Some Investigations on the Cerium-treated Cast Iron

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Synopsis

The effects of the addition of cerium on the macro- and microstructure of hypo--eutectic and eutectic cast iron have been investigated and further, some experiments. were carried out to produce the high strength and rapid-malleable cast iron containing high silicon by the addition of cerium. The results obtained were as follows : (1) With the increase of the cerium content, the structure of cast iron changed from a grey iron to a white iron passing through an inverse chilled iron. When the composition of cast iron was fixed, the amount of cerium necessary to get white cast iron from a deoxidized melt was less than that from an oxidized melt. (2) It was verified that white cast ironization with the addition of cerium was not caused by its alloying such as in the case of manganese or chromium, in which they form special carbides, but by the supercooling of melt accompanied with strong deoxidation by cerium. (3) The mechanical properties of cerium-treated rapid malleable cast iron having the high silicon contents are higher than those of the commercial black heart malleable cast iron, and by controlling the amount of cerium, carbon and silicon in cast iron, the castings of a larger section than the maximum size which has been applied to ordinary malleable cast iron can be made.

I. Introduction

H. Morrogh and W. J. Williams[1] found that a nodular graphite structure. was produced in an as-cast state by adding cerium to the molten cast iron in a ladle. The cerium-treated process is more expensive than the magnesium-treated one because of the high cost of misch metals used as an additive, and therefore,. the latter is more widely used for the production of nodular cast iron. Cerium is only used to reduce the necessary amounts of magnesium and to relieve the inhibiting actions of some impurities when magnesium-treated process is applied for the spheroidization of graphite. From the discussion of Morrogh's paper, in. which he described about the production of nodular graphite by the use of cerium in the hyper-eutectic melts, it is easily approved that the cerium-treatment is also available for the eutectic and the hypo-eutectic melt.

In the present work, the change in structure with the amounts of cerium added, the effect of inoculation after the cerium-treatment, and the shrinkage cavity of castings were investigated to clarify the behaviours of cerium in the hypo-eutectic and the eutectic cast iron. Examination was also made on the manufacture of a rapid malleable cast iron having high silicon by the addition of.

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(1) H. Morrogh and W.J. Williams, J. Iron & Steel, **159** (1947), 306.

cerium, because cerium has the strong action of white ironization.

II. Raw materials and the melting method

Raw materials used for melting were scrap steel and coke pig iron as shown in Table 1. 25~35 kg of steel scraps and gas carbon or pig irons and scrap steels

Table 1. Chemical composition of raw material.

	C %	Si %	Mn %	P %	S %
Coke pig iron	4.05	1.75	0.69	0.159	0.029
Steel scrap	0.22	0.07	0.42	0.015	0.024

were melted in a small basic Héroult furnace. The slag materials charged before melt down were lime stone. After the charge was melted down, silicon content in metal was controlled by adding metallic silicon, and carbon content in metal was rapidly analyzed and controlled by adding pig irons or scrap steels. In the refining period, the reducing slags ($CaCO_2$, SiO_2, Carbon etc.) or the weakly oxidizing slags ($CaCO_3$, SiO_2, etc.) were used according to the purpose.

III. Test specimens and experimental method

1. Spoon test before tapping

For the spoon test, the specimens treated with cerium were cast in 13 and 25 mm ϕ green sand molds. The casting temperature was between 1450 and 1480°C. The relationship between the structural changes of specimens and the amounts of cerium added was investigated by the fracture and the microstructure examination.

In order to determine the relationship between the necessary amount of cerium and the oxygen content in molten iron, the following two methods were used.

(i) Comparison of the addition of cerium together with iron oxide with that of cerium alone to the molten iron reduced by the reducing slag.

(ii) The case of cerium addition to the molten iron oxidized by the weakly oxidizing slag. And the case of cerium addition to the molten iron which was refined by the reducing slag after the weakly oxidizing slag was slagged-off.

In some cases the molten iron was inoculated with Fe–Si alloy after cerium-treatment and then the microstructural change of specimens was investigated.

2. Specimens for shrinkage cavity test

The specimens for a shrinkage cavity test were cast into the molds of poise and spindle-type as shown in Fig. 1. Comparison of shrinkage cavities was made among the cerium-treated cast iron, ordinary cast iron, and ductile cast iron.

