A NEW HIGH STRENGTH CAST IRON

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I. Introduction

Some kinds of high strength cast iron have been researched with the introduction of processes for refining iron. In regard to this, moreover, we found lately a new fact that, when small amount of calcium cyanamide is added into the molten ordinary gray cast iron, the mechanical properties, especially tensile strength of the iron may be improved.

The effects of calcium cyanamide on the mechanical and other properties of cast iron, which are recognized in the above process, will be studied in the following paper.

II. Method of Study

We, for melting iron, using a graphite crucible in the kriptol resistance furnace or high frequency induction furnace, got many kinds of cast iron of different composition. The test piece of tensile strength shown in Fig. 1 was poured in half-dried sand mold. And the measurement of temperature was carried out by optical pyrometer.

The used materials are shown in Table 1. The calcium cyanamide, which we used, being grains of smaller than 3 mm crushed from clinker, was forced into the molten pig to react well.

TABLE 1. Used Materials

Materials	Remarks	Chemical composition, pct.							
		C	Si	Mn	P	S	Cu	Cr	V
Electric-regenerated pig iron (I)	A	3.40	1.59	0.39	0.24	0.018			
Electric-regenerated pig iron (II)	B	3.10	1.40	0.42	0.21	0.030			
Cupola-regenerated pig iron (I)	C	3.50	1.96	0.32	0.096	0.013	0.27	0.08	
Cupola-regenerated pig iron (II)	D	3.50	1.40	0.66	0.105	0.021			
Katsuyama electric pig iron	E	3.70	1.50	0.05	0.24	0.018			
Nisso low phosphoric pig iron	F	3.78	1.37	1.18	0.022	0.008	0.007	0.05	0.034
Mild steel scrap		~0.20	~0.18	~0.40	~0.05	~0.04			
Ferro-silicon			~75						
Ferro-mangan				~45					

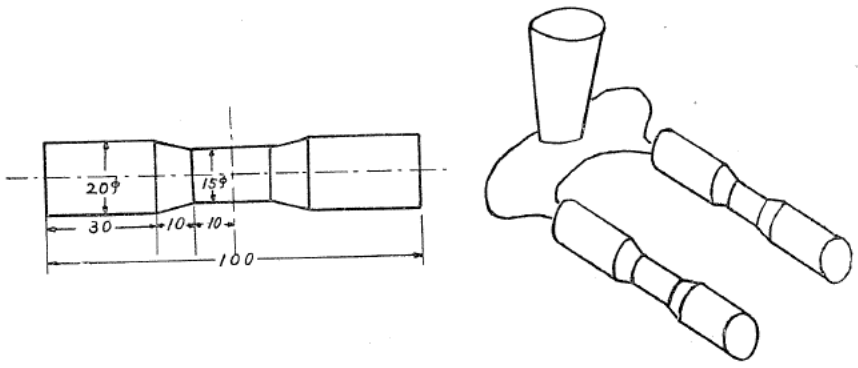


FIG. 1. Test piece of tensile strength.

III. Result of Experiment

(1) Effect of Adding Weight of Calcium Cyanamide:

We investigated about the effect of adding weight of calcium cyanamide on a few cast irons of different composition. The results are shown in Fig. 2.

Fig. 2 (a): Melting pig iron A and steel scrap, we made the molten pig iron containing 2.8 pct. C, 2.0 pct. Si and 1.0 pct. Mn, and added calcium cyanamide to it by 0.2 to 1.0 pct. The I-curve shows the change of tensile strength. In this case, the addition of 0.8 pct. is most desirable. The maximum heating was 1500°C, adding temperature 1450°C and pouring temperature 1400°C.

Fig. 2 (b): Using pig iron F, we made the molten pig containing 3.5 to 3.6 pct. C, 1.8 to 1.9 pct. Si and 1.0 pct. Mn, and added calcium cyanamide up to 3.0 pct.

From the I-curve, the curve of tensile strength, it may be seen that the best result is gained with the addition of 1.5 pct.

Fig. 2 (c): Melting pig iron C, we made the melt containing 2.9 pct. C, 2.0 pct. Si and 1.0 pct. Mn, and added calcium cyanamide by 0.1 to 0.8 pct.

In this case, the additon of 0.1 pct. is pretty effective already, and there is no difference in any case of the additions of 0.1 to 0.3 pct. If it is added by more than 0.5 pct., the blow hole develops, and the tensile strength decreases.

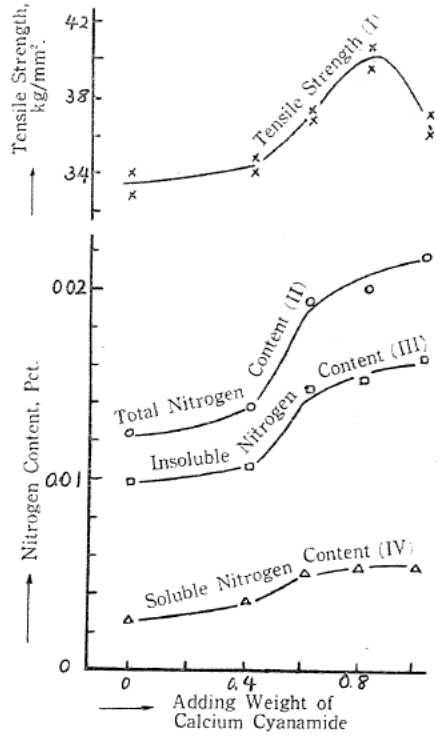
When we take the general view of the results of Fig. 2, the following facts are observed.

(i) According to the change of composition of the cast iron, the adding weight of calcium cyanamide which should give the maximum tensile strength is variable. When the cast iron contains low carbon and low silicon, the small amount of the added calcium cyanamide is effective already, and when high carbon and high silicon, more amount is necessary. But when it is added excessively, pin-holes and blow-holes are developed. From the result of measurement of the specific gravity, we can see later on, based on the fact of the decrease of the specific gravity, that when it is added excessively, the microscopic pin-holes develope even if the visible pin-holes do not appear.

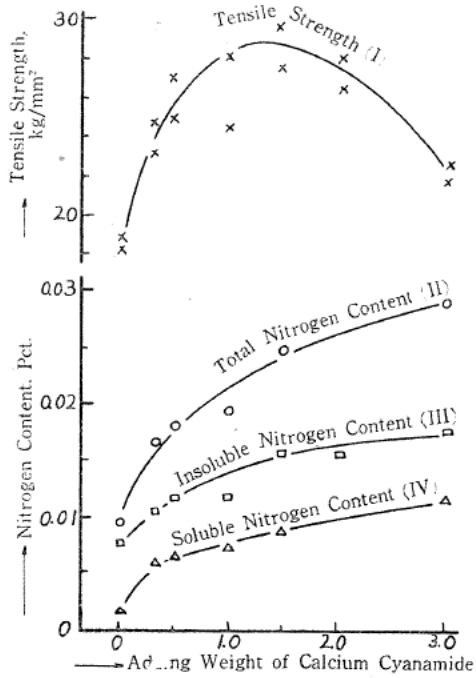
(ii) Even if the compositions of the cast iron made of different pig irons are same, the suitable adding weight of calcium cyanamide is variable, and the effect, accordingly, may not be constant.

(iii) According to the quality of the calcium cyanamide, the effect of adding

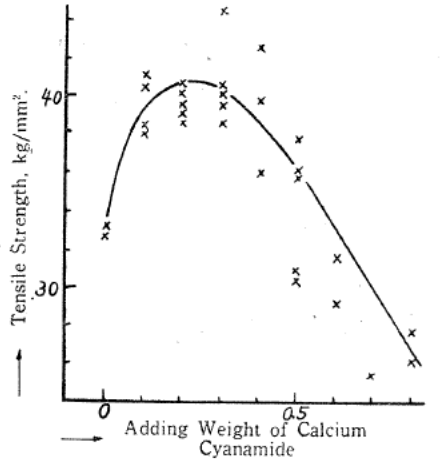
weight seems to be variable. Therefore, we, in using calcium cyanamide practically, must decide at first the most suitable adding weight.



