Research on the High Silicon Malleable Cast Iron by the Addition of Bismuth

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(Received July 30, 1964)

Synopsis

High silicon malleable cast iron was manufactured by adding 0.05 per cent of bismuth. The mechanical properties of this iron are better, and the periods of malleablized heat treatments are shorter than those of conventional malleable cast irons. The chilling tendency caused by the addition of bismuth begins to fade in 5 minutes after its addition to a molten iron.

I. Introduction

To develop the physical and the mechanical properties of malleable cast irons many works have been reported[(1)-(8)]. The increase of silicon content in cast irons is easily understandable to be effective because of increasing malleablizing speed and tensile strength of irons, but the amount is restricted for the purpose of obtaining white cast iron structure in as-cast condition, though the increase of silicon for this purpose is possibly by the decrease of carbon content of a malleable cast iron. It is, however, more important and interesting to research the increase of silicon amount up to about 2 per cent in the range of the ordinary carbon content, say $2.3\sim2.6$ per cent, of a malleable cast iron.

To develop the mechanical properties and to raise the malleablizing speed of malleable cast iron, our several works have been reported: for example, study[(9)]

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* The 1120th report of the Research Institute for Iron, Steel and Other Metals.

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(8) AFS Malleable Div. Heat Treatment Committee, Modern Castings, **45** (1964), 749.

(9) M. Homma, A. Minato, H. Meguro and Y. Abe, Sci. Rep. RITU, **A 12** (1960), 500.

of the high silicon malleable cast iron by the addition of cerium, study[10] of the spheroidal graphite hypereutectoid cast steel, and study[11] of the high silicon malleable cast iron controlling the relation among silicon, manganese and sulphur. The present report describes the rapid malleablizing and high tensile malleable cast iron manufactured by adding 0.05 per cent of bismuth to the molten iron, being super-cooled by reducing refining.

The studies of the relation between bismuth and a malleable cast iron have been heretofore reported many times, and especially, it is noticeable that a malleable cast iron, "Centra Steel"[12], as it is called, having a hypereutectoid composition and a high elastic modulus can be manufactured by the addition of boron, tellurium and bismuth; of these bismuth has been found in some cases to produce a "lacy" type of flak graphite, and for this reason tellurium is preferred.

II. Experimental methods

The chemical compositions of raw materials used are shown in Table 1.

Table 1. Chemical compositions of raw material.

Materials	Chemical composition %				
	C	Si	Mn	P	S
Steel	0.35	0.12	0.53	0.007	0.015
Coke pig iron	4.15	2.09	0.53	0.130	0.026

The specimens were prepared in a small electric furnace of Héroult type capable of melting about 50 kg. The charged raw materials were steel scrap and carbon in one case, and coke pig iron and steel scrap in the other. These materials were refined by the reducing slag composed of $CaCO_3$, SiO_2 and carbon.

The test-pieces, 30 ∼ 50 mm in diameter, for the fracture examination and those for the mechanical property without the addition of bismuth and with the addition of bismuth of 0.05 per cent were all cast in green sand moulds. The mechanical test-pieces, 40 mm in parallel part and 14 mm in diameter, were malleablized as in as-cast condition. The tapping and the casting temperature were 1490 ∼ 1520°C and 1440 ∼ 1470°C, respectively.

Both commercial bismuth (99.9 per cent) and specially qualified one (99.999 per cent) were used, but the difference between their effects was hardly detectable. The melting and the boiling temperature of bismuth are 291°C and 1560°C, respectively, and therefore, an attention must be paid to the operation of its addition and the disappearance of its effects by the evaporation, which will be described in IV.

(10) M. Homma, H. Meguro, A. Minato and Y. Abe, Sci. Rep. RITU, **A 12** (1960), 201.
(11) M. Homma, Y. Abe, H. Meguro and A. Minato, Sci. Rep. RITU, **A 13** (1961), 82.
(12) W.B. Larson and Others, Modern Castings, **35** (1959), 47.

III. Result of experiments and considerations

1. Chemical compositions of specimens and their fractures in as-cast condition

The results are shown in Table 2.

Table 2. Chemical compositions of specimens and fractures of as-cast condition.