3. Tensile strength test specimens and heat-treatment

For the same molten iron as that for spoon test, the minimum amount of cerium, by which white ironization could be realized in 25 mm ϕ specimen, was added to the ladle. When about 70 per cent of the ladle of 8 kg capacity was filled by the molten iron, the cerium metal was added to the melt, its oxidation

being avoided by immersing it with a holder wire.

Test specimens were cast in JIS (Japanese Industrial Standard) No. 4 type (parallel part 50 mm × 14 mm ϕ) green sand mold. Tensile strength was measured
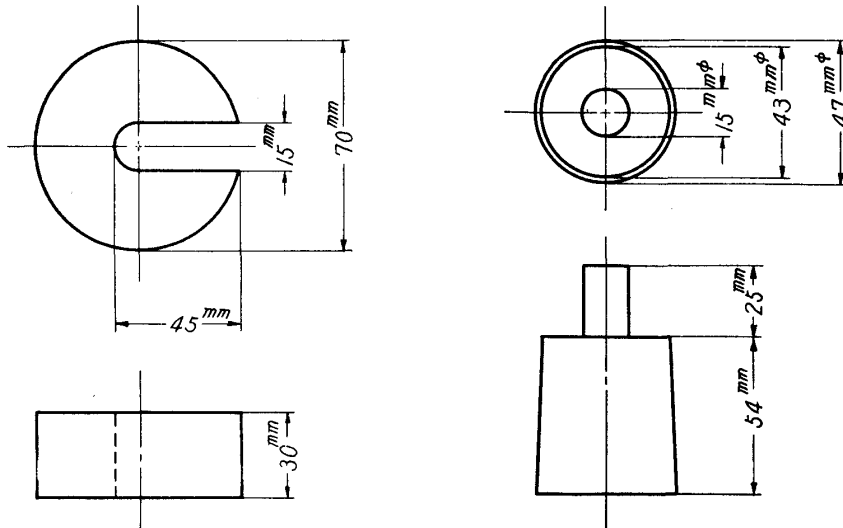

Fig. 1. Size of shrinkage cavity test specimens. (Green sand mold)

after annealing. Annealing was carried out at 850°C for the first stage and then at 750°C for the second stage in an industrial muffle furnace.

4. Chemical compositions of cerium alloy

The cerium metal was the commercial one with the name of misch metal. The compositions of this metal are shown in Table 2. This metal contains several

Table 2. Chemical composition of cerium alloy.

Ce %	La %	Nd %	Pr %	Sm %	Other rare earth metals%
50~55	22~26	15~17	5~7	2	rest

elements, but these are rare earth elements of the same group and the chemical properties are similar to that of cerium, so those can be regarded to have the same effect. The adding amounts of cerium cited in this paper are those of misch metal.

IV. Experimental results and consideration

1. Spoon test before tapping

In the case of after-treatment of molten iron tapped from the furnace, the effect of treatment is remarkably influenced by the character of molten metal. For example, in the case of ductile cast iron, the necessary amount of magnesium is remarkably influenced by the oxygen content of molten metal, decreasing with the increase of the degree of deoxidation and desulfurization of molten iron[2].

(2) M. Homma, H. Meguro, R. Ohno and Y. Abe, J. Jap. Foundrymen's Soc., 30 (1958), 597 ; Sci. Rep. RITU, A11 (1959), 466.

The standard free energy of formation of various oxide are shown in Fig. 2[3]. The deoxidizing ability of cerium is close to those of calcium and magnesium. It is expected that the structures vary with the dissolved oxygen content in the untreated molten metal, so the examination was attempted for the reduced molten metal and the oxidized metal by adding oxide. The chemical compositions of samples are shown in Table 3 (In the melting mark D, the effect of inoculation was examined). The fractures and micro-structures are shown in Table 4.