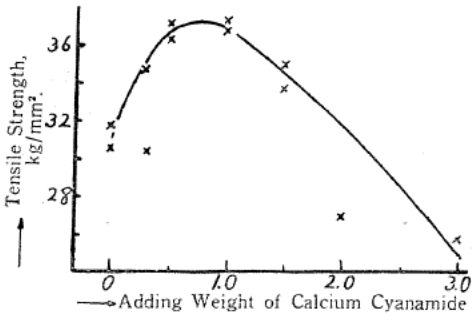
(a) Pig iron "A" is used. Composition; C: 2.8 pct., Si: 2.0 pct., Mn: 1.0 pct.



(b) Pig iron "F" is used. Composition; C: 3.5~3.6 pct., Si: 1.8~1.9 pct., Mn: 1.0 pct.



(c) Pig iron "C" is used. Composition; C: 2.9 pct., Si: 2.0 pct., Mn: 1.0 pct.



(d) Pig iron "B" is used. Composition; C: 2.6~2.8 pct., Si: 2.7~2.9 pct., Mn: 1.0 pct.

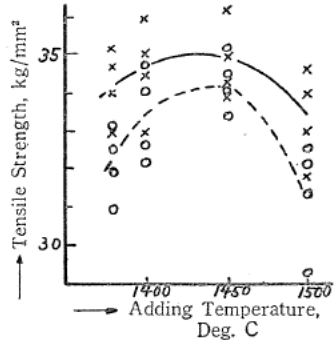
FIG. 2. Effect of adding weight of calcium cyanamide.

(2) *Effect of Adding Temperature:*

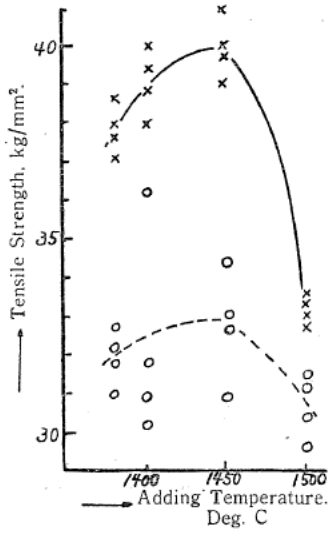
To decide the best adding temperature, we made four kinds of molten pig of different composition out of pig iron A, namely:

(I) 2.8 to 2.9 pct. C, 2.5 pct. Si and 0.6 pct. Mn,
(II) 2.8 to 2.9 pct. C, 3.0 pct. Si and 0.6 pct. Mn,
(III) 2.8 to 2.9 pct. C, 2.0 pct. Si and 1.0 pct. Mn,
(IV) 3.2 to 3.3 pct. C, 2.4 pct. Si and 1.0 pct. Mn.

Calcium cyanamide was added by 0.8 pct. Treating temperature were 1380, 1400, 1450 and 1500°C. The results for tensile strength are shown in Fig. 3. All through these four compositions, the treating temperature of 1450°C is most effective, the tensions of the cast iron treated at 1380 and 1500°C are low, and those at 1400 and 1450°C are almost equal with each other.



(a) ×——×; C: 2.8~2.9 pct., Si: 2.5 pct., Mn: 0.6 pct. ○·····○; C: 2.8~2.9 pct., Si: 3.0 pct, Mn: 0.6 pct. With addition of calcium cyanamide by 0.8 pct.



(b) ×——×; C: 2.8~2.9 pct., Si: 2.0 pct.. Mn: 1.0 pct. ○·····○; C: 3.2~3.3 pct., Si: 2.4 pct, Mn: 1.0 pct. With addition of calcium cyanamide by 0.8 pct.

FIG. 3. Effect of adding temperature of calcium cyanamide (pig iron "A" is used).

The low tensile strength at 1380°C may come from the imperfect decomposition of the calcium cyanamide, and that at 1500°C will be due to the hasty decomposition and much loss of the vapour of calcium cyanamide.

Therefore, we took always the adding temperature of 1450°C.

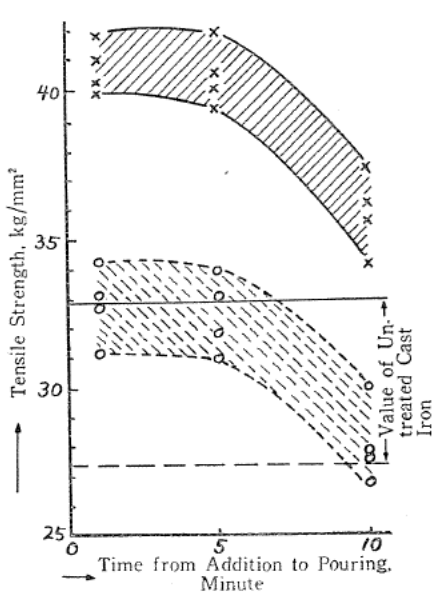
(3) *Effect of Holding Time from Addition of Calcium Cyanamide until Pouring:*

Using pig iron A, we examined the effect of the holding time from the addition of calcium cyanamide until the puring on the tensile strength which should be resulted. The holding was to keep the molten pigs in the furnace at 1450°C (±20°C) for 5 minutes or 10 minutes. The results are represented in Fig. 4.

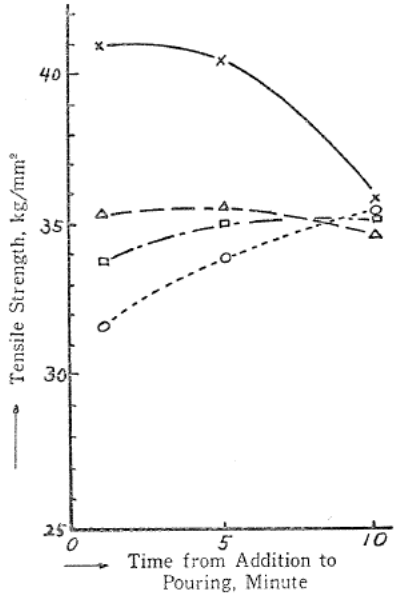
Fig. 4 (a) is the results of two kinds of cast iron, one containing 2.8 to 2.9 pct. C, 2.0 pct. Si and 1.0 pct. Mn, and the other containing 3.2 to 3.3 pct. C, 2.4 pct. Si and 1.0 pct. Mn. The value of the tensile strength after the holding of 5 minutes

is little different, but 10 minutes after the improved effect is almost destroyed.

Fig. 4 (b) represents the effect of the holding time on the molten pig iron treated with the different weight of the calcium cyanamide. The used cast iron contains 2.8 to 2.9 pct. C, 2.0 pct. Si and 1.0 pct. Mn. By the addition of 0.8 pct., the improved effect is diminished as the holding time increases same as Fig. 4 (a). But by the additions of 2.0 pct. and 3.0 pct., the tensile strength increases as the holding time increases. This is due to the diminution of the pin-holes. Each value 10 minutes after becomes almost resemble.



(a) Change of composition. ×; C: 2.8 ~2.9 pct., Si: 2.0 pct., Mn: 1.0 pct. ○; C: 3.2 ~3.3 pct., Si: 2.4 pct., Mn: 1.0 pct. With addition of calcium cyanamide by 0.8 pct.



(b) Change of adding weight of calcium cyanamide. Composition; C: 2.8~2.9 pct., Si: 2.0 pct., Mn: 1.0 pct. ×——×: with addition of calcium cyanamide by 0.8 pct. △——△: // 1.5 pct. □- - -□: // 2.0 pct. ○·····○: // 3.0 pct.

FIG. 4. Effect of holding time from addition to pouring.

