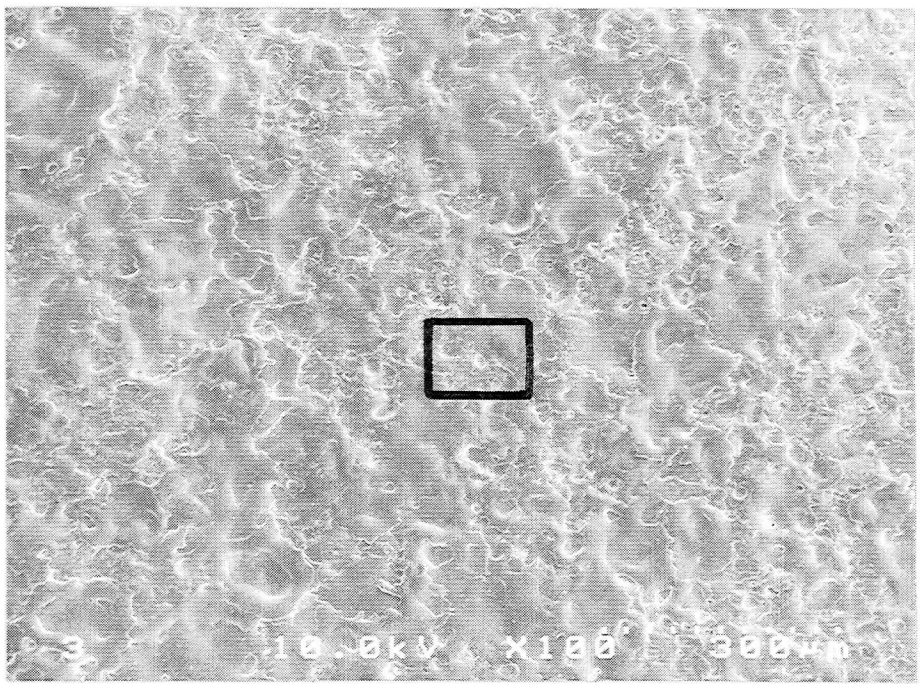
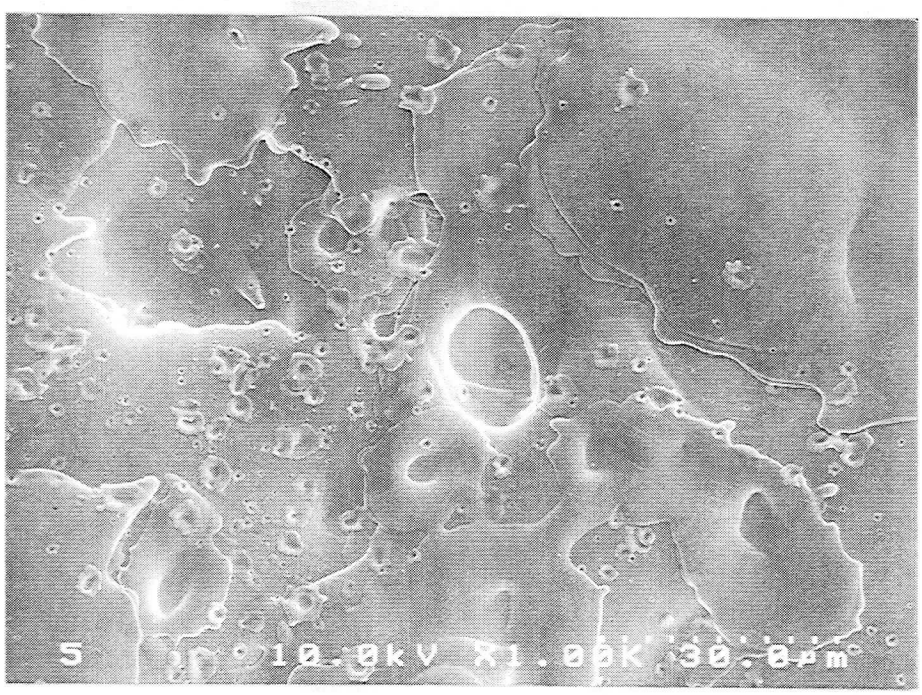


Fig.9 Calibration curve for magnesium phase analysis by emission spectrometer.



