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著者	HOMMA Masao, MEGURO Hiroshi, ABE Yoshihiko, OHNO Reiichi
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Study of Magnesium Treated Nodular Cast Iron by Reducing Refining in the Electric-Arc Furnace*

Masao HOMMA, Hiroshi MEGURO, Yoshihiko ABE and Reiichi OHNO

The Research Institute for Iron, Steel and Other Metals

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Synopsis

Magnesium treated nodular cast iron (D.C.I.) was investigated by the reducing refining in the acid and the basic electric-arc furnace. By the reducing refining in arc furnace the oxygen and sulfur contents in molten metal were decreased, and so magnesium amounts necessary for the ductilization of graphite decreased. This reducing degree of magnesium amounts were examined. Further, the shrinkage cavities in the basic and the acid furnace were compared.

I. Introduction

At present, there are many important problems in the industrialization of magnesium treated nodular cast iron (ductile cast iron D. C. I.). The effects of raw material and inhibiting elements, the kind and quantity of nodulizing alloys, the suitable melting method, the mass effect, the prohibition of mixing with dross, the improvement of casting surface and the counter-measure to shrinkage cavity are complex factors, and many studies must be performed to its development in the future. One of the most important projects will be the study of reducing the necessary magnesium for ductilization. It is expected that the reduction of magnesium alloy additions and accordingly, the reductions of mixing dross and shrinkage cavity in castings can be obtained as results of deoxidization and desulfurization by applying reducing refining of molten iron to the manufacture of ductile cast iron. Of high carbon cast irons ductile cast iron is ideal and of high grade. For the manufacturing furnace with high grade steels, an arc furnace is more suitable than the furnace of open hearth type and similarly, it is suitable for the manufacture of such a high grade cast iron as ductile cast iron than a cupola furnace, with which refining is almost impossible. In early days, as the manufacturing furnace with ductile cast iron, the arc furnace was used and then cupola was possible to be used after studying melting method, but it tends to come back to use arc furnace again, with which molten iron is deoxidized and desulfurized and then treated with magnesium. One third of factories in the United States seem to manufacture ductile cast iron with arc furnace. In the present study, the reduction of magnesium additions were investigated in manufacturing ductile cast iron after reducing refining in both acid and basic small

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Héroult type arc furnaces of 30~50 kg in capacity.

II. Considerations on the conventional melting methods

In the conventional smelting method with an acid cupola furnace it is usually necessary to select adequate raw materials and cokes of low sulfur content. But the sulfur content in molten iron increased inevitably and the degree of deoxidation was poor, so that magnesium alloy additions must be increased, and dross and shrinkage cavity both tended to increase.

The cupola furnace for ductile cast iron melting in England is being used almost with acid-lining, and sulfur content are 0.08~0.14 per cent. It was reported that when basic-lining was used, sulfur content decreased to 0.01~0.04 per cent and the addition of magnesium and cerium could be reduced and the lowering of price was obtained[1]. In the United States basic-lining is used in almost cupola furnaces for ductile cast iron[2].

When the structure is of spheroidized graphite, sulfur content is below 0.025 per cent. Even if sulfur exists about 0.1 per cent, sulfur can be desulfurized sufficiently and graphite is spheroidized by the addition of much magnesium in quantities 1.0~1.2 per cent, in use of a little explosive Ni-Mg (50-50) alloy or Cu-Mg (50-50) alloy[3]. The quantity of magnesium can be reduced by soda ash treatment[4] before adding magnesium. Remelted molten iron with graphite crucible furnace after melting the whole steel block raw materials with acid cupola furnace required the addition of 0.8 per cent pure magnesium to spheroidize graphite perfectly, but it is reported that according to the carburizing and desulfurizing treatment by the injection process graphite was spheroidized by 0.2 per cent magnesium additions[5].