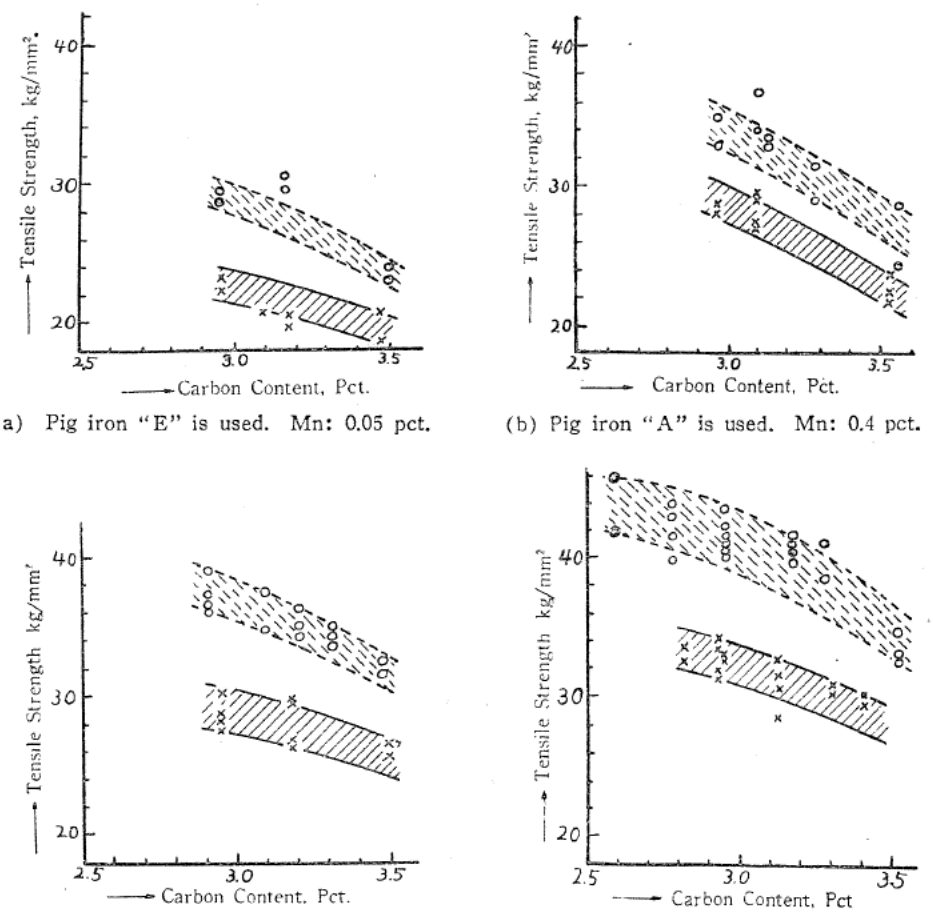
(4) *Influence of Component:*

(a) Influence of Carbon.

Using pig iron A (pig iron E when 0.05 pct. Mn only), we melted the cast iron with constant silicon content of 2.0 pct. and manganese content of 0.05, 0.4, 0.6 or 1.0 pct. The change of the tensile strength accomapnied by the change of the carbon content of these cast irons is indicated in Fig. 5. There are represented the tensile strength of the cast iron untreated or treated with the calcium cyanamide of 0.8 pct. in this figure. (a) is with 0.05 pct. Mn content, (b) is with 0.4 pct. Mn content, (c) is with 0.6 pct. Mn content and (d) is with 1.0 pct. Mn content.

From these figures, it is apparent that the tensile strength decreases with the increase of the carbon content, and this is the common property of the cast iron with flaky graphite.

The tensile strength of the cast iron treated with calcium cyanamide exceeds that of the untreated by 5 to 8 kg/mm², all through Figs. (a), (b), (c) and (d).



(a) Pig iron "E" is used. Mn: 0.05 pct. (b) Pig iron "A" is used. Mn: 0.4 pct.

(c) Pig iron "A" is used. Mn: 0.6 pct. (d) Pig iron "A" is used. Mn: 1.0 pct.

o: with addition of calcium cyanamide by 0.8 pct. ×: untreated. Si: 2.0 pct.

FIG. 5. Effect of carbon content.

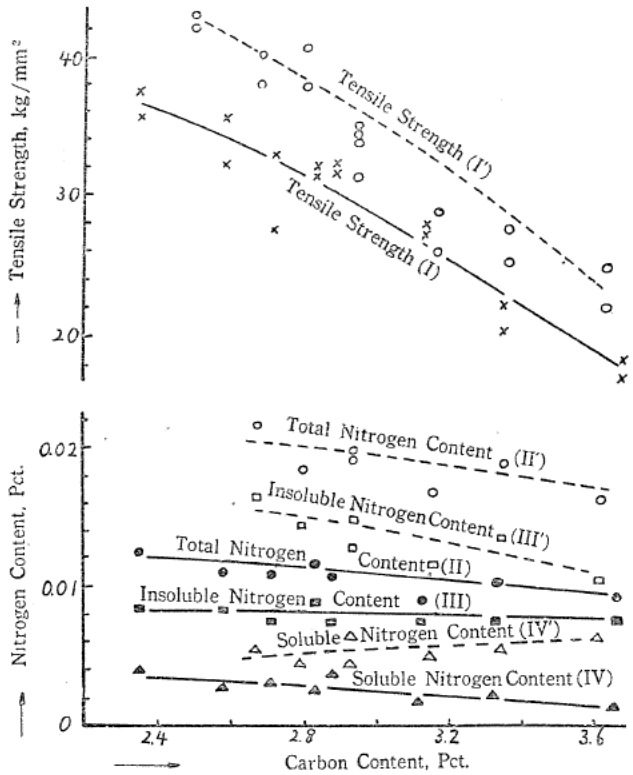
Fig. 6. is the result of other pig irons B and F. Silicon content is 2.0 pct. (1.7 to 2.0 pct. Si in analysis), manganese content is 1.0 pct., and carbon content is in the range of 2.4 and 3.6 pct. Calcium cyanamide is added by 0.3 pct.

In this result (I- and I′-curve), the tensile strength of the treated cast iron is greater by about 6 kg/mm² than that of the untreated. But as the carbon content increases, the effect is to be likely to decrease slightly. And the absolute values of I- and I′-curve are smaller than that of Fig. 5 (d). It is supposed that the difference comes from the properties of the material pig iron.

(b) Influence of Silicon.

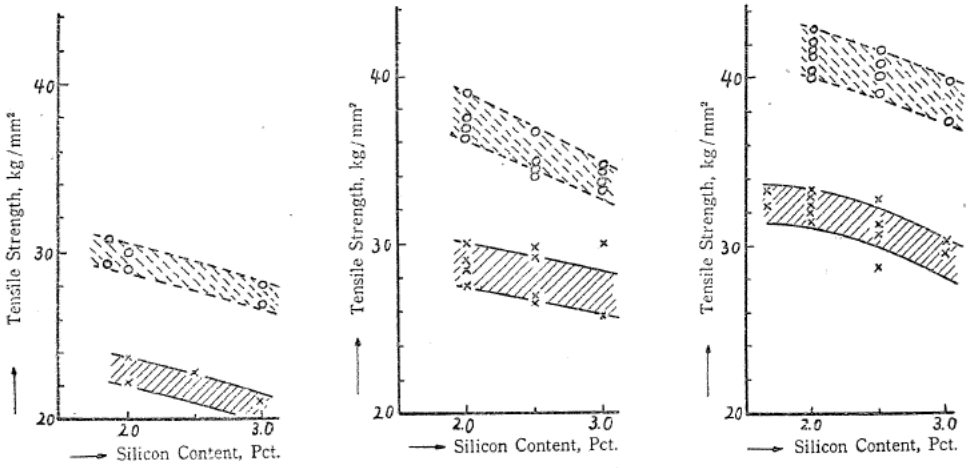
Using pig iron A (pig iron E when 0.05 pct. Mn only), we made the cast irons with constant carbon content of 2.9 pct. and manganese content of 0.05, 0.6 or 1.0 pct. Silicon content was changed between 2.0 and 3.0 pct. Calcium cyanamide added by 0.8 pct. In Fig. 7, there is indicated the result in the tensile strength.