300μm

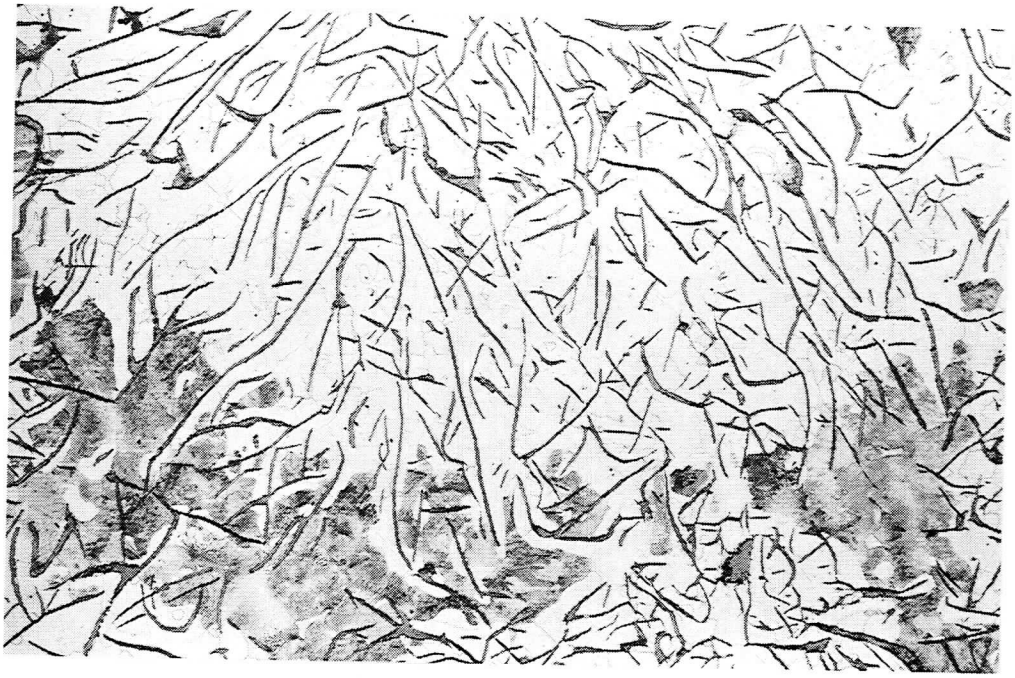
a. Low magnification



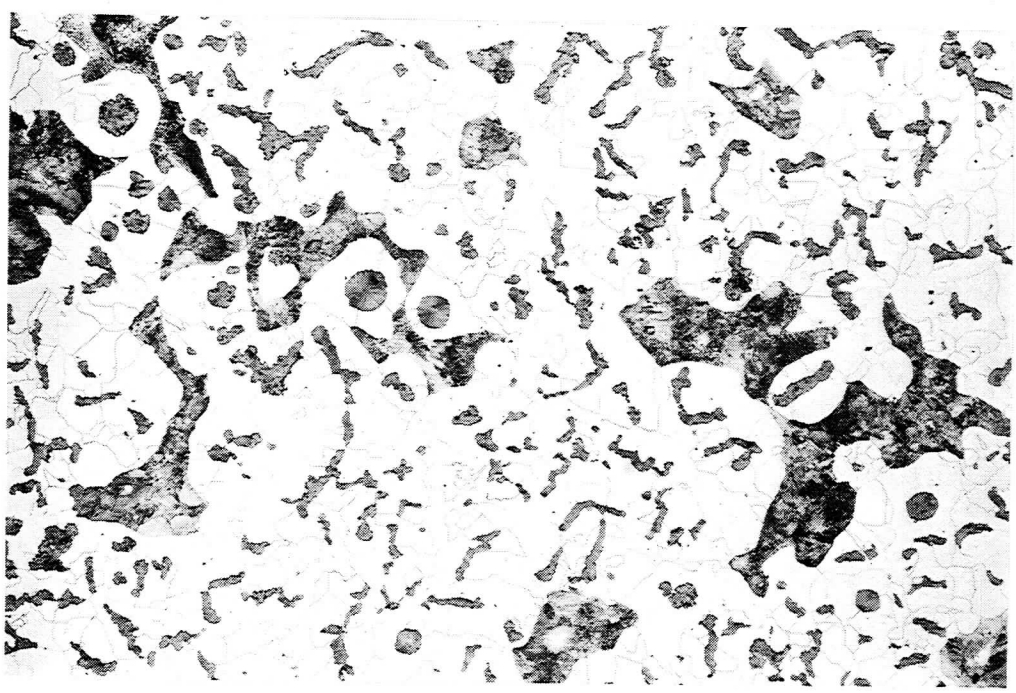
30μm

b. High magnification

Fig.10 SEM photograph of analysis mark in chilled sample No.6.