Furnace	Charge No.	Raw material	Tap No.	Chemical composition (%)							Fractures after bismuth addition 0.05 %, mmφ		Fractures before bismuth addition, 30mmφ
				C	Si	Mn	P	S	Cr	Bi	30	50	
Basic lining	419A	Steel and coke pig iron	1	2.28	1.84	0.59	0.017	0.012	0.038	0.006	W	W	Mo (W)
			2	2.18	1.78	0.61	0.017	0.019	—	0.005	W	W	W
	426A		1	2.57	1.92	0.58	0.015	0.023	—	0.008	W	W	Mo (G)
			2	2.40	1.88	0.58	0.016	0.020	—	0.007	W	W	G
	510A		1	2.56	2.08	0.57	0.017	0.025	—	0.011	W	W	G
			2	2.45	2.04	0.57	0.023	0.015	—	0.011	W	Mo	G
	607B	Coke pig iron and steel	1	2.35	2.22	0.56	0.079	0.020	0.029	0.007 0.015	W	Mo	G
			2	2.35	2.14	0.56	0.073	0.019	—	0.014 0.009	W	Mo	G
Acid lining	822		1	2.44	2.06	0.47	0.074	0.063	—	0.006	W	W	Mo (W)

Note W: White iron, G: Grey iron, Mo: Mottled iron.
The fracture of mottled iron closed to that of white or grey iron is shown by Mo(W) or Mo(G), respectively.

The ratio of amounts manganese/sulfur was 22.8～49.2 in the basic furnace operation and 7.5 in the acid one, and so the amount of manganese in these cases was sufficient, according to the formula of Gilmore(13). Though this ratio has, in general, a large effect on the malleablization, the specimens in the present research were hardly influenced by this ratio because of a large content of silicon of 1.8～2.2 per cent, due to having a much wider range of this ratio compared with conventional malleable irons.

The specimens of 30 mm in diameter, containing no bismuth showed the mottled fracture, when silicon content increased, over 1.8 per cent, but those of 30～50 mm in diameter, to which 0.05 per cent of bismuth was added, throughout the range of carbon and silicon in the present case, showed the white iron fracture in as-cast condition, because of both actions of the super-cooling effects of the molten iron caused by the reductions of oxygen and sulfur, and by the addition of bismuth.

The analytical amount of bismuth was 0.005～0.015 per cent, and that of oxygen was 0.0010～0.0030 per cent in the specimens adopted by permanent

(13) L.E. Gilmore, Foundry, **55** (1925), 734.

mould.

In high silicon malleable cast irons reported by Roesch(14) the total sum of carbon and silicon is 3.7～3.9 per cent and the amount of silicon is in the range of 1.4～1.55 per cent, and the ratio maganese/sulfur is 17.2～3.9 per cent. On the other hand, the total sum of carbon and silicon and the amount of silicon are respectively 4.0～4.7 per cent and 1.8～2.2 per cent in the present research, as shown in Fig. 1.

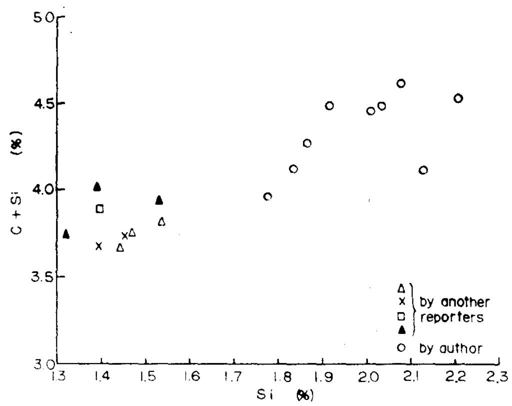


Fig. 1. The relation between carbon and silicon in the high silicon malleable cast irons.

It was shown by the present research that the increase of silicon did not cause the mottled or the gray fracture, co-operated with the addition of bismuth, and also it could be presumed that the fluidity of molten iron would be developed by the increase of silicon.

2. Heat treatments and mechanical properties

The heat treatments and the structures obtained are shown in Table 3. The

Table 3. Heat treatment temperature and holding time.

Matrix	First stage graphitization	Second stage graphitization
Globular pearlite type	850°～900°C×6～10hr Air cool	650°C×6hr Air cool
Ferrite type	850°～900°C×6～10hr Furnace cool	750°C×14～20hr Furnace cool

spheroidizing of pearlite was completed by heating for 6 hours at 650°C. On the other hand, the increase of silicon caused the increase of the area of the ferrite around tempered graphite but it could be controlled by fixing the spheroidizing temperature and the amount of silicon to the constant value. Though the perlite structures were apt to remain in the ferritizing treatment, caused by bismuth, they

(14) K. Roesch, Foundry Trade J., **104** (1958), 479.

could be decomposed by the control of heating time.