As with the carbon content, when the silicon content increases, the tensile strength



Pig iron "B" and "F" are used. Si: 1.7~2.0 pct., Mn: 1.0 pct.
------: with addition of calcium cyanamide by 0.3 pct. ——: untreated.

FIG. 6. Effect of carbon content.



(a) Pig iron "E" is used. Mn: 0.05 pct.
(b) Pig iron "A" is used. Mn: 0.6 pct.
(c) Pig iron "A" is used. Mn: 1.0 pct.

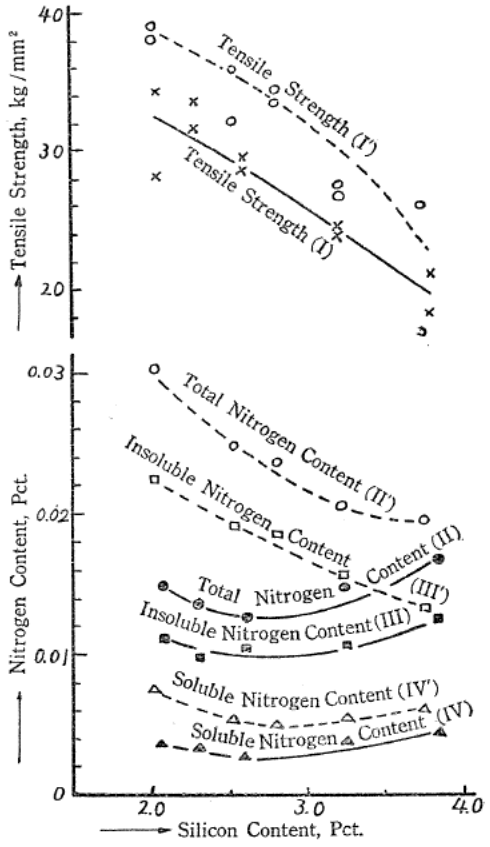
C: 2.9 pct. ○: with addition of calcium cyanamide by 0.8 pct. ×: untreated.

FIG. 7. Effect of silicon content.

decreases. In this case, also, the tensile strength of the treated cast iron is greater by 5 to 8 kg/mm² than that of the untreated.

Another pig iron B being melted, the cast iron with 2.9 pct. C (2.8 to 2.9 pct. in analysis) and 1.0 pct. Mn content was made. The silicon content is changed between 2.0 and 4.0 pct., and the added calcium cyanamide is 1.0 pct. The result is represented in Fig. 8.

Seeing this result, too, in the range of 2.0 to 3.0 pct. Si content, the tensile strength of the treated cast iron (I'-curve) is greater by about 6 kg/mm² than that of the untreated (I-curve), but in the range beyond 3.0 pct. Si, the increase of the tensile strength is small. And in the range of 2.0 to 3.0 pct. Si, the absolute value of the tensile strength in Fig. 8 is smaller than that of Fig. 7 (c). The difference may come from the property of used pig iron, in the same way as the carbon content.



Pig iron "B" is used. C: 2.8~3.0 pct. ——: untreated. ·····: with addition of calcium cyanamide by 1.0 pct.

FIG. 8. Effect of silicon content.

(c) Influence of Manganese.

Melting pig iron A (pig iron E when 0.05 pct. Mn only), we made the molten cast iron containing constant carbon of 2.9 pct. and silicon of 2.0, 2.5 or 3.0 pct., and added the ferro-mangan up to the aimed content. Calcium cyanamide was added by 0.8 pct. The results are shown in Fig. 9. (a) is with 2.0 pct. Si content, (b) is with 2.5 pct. Si content and (c) is with 3.0 pct. Si content.

This result is different from those of the carbon and silicon content, and the tensile strength increases as the manganese content increases, but when manganese content becomes more than 1.2 pct., there appears the mottled cast iron. Therefore, we made this experiment mostly with less than 1.0 pct. Mn content.

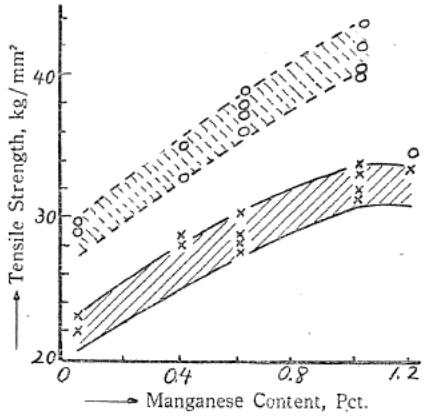
The treated tensile strength is improved by 6 to 8 kg/mm² from the untreated.

Fig. 10 shows the result with the cast iron, containing 2.8 to 3.0 pct. C and 2.2 pct. Si, made of the same pig iron A (pig iron E when 0.05 pct. Mn only).

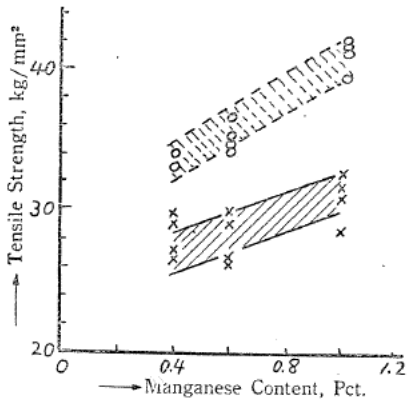
The curves of the tensile strength (I- and I'-curve) show the same fact as said above.

(d) Influence of Phosphor.

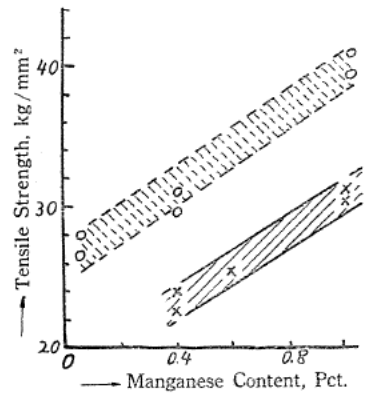
By using pig iron A, we made the molten pig containing 2.9 pct. C, 2.0 pct. Si and 1.0 pct. Mn, and added ferro-phosphor (15 pct. P) to make the aimed phosphor content in the range of 0.4 to 1.0 pct. Calcium cyanamide was added by 0.8 pct., and the results are indicated in Fig. 11.



(a) Si: 2.0 pct.



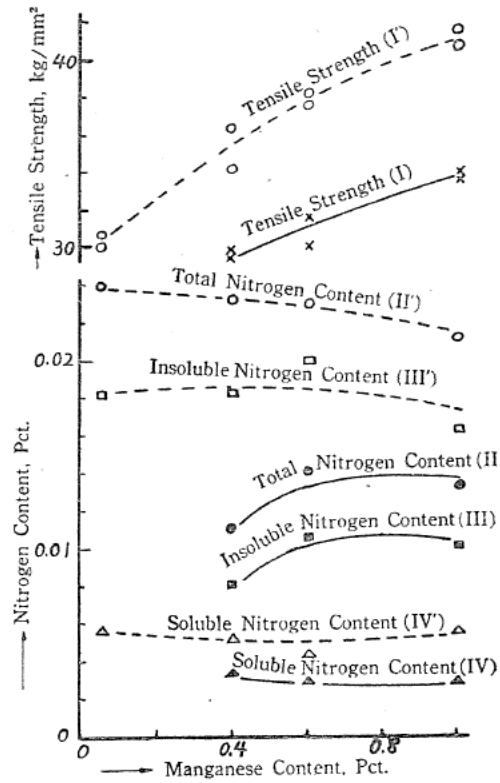
(b) Si: 2.5 pct.



(c) Si: 3.0 pct.