III. Experiment of refining with electric-arc furnace

The method of adding magnesium alloy in ductile cast iron can be considered as a kind of forced deoxidization, accompanied with desulfurization[6]. There is a report[7] that pointed out the bad effect of oxygen in ductile cast iron. If the raw material iron contains much oxygen and sulfur, considerable amounts of magnesium will be consumed for deoxidization and simultaneous desulfurization. On applying refining method of deoxidation and desulfurization, the additional amount of magnesium alloy can be reduced and a ductile cast iron of better

(1) S. B. Bailey, Foundry Trade J., **96** (1954), 577.
(2) P. K. Figge, Giesserei, **42** (1955), 26 ; 701.
(3) Kusakawa, J. Jap. Foundrymen's Soc., **26** (1954), 290.
(4) Morita and Ozaki, J. Iron and Steel Inst. Jap., **39** (1953), 835.
W. Patterson, Giesserei, **44** (1957), No. 9, 216.
(5) Kawabata, J. Jap. Foundrymen's Soc., **28** (1956), 573.
(6) M. Homma and Y. Hashimoto, J. Jap. Inst. Met., **16** (1952), 486 ; 547.
F. H. Butter, H. F. Taylor and J. Wulff, Amer. Foundrymen, **20** (1951), Oct., 49.
I. C. H. Hughes, Foundry Trade J., **93** (1952), 349 ; 385 ; 417.
(7) G. Darge, Foundry, **79** (1951), 122.
Tanimura, Matsuda, Taniguchi and Izu, *Study on Dnctile Cast Iron* (I) (1952), 43.

quality having less mixing of dross and shrinkage cavity can be obtained, not only with basic arc furnace of Héroult type but also with acid one compared with melting methods by using cupola. However, in the case of reducing refining with arc furnace, the differences in the degree of deoxidation and desulfurization are observed by slag forming method. Therefore, much consideration must be done on slag forming method, because of the reduced degree of necessary amount of magnesium for manufacturing of ductile cast iron is also different.

1. The outline of melting method

Raw material for melting was used scrap steels as shown in Table 1. At first,

Table 1. Chemical composition of steel scraps.

C%	Si%	Mn%	P%	S%
0.22-0.27	0.07-0.86	0.42-0.44	0.015-0.023	0.024-0.031

it was smelted in the addition of gas carbon with acid-lined (silica sand and quarts mortar lining) or basic-lined (magnesia lining) Héroult arc furnaces and it is slagged-off as soon as the charge was melted down.

Next, secondary slag was thrown into the molten metal and started reducing by deoxidation and desulfurization. Silicon content in metal was controlled by adding metallic silicon and the necessary magnesium additions were estimated by spoon test, and moten meltal was tapped after about 1 hr refining. Tapping temperature was between 1430 and 1470°C, and then Fe-Si-Mg (18 per cent) alloy was added and 0.4 per cent of Fe-Si alloy (75 per cent Si) was inoculated after reducing reaction. Casting temperature of specimens was between 1350 and 1400°C.

2. Adding method and the size of magnesium alloy

One charge of molten metal was 7 to 8 kg and the adding method of alloy is shown in Fig. 1. A cover made of cast iron was put on a ladle of 10 kg capacity to protect the splashing of molten metal, and at the bottom of a graphite crucible setting in the middle of cover, a hole was drilled through which molten metal can be poured into the ladle. For the purpose of protecting to burn up the alloy in the ladle, another graphite crucible was upset and a hole was drilled on the top of it. As a result obtained from many investigations, this adding method was found to be very effective.