Scrap steel and pig iron were used as the raw materials of mark A. Mark A was treated with cerium of 0 to 0.1 per cent after oxidizing or reducing refining, and the results obtained were as follows: The specimens of 13 mm and 25 mm dia. of untreated A-1 were grey iron and these structures were eutectic graphite. The specimens A-2 and A-5 which were treated with 0.05
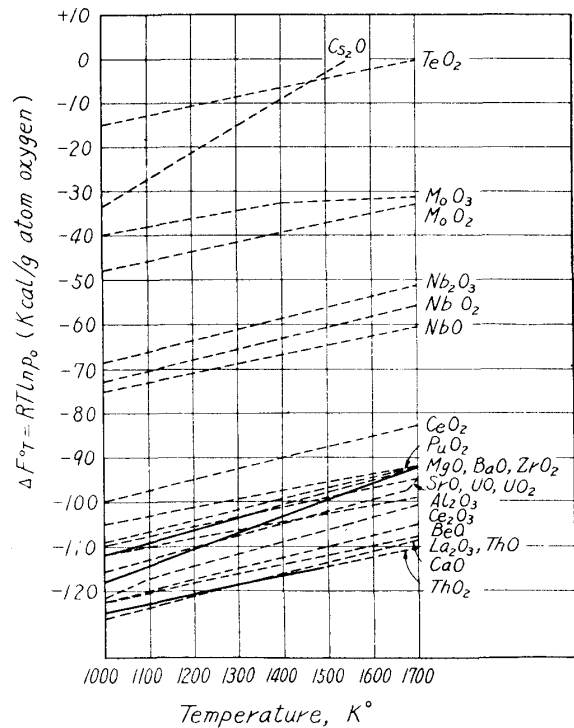
Fig. 2. Standard free energy of formation of oxides.

Table 3. Chemical composition of samples.

Mark	C %	Si %	Mn %	P %	S %	Cr %
A	2.38	1.92	0.44	0.084	0.008	0.038
B	2.64	2.45	0.42	0.100	0.019	0.024
C	3.39	2.35	0.41	0.020	0.009	—
D	3.69	2.71	0.36	0.018	0.007	none

per cent of cerium became an inverse chilled structure which solidified into grey (eutectic graphite) structure at the outside layer and white at the core, but the sphere of grey iron structure in A-2 was wider than that in A-5. With cerium of 0.08 per cent, specimen of A-3 showed the inverse chilled structure, whereas the fracture of A-6 was perfectly white in 13 mm dia. and had only very thin grey layer at the rim in 25 mm dia. specimen. Further, by treating with 0.1 per cent cerium, very small amount of eutectic graphite was observed at the rim of A-4, but the fracture of A-7 became entirely white.

(3) Progress in nuclear energy, Series III. Progress of chemistry, Vol. 1, 296.

Table 4. Relation between the amounts of cerium addition and structures.

| Mark	Refining method	Specimen No.	Ce added quantity (%)	Fe$_2$O$_3$ added quantity (%)	Fracture 13 mm ϕ	Fracture 25 mm ϕ	Microstructure
A	Oxidizing	A—1	—	—	●	●	E.G+P
		A—2	0.05	—	○	○	I.C
		A—3	0.08	—	○	○	I.C
		A—4	0.1	—	○	○	I.C
	Reducing	A—5	0.05	—	○	○	I.C
		A—6	0.08	—	○	○	13ϕL, 25ϕI.C
		A—7	0.1	—	○	○	L
B	Reducing	B—1	—	—	●	●	E.G+P
		B—2	0.1	—	●	●	F.G+N.G+P
		B—3	0.3	—	○	○	L
		B—4	0.5	—	○	○	L
		B—5	0.1	0.1	●	●	F.G+P
		B—6	0.3	0.1	○	○	I.C
		B—7	0.5	0.1	○	○	L
		B—8	0.1	0.3	●	●	F.G+P
		B—9	0.3	0.3	○	○	13ϕL, 25ϕI.C
		B—10	0.5	0.3	○	○	L
C	Reducing	C—1	—	—	●	●	R.G+P
		C—2	0.03	—	●	●	E.G+P
		C—3	0.04	—	○	○	I.C
		C—4	0.05	—	○	○	I.C
		C—5	0.06	—	○	○	I.C
		C—6	0.1	—	○	○	L
		C—7	0.03	0.5	●	●	R.G+E.G+P
		C—8	0.04	0.5	○	●	I.C
		C—9	0.05	0.5	○	●	I.C
		C—10	0.06	0.5	○	○	I.C
		C—11	0.1	0.5	○	○	L

Note   F.G : Flake graphite ; R.G : Rosette graphite ; E.G : Eutectic graphite ;
N.G : Nodular graphite ; P : Pearlite ; L : Ledeburite ; I.C : Inverse chill.