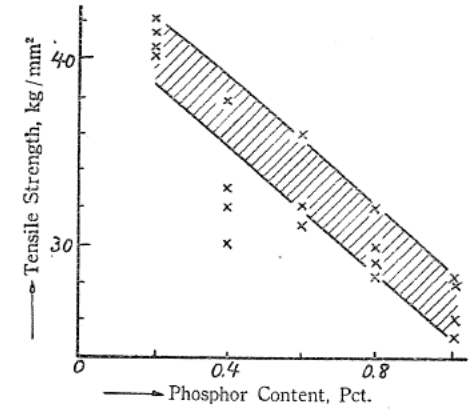
Pig iron "A" and "E" are used. C: 2.9 pct. ○: with addition of calcium cyanamide by 0.8 pct. ×: untreated.

FIG. 9. Effect of manganese content.



Pig iron "A" and "E" are used. C: 2.8~3.0 pct., Si: 2.2 pct. ——: untreated. ------: with addition of calcium cyanamide by 0.8 pct.

FIG. 10. Effect of manganese content.



Pig iron "A" is used. C: 2.8~2.9 pct., Si: 2.0 pct., Mn: 1.0 pct. With addition of calcium cyanamide by 0.8 pct.

FIG. 11. Effect of phosphor content.

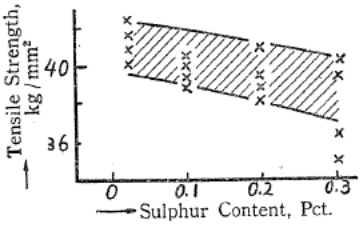
The tensile strength decreases linearly as phosphor content increases. This fact may be understood from the increasing steadite in the microstructure.

The phosphor content less than 0.2 pct. is not harmful.

(e) Influence of Sulphur.

Using pig iron A, we made the molten pig containing 2.9 pct. C, 2.0 pct. Si and 1.0 pct. Mn, and added the ferrous sulphide to it by 0.1, 0.2 or 0.3 pct. S content. Calcium cyanamide was added by 0.8 pct. The result is shown in Fig. 12.

In the range of this experiment, the decrease of the tensile strength is pretty small. Because of the high manganese content, all the sulphur contained grows into the manganese sulphide, and only little effect in strength is appeared. The value of 0.3 pct. S is wide-spattered. This may be because of the segregation of the manganese sulphide.



Pig iron "A" is used. C: 2.8~2.9 pct., Si: 2.0 pct., Mn: 1.0 pct. With addition of calcium cyanamide by 0.8 pct.

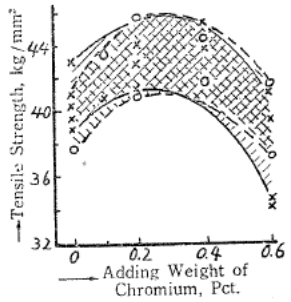
FIG. 12. Effect of sulphur content.

(f) Influence of Chromium.

Using pig iron C, we made two kinds of molten pig, one containing 2.9 pct. C, 2.0 pct. Si and 1.0 pct. Mn, and the other containing 2.9 pct. C, 2.0 pct. Si and 0.6 pct. Mn. With ferro-chrome (95 pct. Cr), we added 0.1, 0.2, 0.4 or 0.6 pct. Cr to them, and calcium cyanamide is added by 0.3 pct. The results are shown in Fig. 13.

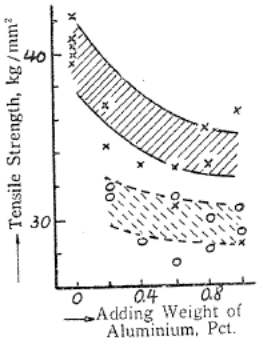
In both case of the Mn content of 0.6 and 1.0 pct., the tensile strength of less than 0.3 pct. Cr increases with the Cr content, and in case where the Cr content is more than 0.3 pct., the cementite increases, and at 0.6 pct Cr content, we see the mottled iron and tensile strength decreases.

When the cast iron contains such amount of carbon and silicon, the maximum tensile strength is obtained at 0.3 pct. Cr content, but in this case hardness increases, and the machinability becomes worse.



Pig iron "C" is used. ×; C: 2.9 pct., Si: 2.0 pct., Mn: 1.0 pct. ○; C: 2.9 pct., Si: 2.0 pct., Mn: 0.6 pct. With addition of calcium cyanamide by 0.3 pct.

FIG. 13. Effect of chromium.



Pig iron "C" is used. ×; C: 2.9 pct., Si: 2.0 pct., Mn: 1.0 pct. ○; C: 2.9 pct., Si: 1.7 pct., Mn: 1.0 pct. With addition of calcium cyanamide by 0.3 pct.

FIG. 14. Effect of aluminium.

(g) Influence of Aluminium.

Using pig iron C, we made two kinds of molten pig, one containing 2.9 pct. C, 2.0 pct. Si and 1.0 pct. Mn, and the other containing 2.9 pct. C, 1.7 pct. Si and 1.0 pct. Mn, and added them pure aluminium by 0.2 to 1.0 pct. Calcium cyanamide was added by 0.3 pct. The result is represented in Fig. 14.

Looking these results in two kinds of melt, in case of less than 0.6 pct. Al, the tensile strength decreases as aluminium content increases, and after then it is almost constant.

(h) Influence of Tin.

Using pig iron C, we made the melt containing 2.9 pct. C, 2.0 pct. Si and 1.0 pct. Mn, and added pure tin by less than 0.3 pct. Calcium cyanamide was added by 0.2 pct. The result is shown in Fig. 15.

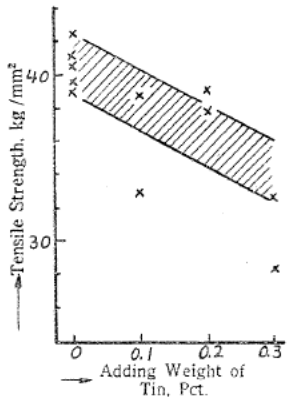
In this figure, it is found that the tensile strength decreases as the tin content increases.

(i) Influence of Lead.

Using pig iron C, we melted the cast iron containing 2.9 pct. C, 2.0 pct. Si and 1.0 pct. Mn, and added lead by 0.05, 0.1, 0.2 or 0.3 pct. Fig. 16 is the result in the tensile strength of both the cast iron treated with 0.2 pct. calcium cyanamide and the one untreated.

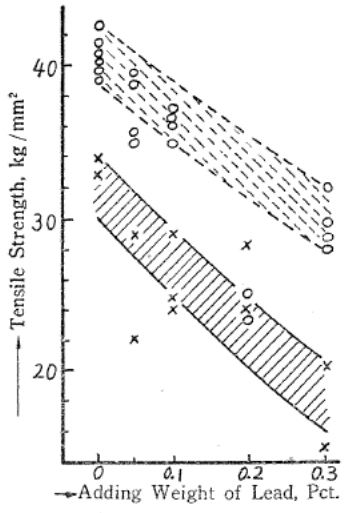
When lead was added, the brown fume arose, and the lead recovery might be low, but as shown in Fig. 16, the tensile strength decreases with addition of lead, and the tensile strength of the treated cast iron is greater by 8 to 9 kg/mm^2 than that of the untreated.

And then, with the increase of the lead addition, the chilling effect is found.



Pig iron "C" is used. C: 2.9 pct., Si: 2.0 pct., Mn: 1.0 pct. With addition of calcium cyanamide by 0.2 pct.

FIG. 15. Effect of tin.



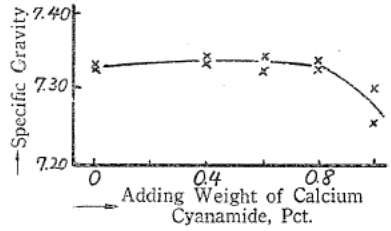
Pig iron "C" is used. C: 2.9 pct., Si: 2.0 pct., Mn: 1.0 pct. ○: with addition of calcium cyanamide by 0.2 pct. ×: untreated.