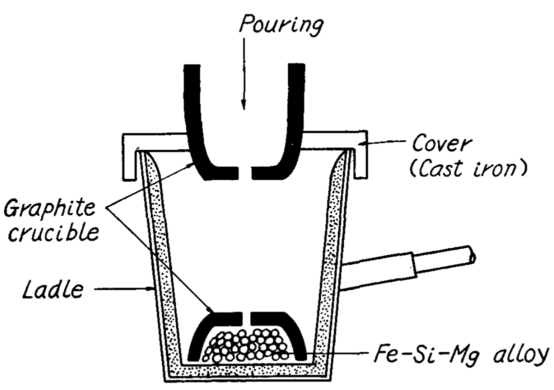
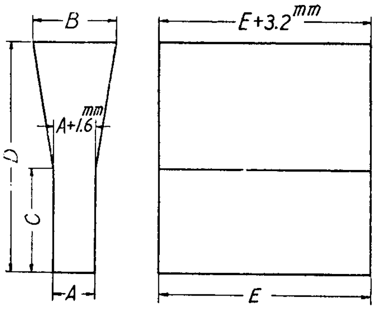


Fig. 1. Arrangement for Mg alloy addition.

Fine powder or beans-size Fe-Si-Mg alloy was relatively easy to burn up and its larger bulk was reacted vigorously and both yields were not good. Little finger size of alloy showed a trend of the best yielding of magnesium in metal, on treating the ladle of 10 kg capacity.

3. Preparation of tensile test specimens

Test specimens of ductile cast iron were made in keel block dry sand mold, and this method is similar in the case of cast steel, also. According to A.S.T.M. (1951) A-399-51T Standard[8], specimens are cast in various open-end keel block Y type molds made by adequate core sand as shown in Fig. 2, and sand of 38 mm



Dimension mm	Size of Y-block		
	13mm	25mm	76mm
A	13	25	76
B	41	54	127
C	19	38	67
D	137	137	143
E	152	152	152

Fig. 2. Keel block of A.S.T.M. (1951) standard.

thick may be used for casting metal of 13 and 25 mm . thick; sand of 76 mm. thick may be used for casting metal of 76 mm. thick and tensile and transverse test specimens may be machined from the lower rectangular part. It is understood that the preparation of ductile cast iron specimens itself contains much more difficult problems, i.e., about the shrinkage cavity, dross and pin hole and castability than other high grade cast irons.

On the other hand, tensile test specimens of ductile cast iron for this experiment was based on the casting plan determined by JIS (Japanese Industrial Standard) for malleable cast iron, and were cast in JIS No. 4 test specimen (parallel part 50 mm × 14 ϕ mm) green sand mold. Green sand were composed of skin sand and back sand.

4. Result of tensile tests

Tensile specimens were cast in green sand mold for JIS No. 4 specimen, after adding magnesium alloy to molten metal being refined by acid or basic furnace, and annealed with an industrial muffle furnace. On annealed specimens, elongation, tensile strength and yield point were measured. Results obtained are shown in Table 2. Annealing was carried out at 850°C for 2 hrs and then at 760°C for 5 hrs, furnace-cooled. Matrix of specimen was almost ferrite structure. It has been said that perfect spheroidal graphite cannot be obtained unless about 0.4 per cent magnesium are added by the conventional method.

In melting with basic furnace, desulfurizing rate was better, and 44 to 48 kg/mm^2 in tensile strength, 31 to 35 kg/mm^2 in yield point and 10 to 15 per cent in elongation were obtained after annealing, by about 0.11 to 0.17 per cent magnesium additions. A good result was obtained as Fe-Si-Mg alloy, that is, analytical value of magnesium in metal was 0.026 to 0.04 per cent, the yield of magnesium was 20 to 30 per cent.

(8) Saitô, Sawamura and Morita, *Metallic Materials and their Working Methods, Cast Iron* (1953), 482.

Table 2. Analytical values of magnesium and mechanical properties.