Similarly to the case of mark A, the raw materials for mark B were scrap steel and pig iron. In the series of mark B, experiments were undertaken to compare the microstructure and the fracture of the reducing refined cast iron which were added by 0 to 0.5 per cent cerium, with those of the iron which were added by 0.1 to 0.5 per cent cerium together with 0.1 and 0.3 per cent iron oxide. The fracture of untreated B-1 was grey iron, and its graphite structure was eutectic as shown in Photo. 1-a. B-2 which was treated with 0.1 per cent cerium
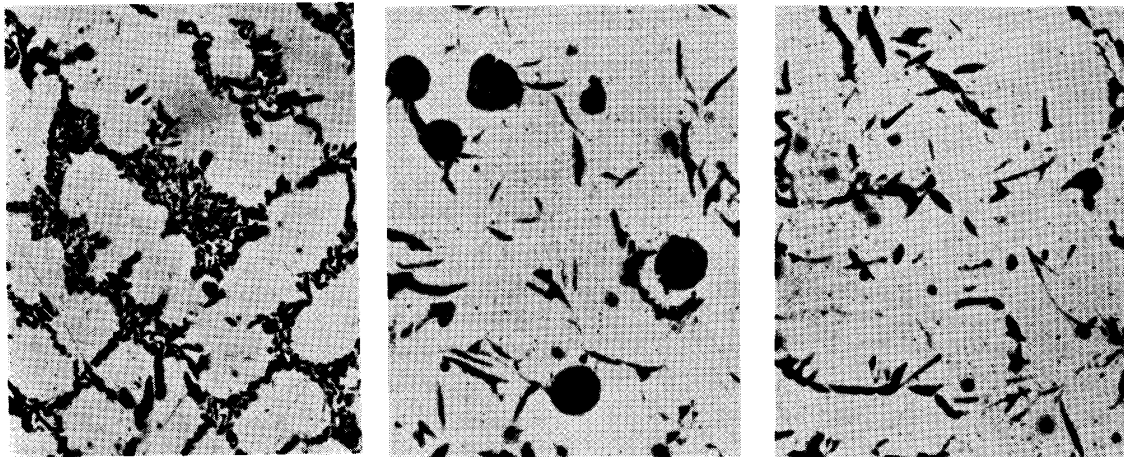
(a) Ce 0%   (b) Ce 0.1%   (c) Ce 0.1%,
                                              Fe$_2$O$_3$ 0.1%

(d) Ce 0.3%,   (e) Ce 0.5%
    Fe$_2$O$_3$ 0.1%
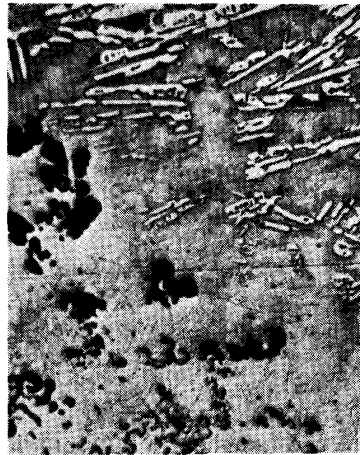
Photo. 1.   The effect of additional amounts of cerium with iron oxide
and cerium alone. (×200)

was grey iron as well as B-1. However, as shown in Photo. 1-b, the graphite structure of B-2 was composed of flakes and spheroids. In the structure of both B-5 and B-8 which were treated with 0.1 per cent cerium together with 0.1 and 0.3 per cent iron oxide, spheroidal graphite was not observed but flaky graphites alone as shown in Photo. 1-c (B-5). B-3 treated with 0.3 per cent cerium had only very small graphites and a few spheroidal graphites, and its fracture became to show perfectly white iron. B-6 which was treated with 0.3 per cent cerium together with 0.1 per cent iron oxide resulted in an inverse chilled iron, and B-9

which was treated with 0.3 per cent cerium together with 0.3 per cent iron oxide changed into white iron in 13 mm dia. and inverse chilled iron in 25 mm dia. specimen. Photo. 1-d shows the intermediate layer of the eutectic graphite and the white cast iron structure of B-6 (13 mm dia.). Further, B-4, B-7, and B-10 which were treated with cerium of 0.5 per cent showed white iron independently of the addition of iron oxide of 0 to 0.3 per cent. All of these specimens were composed of pearlite and eutectic cementite in the matrix, and had only very small graphites and a few spheroidal graphites as seen in Photo. 1-e (B-4), and these microstructures were the same as that of the white iron part of the inverse chilled structure.