FIG. 16. Effect of lead.

(5) *Specific Gravity:*

Using the sample used in Fig. 2 (a), we measured the specific gravity. The result is shown in Fig. 17.

Until the addition of calcium cyanamide comes up to 0.8 pct., the specific gravity does not change. Therefore, until the adding weight of calcium cyanamide becomes suitable to the maximum tensile strength, the blow-holes do not develop. But when, by the addition of 1.0 pct. calcium cyanamide, the tensile strength decreases, the specific gravity decreases. Thus we can see the development of the microscopic blow-holes.



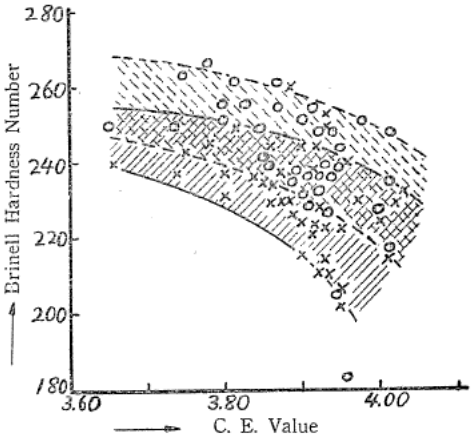
Pig iron "A" is used. C: 2.8 pct., Si: 2.0 pct., Mn: 1.0 pct.

FIG. 17. Relation between specific gravity and adding weight of calcium cyanamide.

(6) *Effect of Calcium Cyanamide on Hardness of Cast Iron:*

We examined what change happened in hardness of the cast iron when calcium cyanamide was added. The result is shown in Fig. 18. Calcium cyanamide was added by 0.5 pct., and the test piece of 20 mm ϕ was cast in the green sand mold. In this figure, the horizontal co-ordinate indicates the carbon equivalent value, or C.E. value (T.C. + Si/3 + P/3).

According to this result, the hardness of the cast iron treated with the calcium cyanamide increases by about 10 in Brinell Hardness Number.



×: untreated. ○: with addition of calcium cyanamide by 0.5 pct.

FIG. 18. Effect of calcium cyanamide on hardness.

(7) *Effect of Calcium Cyanamide on Chilling:*

As was seen in the preceding experiment, the addition of calcium cyanamide bring about increase of hardness. And it is supposed that the addition of calcium cyanamide has the chilling effect. Then we tested about this fact. The test piece for chilling is wedge-shaped, as shown in Fig. 19.

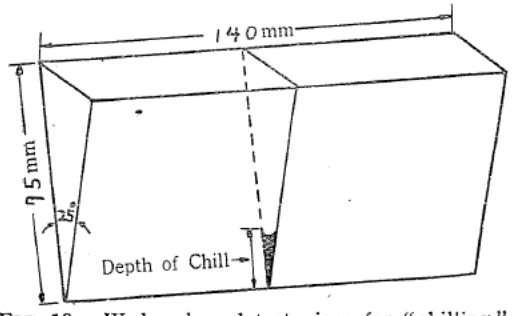


FIG. 19. Wedge-shaped test piece for "chilling."

Using pig iron C, we made the molten pig containing 2.9 pct. C, 2.0 pct. Si and 1.0 pct. Mn, and tested the chilling effect. This result is shown in the upper part of Table 2. Next melting pig iron D, we made the molten pig containing 2.7 to 2.8 pct. C, 2.0 pct. Si and 1.0 pct. Mn, and tested the chilling effect. The result is indicated in the lower part of Table 2.

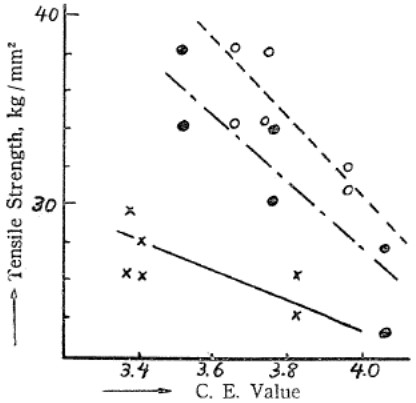
TABLE 2. Result of Chilling Test

Chemical composition (pct.)			Material pig iron	Adding weight of calcium cyanamide (pct.)	Inoculation of silicon (pct.)	Depth of chilling (mm)
C	Si	Mn				
2.9	2.0	1.0	C	0	0	5
2.9	2.0	1.0	C	0.8	0	14
2.9	2.0	1.0	C	0	0.6	0
2.9	2.0	1.0	C	0.8	0.6	4
2.7	2.0	1.0	D	0	0	9
2.8	2.0	1.0	D	0.5	0	20
2.7	2.0	1.0	D	0.5	0.8	8

Saying from these two results, the depth of chilling becomes about twice in the treated cast iron, but if a part of the silicon content is added as an inoculant after the treatment of calcium cyanamide, the chilling effect may be prevented.

(8) *Effect of Inoculation with Silicon:*

As was said in the above test, if a part of the silicon content is added as an inoculant, the chilling effect of calcium cyanamide may be prevented. And we examined how the inoculation of silicon effects on the tensile strength which should be resulted. Namely, using pig iron D, we made the melt containing 2.7 to 3.3 pct. C, 1.9 to 2.1 pct. Si and 1.0 pct. Mn, and tested the tensile strength of three kinds of cast iron, the first being the one untreated, the second being the one treated with 0.5 pct. calcium cyanamide and the last being the one treated with 0.5 pct. calcium cyanamide and then inoculated with 0.7 to 0.8 pct. Si (ferro-silicon) cast irons. Fig. 20 shows the result in C.E. value on horizontal co-ordinate and in tensile strength on vertical co-ordinate.



Pig iron "D" is used. Mn: 1.0 pct. ×——×: untreated. o·····o: with addition of calcium cyanamide by 0.5 pct. ●– – –●: with addition of 0.5 pct. calcium cyanamide and inoculation of 0.7 to 0.8 pct. Si.

FIG. 20. Effect of inoculating silicon.

From this result, it is recognized that the tensile strength of the inoculated cast iron is lower by 2 to 3 kg/mm² than that of the uninoculated, but the chilling effect is prevented perfectly.

In this way, the tensile strength of the cast iron, a part of silicon content of which was added as an inoculant after the treatment of calcium cyanamide, is somewhat lower than that of the cast iron with the treatment of calcium cyanamide only, but it is much larger than that of the untreated. And in the inoculated cast iron, there are effective results of the decreasing of hardness and improvement of machinability, etc. Thus, when, according to composition of cast iron which is required, treatment with calcium cyanamide and inoculation with silicon are carried on, the high strength cast iron of good machinability may be obtained.

(9) *Micro-Structure:*

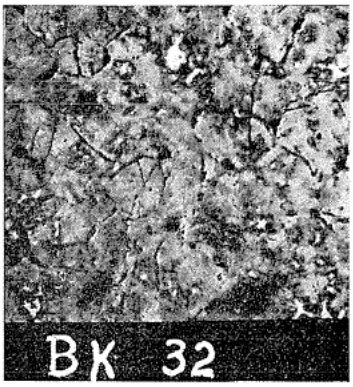
The change of micro-structure by the treatment of calcium cyanamide are shown in the microphotographs of No. 1 to No. 8. No. 1 and No. 2, No. 3 and No. 4, No. 5 and No. 6, No. 7 and No. 8 are, respectively in four pairs, structures of the cast iron of similar composition made of the same pig iron, and the pictures of odd number show the structure of the untreated cast iron and the pictures of even number show those of the treated with calcium cyanamide. Comparing each picture, we can see the followings, namely:

(i) By the treatment of calcium cyanamide, the graphite becomes finer and smaller.

(ii) It seems that the matrix of pearlite becomes finer.