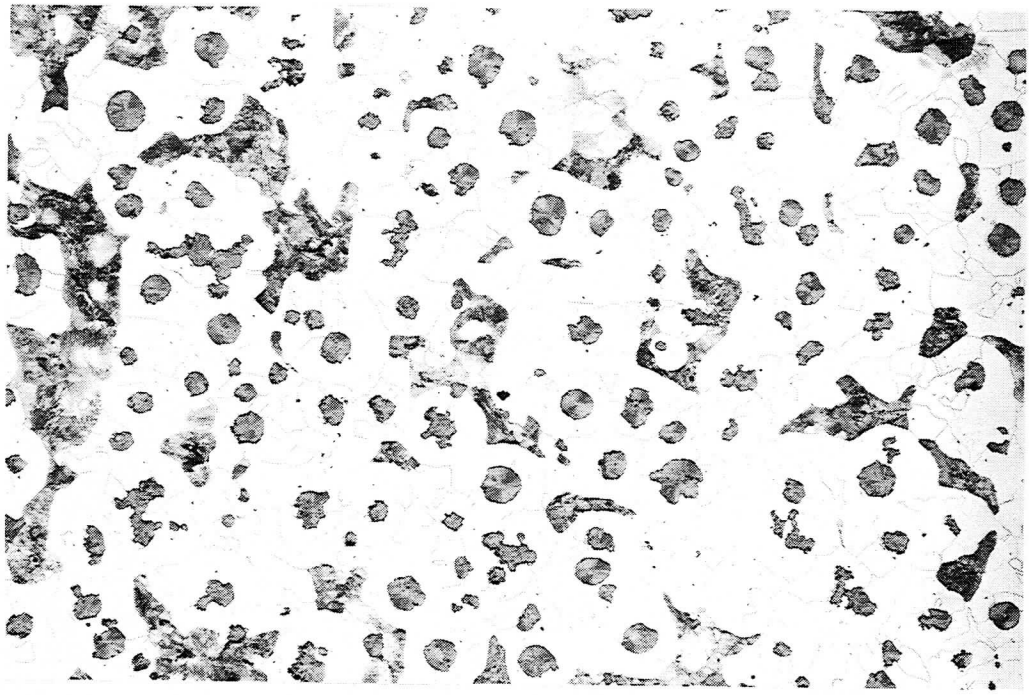


a.0.0114T•Mg, 0.0038F•Mg

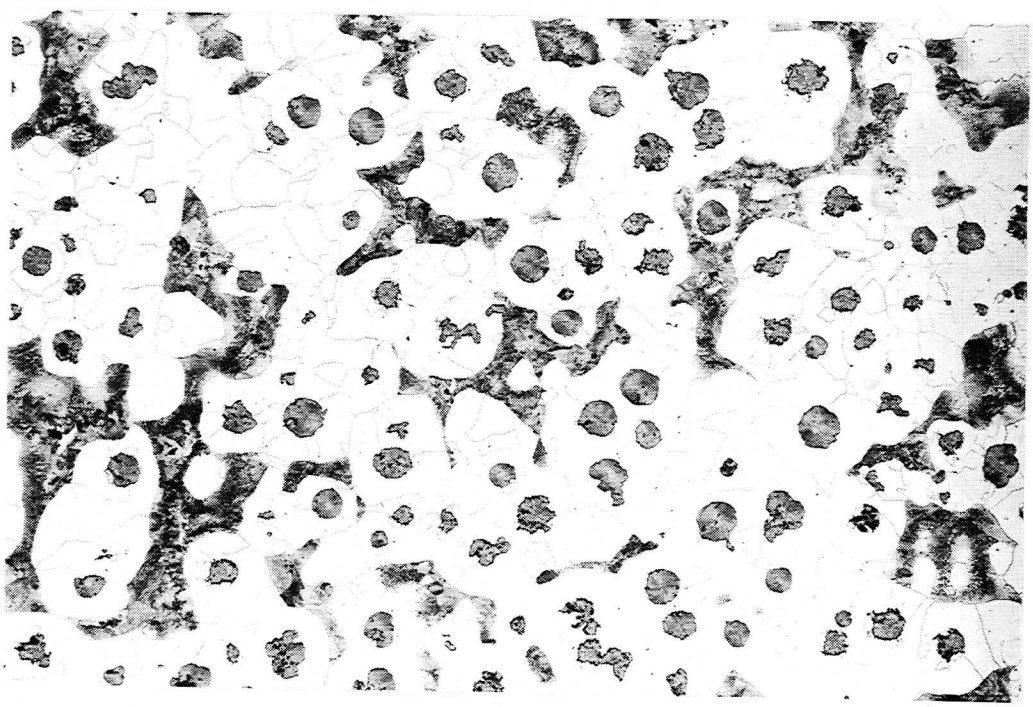


b.0.0185T•Mg, 0.0120F•Mg

Fig.11 Microstructure of 50mm Y-block in each magnesium level. Result of chemical analysis is described.