As the raw material of mark C, scrap steel alone was used. The specimen of mark C contained higher amount of carbon than those of marks A and B, and was almost of eutectic composition. In this series, the investigations were also carried out on the effect of the addition of 0 to 0.1 per cent cerium, and 0 to 0.1 per cent cerium together with 0.5 per cent iron oxide on the fracture and the structure of the reducing refined cast iron. Similarly to the cases of specimens of marks A and B, when the same amount of cerium was added to the melt, the white cast ironization was more easily obtained in the case of deoxidized melt than in the case of oxidized melt. Moreover, a tendency was observed that the structure changed from the grey iron to the white cast iron through an inverse chilled cast iron with increasing amount of cerium added. Though $Sc \left(\dfrac{Total\ C}{4.23 - \dfrac{Si+P}{3.2}} \right)$ of the specimen mark C is larger than that of mark B, the amount of cerium necessary to get white cast iron was less. The reason for this fact may be that the sulfur content in the specimen of mark C is less than that of mark B.

As mentioned above, cerium has an effect of white cast ironization. Most of the carbide-forming elements such as manganese, chromium, and tungsten restrain graphitization or stabilize cementite by forming double carbides with iron, whereas cerium does not form any double carbide with iron. The white cast ironizing action of cerium is probably due to deoxidation and desulfurization and this resembles partly the other deoxidizer such as magnesium.

In the previous papers[4][5][6], one of the present authors systematically examined the relation between the structure of cast iron and its oxygen content, and it was found that the structure of cast iron changed with the minute quantities of oxygen as follows: With gradual decrease in oxygen content in cast iron, the structure changes from the coarse flake graphite which is the most common structure in cast iron to—rose graphite structure—eutectic graphite structure—fine granular graphite structure—inverse chilled structure—super-cooled white cast

(4) M. Homma and Y. Hashimoto, J. Jap. Inst. Met., **16** (1952), 486.

(5) M. Homma and Y. Hashimoto, J. Jap. Inst. Met., **17** (1953), 375. ; Sci. Rep. RITU, A12 (1960), 8.

(6) M. Homma and A. Minato, J. Jap. Foundrymen's Soc., **28** (1956), 712.

iron structure, and inversely with gradual increase in oxygen content, the structure also changes almost symmetrically with the above. The addition of cerium causes the above-mentioned structural changes by the decrease of oxygen content. When the quantities of the carbide stabilizing elements such as manganese, chromium, and tungsten are gradually increased, the structure of cast iron varies from coarse flake graphite to white cast iron through a mottle containing eutectic graphite and cementite. These carbides are very stable and difficult to be graphitized while as will be described later, the white cast iron caused by cerium-treatment is easily graphitized.

Subsequently, the specimen of mark C having eutectic composition and that of mark D having hyper eutectic composition $(C + \frac{1}{3} Si = 4.59)$ were inoculated with 0.2 or 0.4 per cent Fe–Si after the cerium-treatment. The amount of cerium added and Fe–Si inoculant, and microstructures are shown in Table 5. Eutectic

Table 5. The additional amounts of cerium and Fe-Si inoculation, and microstructures.

Mark	Specimen No.	Ce added quantity %	Fe-Si inoculated quantity %	Microstructure
C	C 12	0.1	0.2	Q.F+P
	C 13	0.5	0.2	N.G+P+L
	C 14	0.5	0.4	//
D	D 1	0.1	0.2	N.G(20%)+Q.F(80%)+P+L
	D 2	0.2	0.2	N.G(50%)+Q.F(50%)+P+L
	D 3	1.0	0.2	N.G(50%)+T.C(50%)+P+L
	D 4	2.0	0.2	N.G(90%)+T.C(10%)+P+L
	D 5	3.0	0.2	N.G+P+L

Note   N.G : Nodular graphite ; Q.F : Quasi flake graphite ; T.C : Temper carbon ;
P : Pearlite ; L : Ledeburite

cast iron (mark C) which was inoculated with 0.2 per cent Fe–Si after the addition of 0.1 per cent cerium was free from cementite, and its graphite structure was of quasi-flakes, but in the case of the addition of 0.5 per cent cerium, cementite in the cast iron hardly disappeared even by the inoculation with 0.4 per cent Fe–Si, and the structure was similar to that of the uninoculated one. In the case of hyper-eutectic cast iron (mark D), however, the increase of the amount of cerium added increased the quantity of cementite, and also promoted the spheroidizing tendency of graphite. By the addition of 2 per cent cerium, most of the graphite in the hyper-eutectic cast iron became spheroidal. From the above results, it was seen that, even by the inoculation with Fe–Si, super-cooled ledeburite was liable to appear in the structure of cast iron having hypo-eutectic composition treated with cerium. However, it is easy to malleablize the ledeburite by annealing, because silicon content is high.