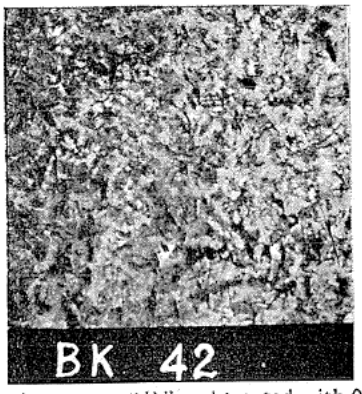
Therefore, such changes in structure may serve the improvement of strength.

No. 1 100×



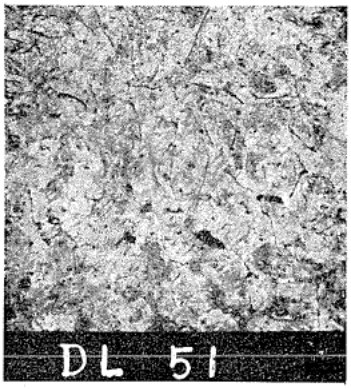
Used pig iron "B," and untreated. C: 2.80 pct., Si: 2.05 pct., Mn: 1.0 pct., Sol.-N: 0.0027 pct., Insol.-N: 0.0091 pct., T.S.: 32 kg/mm^2.

No. 2 100×



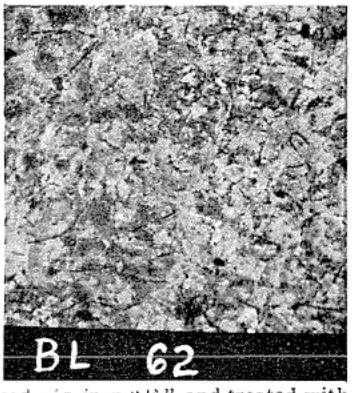
Used pig iron "B," and treated with 0.3 pct. calcium cyanamide. C: 2.78 pct., Si: 1.99 pct., Mn: 1.0 pct., Sol.-N: 0.0043 pct., Insol.-N: 0.0140 pct., T.S.: 41 kg/mm^2.

No. 3 100×



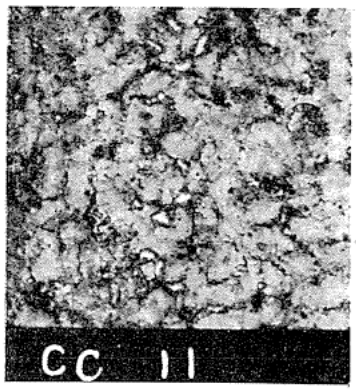
Used pig iron "F," and untreated. C: 3.31 pct., Si: 1.69 pct., Mn: 1.0 pct., Sol.-N: 0.0027 pct., Insol.-N: 0.0076 pct., T.S.: 23 kg/mm^2.

No. 4 100×



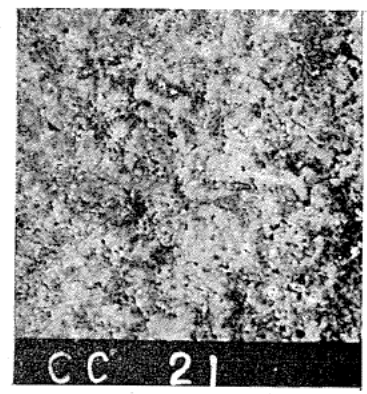
Used pig iron "F," and treated with 0.3 pct. calcium cyanamide. C: 3.31 pct., Si: 1.71 pct., Mn: 1.0 pct., Sol.-N: 0.0054 pct., Insol.-N: 0.0137 pct., T.S.: 28 kg/mm^2.

No. 5 100×



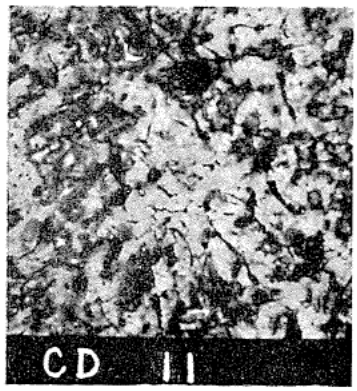
Used pig iron "D," and untreated. C: 2.81 pct., Si: 2.11 pct., Mn: 1.0 pct., T.S.: 28 kg/mm².

No. 6 100×



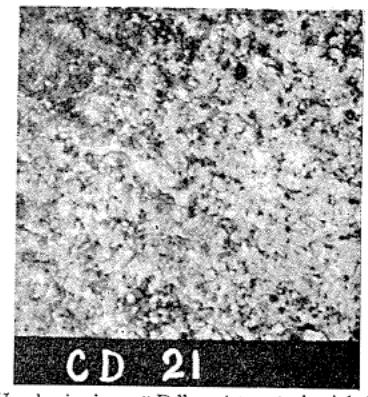
Used pig iron "D," and treated with 0.5 pct. calcium cyanamide. C: 3.09 pct., Si: 2.10 pct., Mn: 1.0 pct., T.S.: 38 kg/mm².

No. 7 100×



Used pig iron "D," and untreated. C: 3.16 pct., Si: 2.02 pct., Mn: 1.0 pct., T.S.: 26 kg/mm².

No. 8 100×



Used pig iron "D," and treated with 0.5 pct. calcium cyanamide. C: 3.23 pct., Si: 2.12 pct., Mn: 1.0 pct., T.S.: 32 kg/mm².

IV. Consideration of Experimental Result

(1) Decomposition of Calcium Cyanamide at High Temperature:

It is said that CO acts to $CaCN_2$ at over about 1120°C, following next formula.[1]

$$CaCN_2 + CO = CaO + 2C + N_2$$

When calcium cyanamide is heated between 900 and 1280°C in the atmosphere of N_2, it sublimates easily at over 1250°C, and at this time the lower calcium carbide does not appear, and this sublimated $CaCN_2$ reacts to the porcelain vessel, and separates free N_2, but that mechanism has been unknown.[2]

In our experiment, the calcium cyanamide is pushed into the molten pig iron at 1450°C as quick as possible, but a part of the calcium cyanamide may react with the adhered oxygen or oxygen in the molten pig, following the above fomula, and the other part may sublimate and decompose as in the case in the atmosphere of N_2. These products of decomposition may react to the molten pig iron.

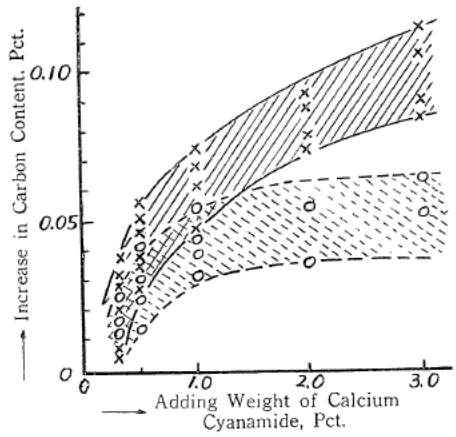
If calcium is produced by this decomposition, the increase of the tensile strength may be understood as the process to the spheroidal graphite cast iron, according to the fact that much addition of calcium products the spheroidal graphite cast iron.[3] But much addition of calcium cyanamide does not yield the change in graphite form almost. And it is recognized that the calcium reacts as a graphitizer.[3] And according to the spectrum analysis, the calcium content is in trace (about 0.005 pct.) in both the cast iron which is treated with calcium cyanamide and the untreated. Therefore, we can see that the calcium has not such effect as the above mentioned.

In this treatment, we suppose that the effect is based on the active nitrogen decomposed from calcium cyanamide (See: IV (3)).

(2) *Increase of Carbon Content According to Addition of Calcium Cyanamide:* When calcium cyanamide decomposes, the free carbon, as indicated in the above formula, develops always. And in the commercial calcium cyanamide there exists free carbon as impurity. Therefore, it is expected that the addition of calcium cyanamide will be accompanied by the increase of carbon content.