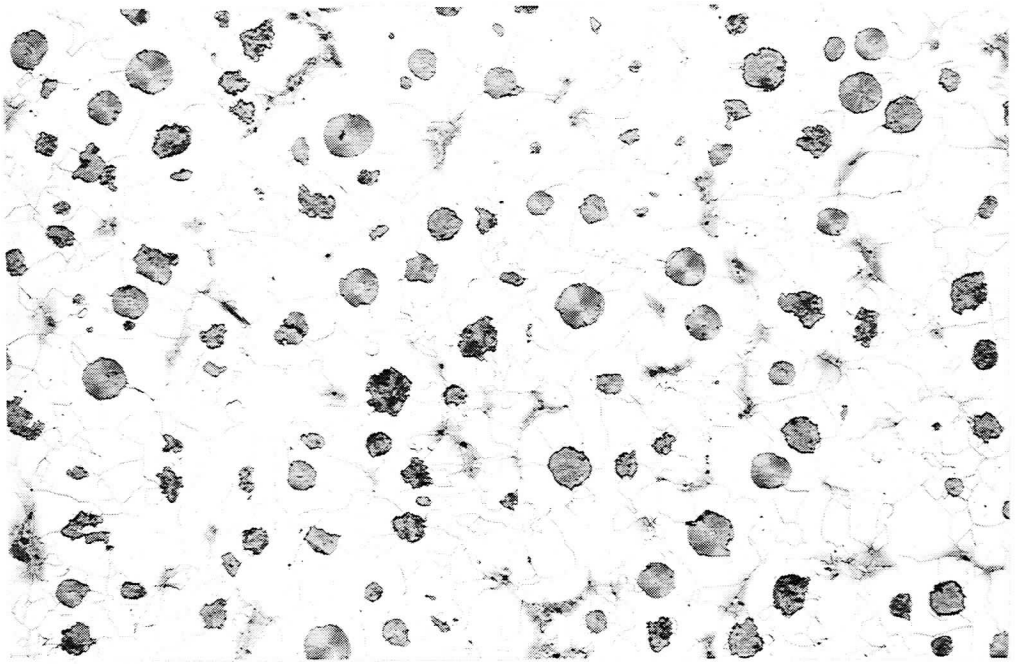


c.0.0316T•Mg, 0.0241F•Mg

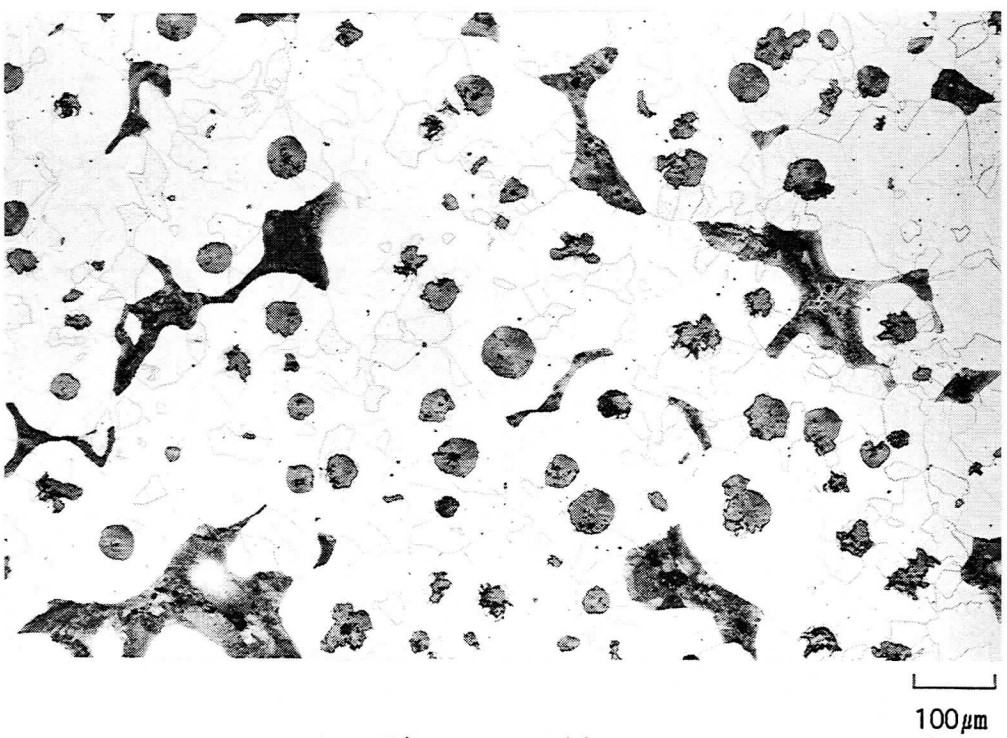


d.0.0368T•Mg, 0.0309F•Mg

Fig.11 Continued



e.0.0500T•Mg, 0.0425F•Mg



f.0.0549T•Mg, 0.0467F•Mg

Fig.11 Continued

Table 1 Results of conventional emission spectrum analysis and free oxygen measurement in magnesium treated liquid irons.

Sample No.	Chemical composition (Mass%)						$\underline{O}$ measurement		
	C	Si	Mn	P	S	Mg	$\underline{O}$ (Mass PPM)	EMF (mV)	Temp. (℃)
1	3.43	2.26	0.11	0.034	0.015	0.011	0.29	−199	1413
2	3.54	2.31	0.20	0.039	0.012	0.022	0.10	−219	1339
3	3.45	2.56	0.21	0.037	0.014	0.031	0.08	−226	1326
4	3.42	2.66	0.21	0.038	0.013	0.040	0.10	−218	1335
5' (base)	3.52	1.43	0.14	0.031	0.019	—	0.93	−137	1434
5	3.49	2.41	0.16	0.031	0.014	0.048	0.09	−239	1363
6	3.52	2.93	0.12	0.039	0.012	0.056	0.07	−259	1370

Table 2 Results of chemical analysis with ICP method on magnesium phases.

Sample No.	Mg (Mass%)		
	Total	Inclusion	Free
1	0.0114	0.0076	0.0038
2	0.0185	0.0065	0.0120
3	0.0316	0.0075	0.0241
4	0.0368	0.0059	0.0309
5' (base)	—	—	—
5	0.0500	0.0075	0.0425
6	0.0549	0.0082	0.0467

Table 3 Relationship among free-Mg content, nodularity and tensile properties.

Free Mg (Mass%)	Nodularity (%)	Tensile properties *		
		Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)
0.0038	7	89	107	2.8
0.0120	49	276	388	7.7
0.0241	89	328	504	18.2
0.0309	87	334	520	21.6
0.0425	89	317	482	22.5
0.0467	82	329	488	22.5

* 4 points average