2. Shrinkage cavity test

One of the defects of D.C.I. is that remarkable shrinkage cavity occurs during

solidification. Therefore, a deep consideration must be taken on the casting plan. In the case of the cerium-treated cast iron, however, a shrinkage depression occurs only slightly, and consequently, in casting the specimen of the cerium-treated cast iron the keel block which is used for casting the specimen of D.C.I. is not needed, and it is sufficient to use the casting plan determined by J.I.S. for the malleable cast iron.

Analysis of cast irons used for the shrinkage cavity test are shown in Table 6. The results are shown in Fig. 3. As can be seen in Fig. 3, D.C.I. showed a

Table 6. Chemical composition of shrinkage cavity test specimens.

	C %	Si %	Mn %	P %	S %	Ce %	Mg %
Ordinary cast iron	2.74	2.24	0.42	0.019	0.008	—	—
Ce-treated cast iron	2.74	2.24	0.42	0.019	0.008	0.3	—
Ductile cast iron	3.34	1.88	0.31	0.008	0.016	—	0.23

Ce and Mg per cent show the amount of addition.

(a) Ordinary cast iron

(b) Cerium treated cast iron

(c) D. C. I.
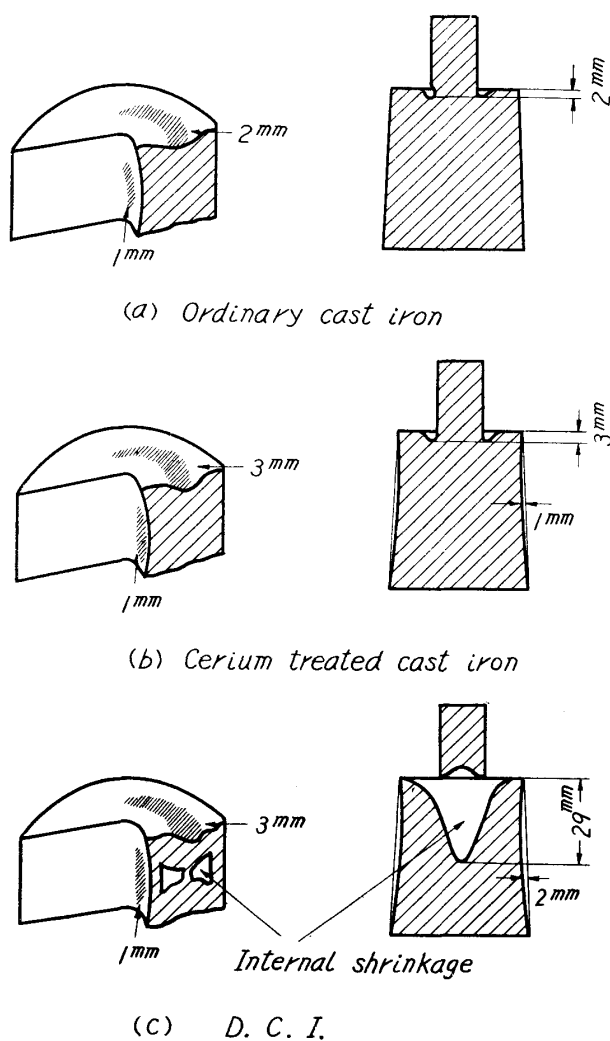
Fig. 3. Shrinkage cavity test.

shrinkage, especially a remarkable internal shrinkage, whereas other two cast irons, those treated with 0.3 per cent cerium (white fracture) and the ordinary cast iron (grey fracture), which all have the same chemical composition, showed a shrinkage depression of about 3 mm in maximum depth, and are free from the internal shrinkage.