The mechanical properties are shown in Fig. 2. The increase of hardness

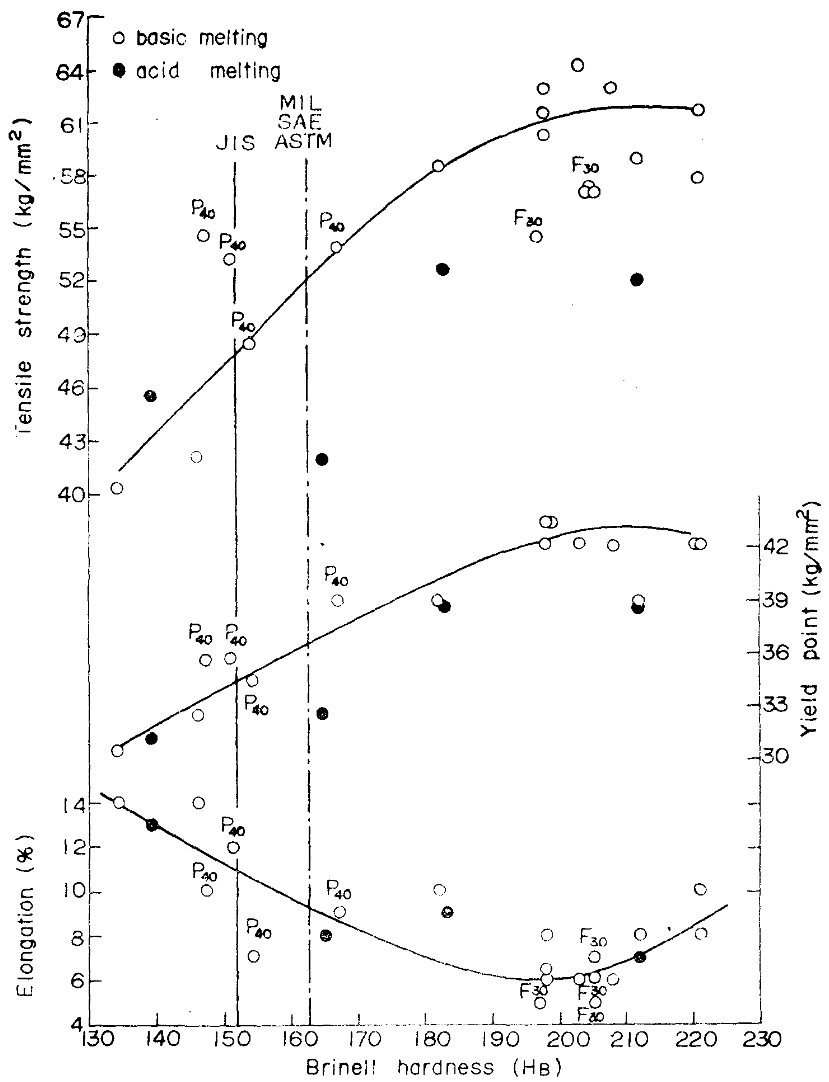


Fig. 2. The relation between hardness and tensile strength, yield point, elongation of the bismuth malleable cast iron.

increases tensile strength and yield point, and decreases elongation.

The black heart malleable irons having ferrite matrix in the present work showed tensile strength of 40～43 kg/mm², yield point of 29～33 kg/mm², elongation of 10～14 per cent, and Brinell hardness of 125～145. The minimum Brinell hardnesses of a pearlite malleable iron stipulated by JIS (Japan Industrial Standard) and SAE are shown by the vertical continuous line and the chain line, respectively. The range above the boundary line of Brinell hardness of 152～163 is the range of pearlite malleable iron, and the range below this line is that of ferrite malleable iron. The marks P_{40} and F_{30} signify the ratio of pearlite being 40 per cent and that of ferrite being 30 per cent in the matrix, respectively. The round marks without number, over than hardness 160 refer to globular pearlite matrix.

The relation between the tensile strength and elongation shown by the under-limited lines of the pearlite malleable iron stipulated by JIS and the standard of United States, and those shown by the round marks signifying having the globular pearlite matrix in the present study, are shown in Fig. 3.