	No. of melting	Mg Added Quantity (%)	Mg Analytical Value (%)	Yield (%)	Mechanical properties (As-annealed) Tensile strength (kg/mm^2)	Yield point (kg/mm^2)	Elongation (%)	Microstructure	Gas analysis by vacuum melting O %	H %
Basic furnace melting	426 A	0.16	0.031	19	40.3	31.2	9.0	N. G+F+P (about 5)	0.0004	0.0002
		0.21	0.048	23	37.7	31.2	7.5	Ditto	0.0006	0.0003
		0.27	0.060	22	38.4	31.2	8.0	Ditto	0.0006	0.0003
	501 A	0.21	0.045	21	44.9	35.1	10.0	N. G+F+P (about 3)	0.0006	0.0002
		0.14	0.035	25	—	—	—	Ditto	0.0004	0.0003
	620 A	0.17	0.035	21	46.2	35.1	15.0	N. G+F+P (about 5)		
		0.17	—	—	46.2	34.5	12.5	Ditto		
		0.13	0.038	30	44.2	34.5	11.0	N. G+Q. N. G+F+P (about 5)		
	705 A	0.13	0.029	22	44.2	29.9	13.0	N. G+F+P (about 10)		
		0.13	—	—	44.2	31.2	13.0	Ditto		
		0.16	0.029	19	44.2	31.9	14.5	N. G+F+P (about 5)		
		0.11	0.026	23	44.2	31.2	11.0	N. G+F+P (about 20)		
		0.11	0.026	23	44.2	31.2	11.5	Ditto		
	719 B	0.12	0.034	28	48.1	34.5	12.0	N. G+Q. N. G+F+P (about 10)		
		0.12	0.028	23	47.5	34.5	19.5	N. G+F		
	803 A	0.17	0.026	15	45.5	34.5	12.0	N. G+Q. N. G+F+P (about 2)		
		0.17	—	—	45.5	34.5	12.0	Ditto		
Acid furnace melting	608 A	0.18	0.042	23	45.5	34.5	11.0	N. G+F+P (about 5)	0.0010	0.0002
		0.18	—	—	44.2	34.5	9.0	Ditto		
		0.17	0.047	28	39.0	32.5	7.0	N. G+F+P (about 15)	0.0009	0.0001
		0.20	0.044	22	39.0	32.5	9.5	N. G+F+P (about 10)		
	719 A	0.27	0.035	13	44.9	35.8	11.0	N. G+F+P (about 3)		
		0.27	—	—	44.9	35.8	11.0	Ditto		
		0.14	0.026	19	47.5	39.0	9.5	N. G+Q. N. G+F		
	802 A	0.24	0.029	12	49.4	41.0	10.5	N. G+F		
		0.22	0.036	16	48.1	39.7	10.0	N. G+Q. N. G+F		
		0.22	—	—	48.1	38.4	10.0	Ditto		
		0.22	0.028	13	47.5	39.0	8.5	N. G+F+P (about 3)		
		0.20	0.028	14	48.8	41.0	11.0	N. G+Q. N. G+F		
		0.20	—	—	47.5	40.0	8.0	Ditto		

Note N. G : Nodular graphite ; Q. N. G : Quasi nodular graphite ; F ; Ferrite ; P : Pearlite ; ( ) shows the quantity of retained pearlite by eye-measurement.

On the other hand, desulfurizing rate of melting with acid furnace was a little worse than that of basic furnace. The magnesium additions were required 0.18 to 0.23 per cent and 40 to 48 kg/mm^2 in tensile strength, 30 to 40 kg/mm^2 in yield point and 9 to 11 per cent in elongation were obtained, and elongation showed a little lower. As a reference, a temporary standard by Japan Cast Iron Technical Committee is shown in Table 3, in which values were measured by specimens

Table 3. Temporary standard by Japan D.C.I. technical committee.

		Tensile strength kg/mm^2	Yield point kg/mm^2	Elongation %
First group	As-Cast	>55	>38	> 2.0
Second group	Annealed	>45	>30	> 5.0
Third group	Annealed	>40	>28	>12

machined from keel block as mentioned above.

It is no doubt that elongation and tensile strength after annealing shown in Table 2 would be improved if test specimens should be machined from keel block made by dried sand mold[9].