3. Application for malleable cast iron

As well known, black heart malleable cast iron is manufactured by the graphitizing heat-treatment of white iron, so the thickness and the chemical compositions are severely restricted to make the white iron in a cast state, and the graphitizing heat-treatment of a long period is necessary. Since the reduction of the period of the heat-treatment is of importance in the manufacture of malleable cast iron, many studies

have been done on the rapid malleablizing.

There are several methods[7] [8] [9] [10] to manufacture the rapid malleable iron, such as a method in which the chemical composition is controlled to be low carbon and high silicon, a method with a special heat-treatment, a method with an improved melting atmosphere, a method in which the special elements are added. Tanimura[11] and Okamoto[12] reported on the effect of the addition of magnesium on the spheroidization of graphite and white ironization. In the present work the addition of cerium was attempted for manufacturing the rapid malleable cast iron containing high silicon, because it was approved that the addition of cerium was effective for the deoxidation, desulfurization and super-cooling of molten metal as well as that of magnesium.

The heat-marks A, B and C in Table 3 were treated by the suitable amount of cerium and cast in the green sand mould of J.I.S. No. 4 tensile test specimen according to the casting plan determined by J.I.S. for malleable cast iron. The amount of cerium added, the temperature and the period of annealing, and the mechanical properties obtained are shown in Table 7. The specimens of marks

Table 7. Mechanical properties.

Mark	Ce added quantity %	Heat-treatment	Tensile strength kg/mm²	Elongation %	Hardness B.H.N
A	0.05	850°C·3 H 750°C·12 H	46.2	10	224
		850°C·3 H 750°C·25 H	41.1	12	142
B	0.3	850°C·3 H 750°C·6 H	49.5	13	152
		850°C·3 H 750°C·10 H	45.5	16	141
C	0.1	850°C·3 H 750°C·8 H	29.5	3	123
	0.3	〃	37.5	6	132

A and B showed especially a higher tensile strength and elongation than the ordinary malleable cast iron. This may be due to the high silicon content of these materials, because the tensile strength is generally increased with silicon content. The mechanical properties of the specimen of mark C showed lower values than those of marks A and B owing to its high carbon contents. In comparison of 0.1 with 0.3 per cent cerium addition, however, the latter showed

(7) H. Tanimura, J. Iron & Steel Inst. Jap., **25** (1937), 559 ; **26** (1940), 860.

(8) C. F. Joseph, Iron Age, **139** (1937), 28.

(9) J. T. Bryce and H. G. Schwab, Metal Progress, **33** (1938), 35.

(10) H. Mikashima, T. Owadano and T. Kobayashi, J. Jap. Foundrymen's Soc., **28** (1956), 328.

(11) H. Tanimura and H. Seki, Study of Ductile Cast Iron (II) (1954), 140.

(12) Okamoto and Tottori, J. Iron & Steel Inst. Jap., **37** (1951), 520.

the improved shape of graphite and the higher mechanical properties than the former.

Although the quantitative determination of graphitizing rate was not performed, the decomposition of cementite at the first stage finished perfectly within 3 hrs at 850°C. On the other hand, the decomposition of pearlite at the second stage was remarkable influenced by the silicon content, that is, in the specimen of mark B, about 5 to 10 per cent of pearlite was retained for 6 hrs at 750°C, and the complete decomposition was obtained within 10 hrs, and in the specimens of mark C the decomposition finished perfectly within 8 hrs. In the specimen of mark A, the matrix showed a bull's eye structure after 12 hrs, and a perfect ferrite structure was obtained after 25 hrs.

(a) Ce 0.1%   (b) Ce 0.3%

Photo. 2.   The effect of cerium amounts on the graphite shape after annealing. (×100)

Summary

The molten metals of hypo-eutectic and eutectic compositions were treated with cerium, and the variation of the structure with the amount of cerium added was examined. The results obtained are as follows:

1. With increasing amount of cerium, the fracture of the cast iron varied from grey to white passing through the inverse chill. Moreover, when the amount of cerium added was fixed, the pre-deoxidized and desulfurized iron showed a relatively easy malleablization.

2. It was surmised that the white ironization with cerium was caused by the deoxidation, the desulfurization and the super-cooling of molten metal, and not by the action of carbide forming elements such as manganese, chromium.

3. By using a very little amount of cerium, the restriction of chemical compositions and thickness for the ordinary malleable cast iron were relieved. Moreover, the white iron containing high silicon manufactured by adding cerium was easily malleablized, and its mechanical properties were superior to those of the ordinary malleable cast iron.