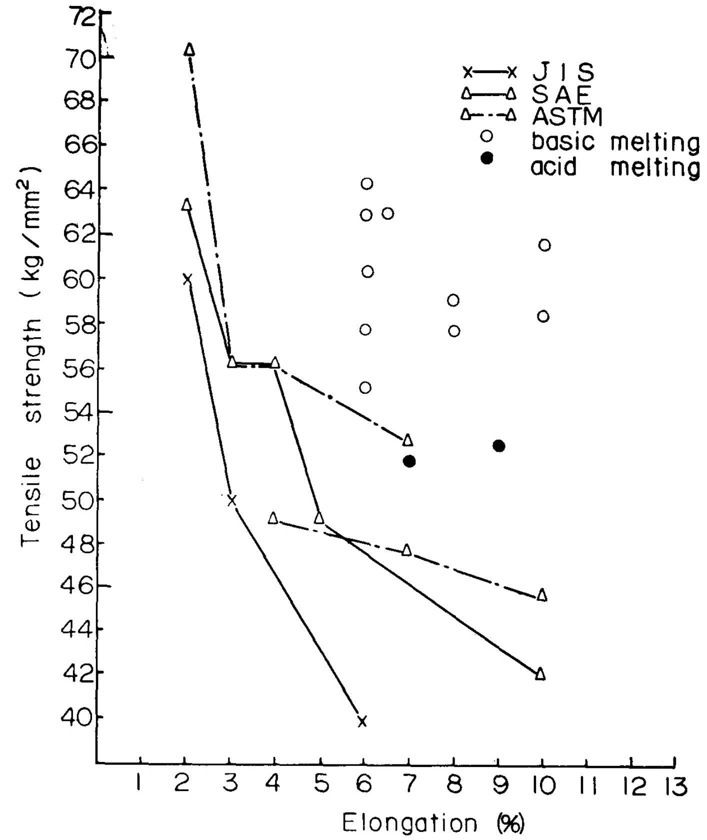


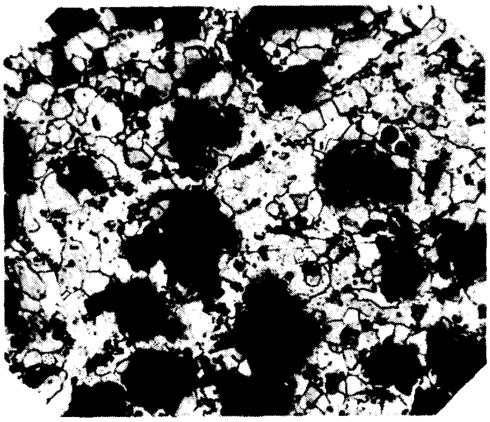
Fig. 3. The relation between tensile strength and elongation of pearlite malleable cast iron stipulated by JIS, SAE and ASTM, and those by present study.

The malleable irons having globular pearlite and prepared in the basic furnace showed tensile strength of 56~64 kg/mm^2, yield point of 39~44 kg/mm^2 and elongation of 6~10 per cent. On the other hand, those prepared in the acid furnace showed the same elongation and a little lower tensile strength, say, 52~53 kg/mm^2.

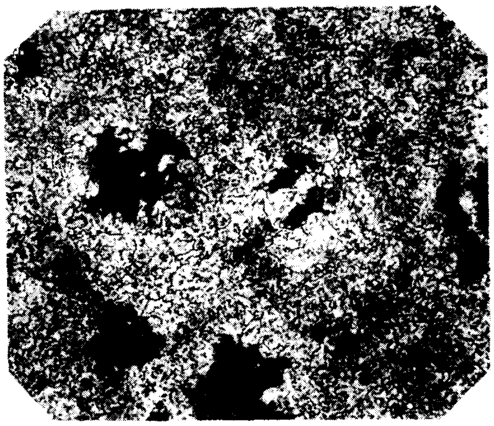
Photo. 1 shows the microstructures of the specimens after heat-treatments.