5. Comparison by shrinkage cavity test specimens

The simple shrinkage cavity test specimens shown in Fig. 3 were cast into green sand mold above which was open. An experimental result is shown in Fig. 4. The lengths of sound part of general shrinkage cavity test specimens, *l*, is shown at the right end of the figure which were obtained by the addition of about 0.4 per cent magnesium with (b) basic electric-arc furnace and (a) acid cupola furnace as the conventional methods. The used magnesium quantity for ductilization was decreased as a result of refining with acid or basic arc furnace, so that the length of sound part of shrinkage cavity test specimens became longer than that of the conventional method. It was shown that magnesium additions were decreased and sounder castings were produced, and moreover, re-

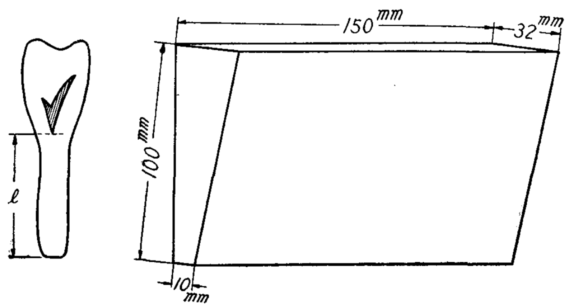


Fig. 3. Seize of shrinkage cavity test specimens (Green sand mold).

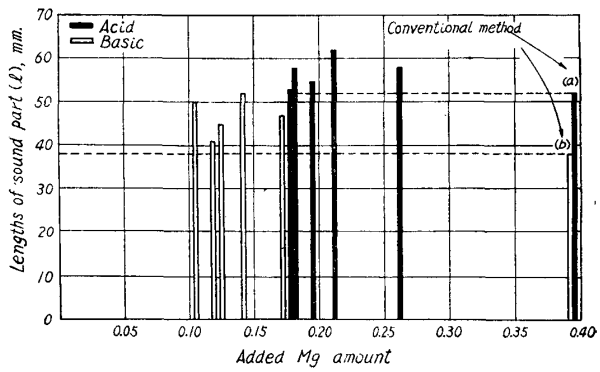


Fig. 4. Comparison between shrinkage cavity test specimens and Mg amounts added in acid and basic furnaces melting.

(9) Shôbayashi and Kumomura, *Study of Ductile Cast Iron* (1952), 135.

gardless the used magnesium quantity was a little more increased in the case of acid furnace, better result was obtained.

6. Desulfurization

Degrees of desulfurizing rate of refining and Fe-Si-Mg alloy additions and degree of carbon saturation are shown in Table 4. Desulfurizing rate by slag

Table 4. Degree of desulfurization and degree of carbon saturation.

Furnace	Melting No.	Original S %	After reducing refining		After magnesium treatment		C %	Si%	Degree of carbon saturation
			S %	Degree of desulfurization	S %	Degree of desulfurization			
Basic furnace	426 A	0.028	0.001	96.42	0.003	—	3.70	2.08	1.03
	501 A	0.030	0.005	83.33	0.002	60.0	3.23	2.62	0.95
	620 A	0.026	0.006	76.92	0.003	50.0	3.21	2.43	0.93
	705 A	0.028	0.010	64.28	0.003	70.0	2.75	2.19	0.77
	719 B	0.027	0.003	88.88	0.001	66.66	2.54	2.48	0.74
	803 A	0.032	0.002	93.75	0.003	—	2.84	2.15	0.80
Acid furnace	608 A	0.030	0.011	63.33	0.011	—	3.59	2.49	1.04
	628 B	*0.050	0.037	26.00	0.017	54.05	3.64	2.61	1.06
	705 B	*0.062	0.027	56.45	0.013	51.85	3.49	3.18	1.08
	712 B	*0.071	0.039	45.07	0.006	84.62	2.94	3.29	0.92
	719 A	0.032	0.006	81.25	0.005	16.66	3.00	2.91	0.90
	802 A	0.028	0.003	89.28	0.003	—	3.18	3.18	0.98

* Analytical value after adding FeS into molten metal.

with basic furnace was good, i.e. 65 to 96 per cent, and sulfur content became 0.001 to 0.010 per cent. Further desulfurization was carried out by magnesium additions and sulfur content became very low, namely, from 0.001 to 0.003 per cent. This fact shows that the rate of consumption of magnesium as MgS and MgO in arc furnace becomes smaller than that in the conventional methods.