IV. Disappearance of the effects of bismuth with time

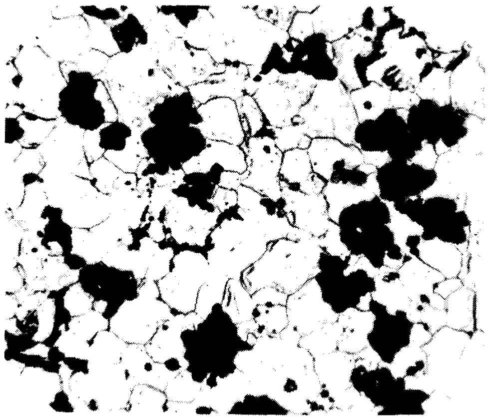
The addition of bismuth has strong effects to render white iron structure at the solidifying point of iron. Bismuth has such a low boiling point as 1560°C and so the yield of its addition to a molten iron is very low. The bismuth alloyed already



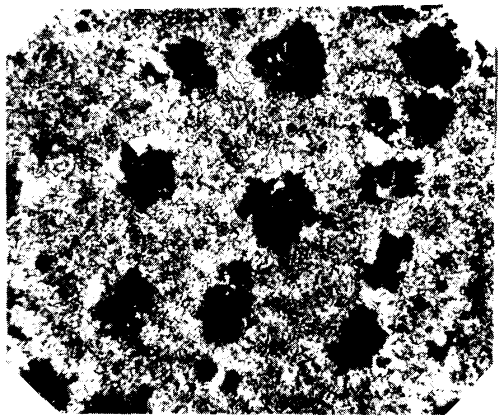
Charge No. 607B, basic melting, ferrite matrix. ×110



Charge No. 426A, basic melting, globular pearlite matrix. ×220



Charge No. 822, acid melting, ferrite matrix. ×285



Charge No. 822, acid melting, globular pearlite matrix. ×285

Photo. 1. The structures of bismuth malleable cast iron.

with a molten iron evaporates and disappears with time. The similar case is well-known in the behaviours of magnesium used for manufacturing a ductile cast iron.

To clarify the fading behaviours of bismuth, the structural change was examined in the range between the white and the gray cast iron, using thin castings which are apt to result in gray iron structure without the addition of bismuth. The structural changes were obtained when the cast iron having the composition of 3.4 per cent C, 2.0 per cent Si, 0.85 per cent Mn, 0.11 per cent P, and 0.03 per cent S was cast in the green sand mould of diameters 3, 5, and 10 mm; the result is shown in Fig. 4.

The specimen Nos. 1, 2, 3, 4, 5, 6 and 7 are those of the non-inoculated, inoculated, inoculated immediately after the addition of bismuth 500 ppm in the melting furnace, inoculated after 5, 10, 15 and 20 minutes of the bismuth addition, respectively. The inoculant was the mixture of Fe-Si 0.2 per cent, Ca-Si 0.2 per cent and CaF_2 0.07 per cent. The temperature of iron in the melting furnace was retained at 1500°C throughout the experiments.

The molten iron solidified with the strong chilling tendency by the addition of bismuth and retained perfectly its tendency for 5 minutes after the addition of bismuth. But after 10 minutes the effects of bismuth addition already disappeared as shown in Fig. 4, except the specimen of 3 mm diameter, in which the effects remained yet a little for 20 minutes.

Fig. 5 shows the structural changes of the cast iron 30 mm in diameter and

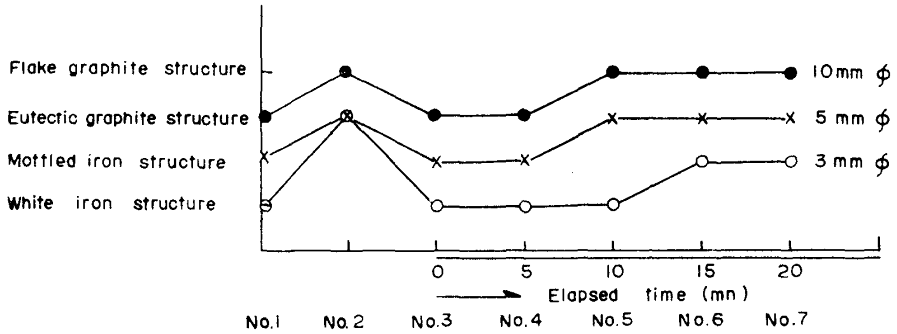


Fig. 4. The structure changes, before and after bismuth addition and with elapse of time.

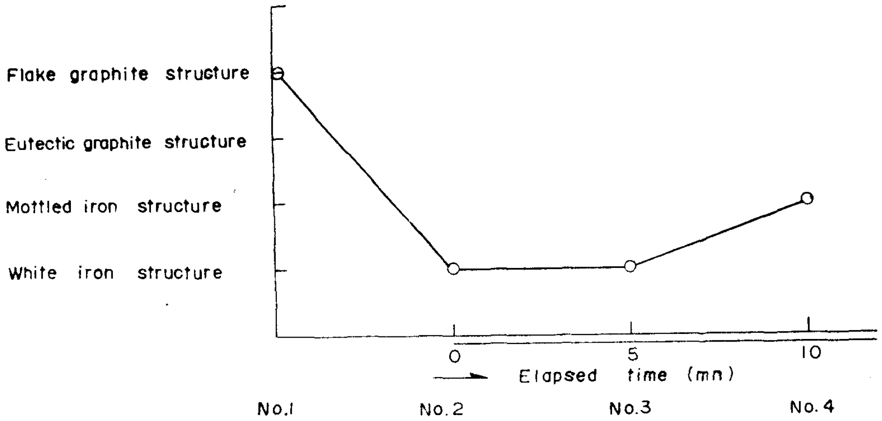


Fig. 5. The structure changes of the cast iron of 30mmϕ thickness before and after bismuth addition and with elapse of time.

having the composition of 2.9 per cent C, 1.89 per cent Si, 0.50 per cent Mn, 0.04 per cent P, and 0.02 per cent S, in which the structure of No. 1 contains no bismuth, No. 2 is the structure immediately after the addition of 1000 ppm of bismuth, and Nos. 3 and 4 are the structures elapsed 5 minutes and 10 minutes, respectively, after the addition of bismuth; all of these were non-inoculated and obtained from the molten iron retained at 1500°C. In any case, after 5 minutes from the addition, the effects of bismuth begin to disappear. The rapid disappearance of the effects of bismuth addition is not industrially unbeneficial in manufacturing these malleable irons, because the addition of bismuth is possible to add to a last transfer ladle immediately before pouring to mould.

The bismuth amounts in iron before the addition, immediately after the addition and after the elapse of 30 minutes from the addition are shown in Table 4, together with the corresponding structural changes. After 30 minutes, they approach nearly their original states, leaving a little difference in the amount of bismuth, but the structures are recovered perfectly to those before the addition of bismuth in the specimens of 3, 5 and 10 mm in diameter.

Table 4. The amounts of bismuth before and after bismuth addition and the structure changes by thickness.

Chemical composition	2.90 %C, 2.35 %Si, 0.57 %Mn, 0.017%P, 0.027%S		
Inoculated quantity	0.47% (Fe-Si, Ca-Si, CaF_2)		
Condition of treatment	Before bismuth addition	Immediately after bismuth addition 100ppm	30min after bismuth addition 100ppm
Analytical value of bismuth (ppm)	7,8,5	60,60,60	10,9,10
Casting diameter (mm)	Structure of iron		
3	Mottled iron	White iron	Mottled iron
5	Eutectic graphite iron	White iron	Eutectic graphite iron
10	Flake graphite iron	Mottled iron	Flake graphite iron

The yield of bismuth in Table 2 will be in the range of 10~30 per cent, considering that the amount of bismuth in the iron before its addition is about 10 ppm as shown in Table 4. Compared with the bismuth amount in Table 2 and the heretofore reported data(3),(4), in which bismuth prevents the iron from the 1st and the 2nd graphitization, accompanied by the increase of its amount from 0.025 to 0.09 per cent, it will be seen that the amount of bismuth used in the present case, say 0.005~0.015 per cent, does not influence the 1st and the 2nd graphitization.

Summary

The high silicon malleable cast irons containing 2.2~2.6 per cent carbon and 1.8~2.2 per cent silicon were studied and the following results were obtained.

(1) By the addition of bismuth having the effect of chilling action to the molten irons which are refined reducingly and have the super-cooled tendency, the iron, which has the same amount of carbon and the more amount of silicon, compared with those of conventional malleable iron, can be obtained as the white iron in a green sand mould. Because of the higher amount of silicon, the malleablizing time can be shorten with the increased tensile strength.

(2) These malleable irons of ferrite type have tensile strength of 40~43 kg/mm^2, yield point of 29~33 kg/mm^2, elongation of 10~14 per cent and hardness of 125~145 H_B. These malleable irons of globular pearlite type have tensile strength of 56~64 kg/mm^2, yield point of 39~44 kg/mm^2, elongation of 6~10 per cent and

hardness of $180 \sim 225 H_B$.

(3) The behaviours of bismuth added to a molten iron were clarified. The effects of bismuth perfectly remained for 5 minutes but even after $20 \sim 30$ minutes of its addition, its effects do not disappear thoroughly, leaving a little difference in the amount of bismuth.

The authors express their thanks for a Grant-in-Aid from the Ministry of Education.