It has been reported that desulfurizing rate in acid furnace is bad. On refining by molten slag, desulfurizing rate was 63 to 89 per cent and sulfur content became 0.003 to 0.11 per cent but further desulfurizing might not be expected in this experiment. Another experiment was carried out by the addition of Fe-S alloy to molten metal with acid furnace and slag was slagged-off once before adding magnesium alloy, and further new slag material was put into molten metal and then magnesium alloy was added.

Desulfurizing rate after slag-off decreased to 26 to 56 per cent, compared with that without Fe-S alloy additions and sulfur content became 0.027 to 0.039 per cent. Then magnesium in Fe-Si-Mg alloy seemed to be consumed and sulfur content became 0.006 to 0.017 per cent. On casting these molten metal, a good result was not obtained by mixing of dross into casting. In this case, the degree of carbon saturation approached to about 1, as silicon content increased inevitably. The retaining of magnesium by means of Fe-Si-Mg alloy additions was worse compared with Ni-Mg, and Cu-Mg alloys and its specific gravity is so small, and its vapor pressure is so large[(2)] that MgS and MgO drosses did not separate from molten metal and floated with Kish graphite and mixed into molten metal on casting. Using of this alloy for hyper-eutectic constituents in melting with acid furnace might not be adequate to make sound casting.

Summary

The manufatcure of ductile cast iron was studied by the deoxidizing and desulfurizing refining of molten iron and further by the addition of Fe-Si-Mg alloy with acid and basic Héroult electric-arc furnaces. The results obtained are as follows.

(1) On refining of molten iron with electric-arc furnace, the deoxidization and desulfurization were well performed, so that the magnesium additions was reduced from about 0.4 per cent in the conventional method to 0.11~0.17 per cent in basic furnace melting and 0.18~0.28 per cent in acid furnace melting. It was found that the mixing of dross was also reduced and the depth of shrinkage cavity was decreased. It is note worthy that the depth of shrinkage cavity in case of acid furnace melting was decreased compared with that of basic furnace melting regardless the reducing rate of used magnesium was smaller.

(2) Tensile strength was tested by JIS No. 4 green sand cast test specimens after annealing. In case of basic furnace melting, 44~48 kg/mm^2 in ultimate tensile strength, 31~35 kg/mm^2 in yield point, 10~15 per cent in elongation were obtained. In case of acid furnace melting, 40~48 kg/mm^2 in ultimate tensile strength, 32~40 kg/mm^2 in yield point, 9~11 per cent in elongation were obtained.

(3) On refining molten iron with electric-arc desulfurizing rate was good. Original sulfur content 0.024~0.031 per cent was reduced to 0.001~0.010 per cent by 65~96 per cent desulfurizing rate in basic furnace and to 0.003~0.011 per cent by 63~89 per cent desulfurizing rate in acid furnace.

(4) Desulfurizing rate by reducing slag of molten metal containing 0.050~0.071 per cent S by adding Fe-S alloy was 26~56 per cent in acid furnace melting. Even if 0.15~1.25 per cent of Fe-Si-Mg alloy added to molten metal, the rate of consumption of magnesium as MgS was increased. On the other hand, in the case of increasing silicon from the lining, the degree of carbon saturation approached to 1, and the dross came to be difficult to separate from Kish graphite, so that the sound casting might not be obtained. In this case, it was necessary that the degree of carbon saturation was taken aim below 1 in the range between 2.5 and 3.2 per cent C, and between 2.0 and 3.0 per cent Si, or that the kind of magnesium alloy must be changed for obtaining better result.

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