Fig. 21 represents the relation of the addition weight of calcium cyanamide and the increase of carbon content. From this result, when cast iron contains less than 3.0 pct. C, the carbon content increases by less than 0.12 pct. with addition by 3.0 pct. of calcium cyanamide. And the increasing rate of the carbon content becomes smaller, as the carbon content increases, and that of the carbon content of about 3.5 pct. is about 0.07 pct., with addition by 3.0 pct. of calcium cyanamide.

These results are related to the cast irons of 1.8 to 2.2 pct. Si content, and if the silicon content decreases, the increase of the carbon content may be larger, and if the silicon content increases, that may be smaller.



×: less than 3.0 pct. C. ○: 3.4~3.6 pct. C.

FIG. 21. Relation between adding weight of calcium cyanamide and increase in carbon content.

(3) *Increase of Nitrogen Content According to Addition of Calcium Cyanamide:*

According to the treatment with calcium cyanamide, the nitrogen content of cast iron increases. This fact is indicated in Fig. 2 (a) and (b), etc. The analysis of the Nitrogen content is due to JES Kjeldahl's method, and the residue of HCl solution is treated by K_2SO_4-$CuSO_4$-H_2SO_4.

As the adding weight of calcium cyanamide increases, the nitrogen content soluble in HCl (hereafter called soluble nitrogen content) and the nitrogen content in the residue of HCl solution (insoluble nitrogen content) increase. According to the comparison of increase of the nitrogen content with that of tensile strength, the insoluble nitrogen content of about 0.015 pct. and total nitrogen content of about 0.020 pct. are effective considerably. With more addition of calcium cyanamide, the nitrogen content increases, but tensile strength becomes smaller by development of

blow holes. Therefore, there exists the most suitable adding weight for maximum tensile strength.

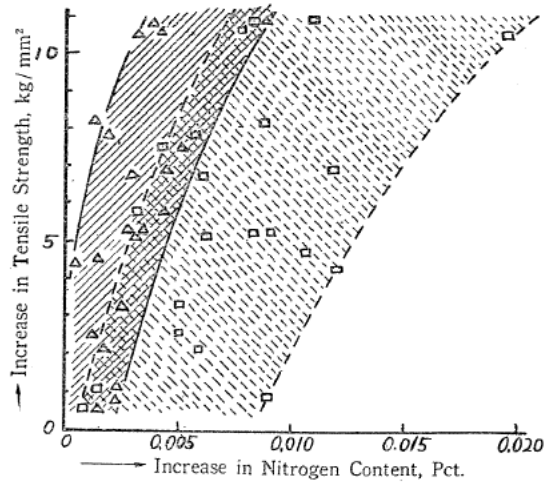
The relation of carbon content and nitrogen content is indicated in the lower group in Fig. 6. The total nitrogen content, whether the iron is treated with calcium cyanamide or not, decreases somewhat with carbon content, and the insoluble nitrogen content in the treated cast iron decreases most greatly, and the increasing rate of tensile strength becomes smaller. When cast iron contains 3.3 to 3.5 pct. C, as shown in Fig. 2 (b), the maximum tensile strength exists with addition by 1.5 pct. of calcium cyanamide. Therefore, when the silicon content of the cast iron is constant, the adding weight of calcium cyanamide to get the same insoluble nitrogen content is small in low carbon content and large in high carbon content. And to gain the maximum tensile strength in the cast iron containing high carbon, we must add more calcium cyanamide than in the cast iron of low carbon content.

The relation of silicon content and nitrogen content is shown in Fig. 8. The insoluble nitrogen content in the untreated cast iron increases with increase of silicon content, and that of the treated cast iron decreases with increase of silicon content. Therefore, if silicon content is more than 3.0 pct. increase of the insoluble nitrogen content according to the addition of calcuim cyanamide is small and improved effect in tensile strength is also small. Therefore, the cast iron with the high silicon content, in the same way as the one with the high carbon content, should be added more calcium cyanamide.

The relation of manganese content and nitrogen content is shown in Fig. 10. The insoluble nitrogen content in the treated cast iron is almost invariable in spite of increases of manganese content. Therefore, without regard to the manganese content, we can expect the effect equally.

The relation of the increasing value of tensile strength and that of nitrogen content is shown in Fig. 22. From this figure, it is recognized that as the nitrogen content (especially insoluble nitrogen content) increases to an extent, the tensile strength increases generally.

Next, we examined the change of the combined carbon content according to the adding treatment of calcium cyanamide. In the results which we got up to the present, the combined-carbon content increases by 0.05 to 0.10 pct. We suppose that this is the result of the remove of the entectoid composition to high carbon side according to increasing of the insoluble nitrogen content. But we are studying about this fact, and shall report it next time. This increase of the insoluble nitrogen content may serve greatly for the increase of tensile strength. And deoxidizing effect, as above mentioned, may be useful also, and these may help



△ : soluble nitrogen content. □ : insoluble nitrogen content.

FIG. 22. Relation between increase in nitrogen content and increase in tensile strength.

together to improve mechanical properties of cast iron.

V. Conclusion

In summarizing the above results, the following facts are observed.

(1) The adding weight of calcium cyanamide is variable with the condition of calcium cyanamide, the carbon and silicon content and the kind of the material pig iron. And we must use the calcium cyanamide after determination of the suitable weight for using material.

(2) In this treatment, the insoluble nitrogen content of 0.015 pct. and the total nitrogen content of 0.020 pct. are pretty effective.

(3) The adding temperature from 1400 to 1450°C is suitable.

(4) If the holding time from the treatment with calcium cyanamide to the pouring is within 5 minutes, it does not affect to the tensile strength which should be resulted, but if it is more than 5 minutes, improving effect may be decreased.

(5) The tensile strength becomes smaller with the increase of carbon content and silicon content, and becomes larger with the increase of manganese content by less than 1.0 pct. Therefore, when we expect the maximum tensile strength, the carbon and silicon content must be lowered as possible without mottled iron, and the manganese content must be 1.0 pct. When the adding weight of calcium cyanamide is equal, the insoluble nitrogen content becomes smaller with the increase of carbon and silicon content, and the increase of tensile strength becomes smaller also. Therefore, as the carbon and silicon content increases, the adding weight of calcium cyanamide must be increased. When the manganese content changes, the insoluble nitrogen content of the treated cast iron is almost invariable. And without regard to the manganese content, we can expect the effect equally.

(6) Tensile strength decreases with the increase of phosphor, sulphur, lead or tin. Chromium increases tensile strength to an extent, but much addition of chromium increases the chilling effect. Aluminium lowers tensile strength to an extent, and after then it is almost invariable.

(7) The specific gravity is almost invariable until the adding weight of calcium cyanamide becomes most suitable to tensile strength which should be resulted, and by more addition, it is lowered with the development of the micro and macro blow holes.

(8) By the treatment with calcium cyanamide, hardness of cast iron increases by about 5 to 10 in B.H.N., and in the wedge-shaped test piece, the depth of chilling is about twice. These are prevented by adding a part of the silicon content as an inoculant, but in this case the tensile strength decreases slightly.

(9) Mechanism of the decomposition of calcium cyanamide is not apparent, but when calcium cyanamide is added, the carbon and nitrogen content increases. And when the nitrogen content, especially insoluble nitrogen, increases to an extent the increase of tensile strength becomes larger.

(10) According to the treatment of calcium cyanamide, the combined-carbon content increases by 0.05 to 0.10 pct. This fact and the deoxidizing effect may help together to increase the mechanical properties.

(11) In the microstructure, the graphite in the treated cast iron is finer and smaller than that of the untreated, and the pearlitic matrix is finer in the treated.

Acknowledgment

A part of this research was performed with the grant of Developmental Scientific Research of the Educational Department of Japan. Grateful acknowledgment must be made here to Mitsubishi Electric and Machine Co., Ltd., Nisso Steel Making Co., Ltd. and Katsuyama Electro-Chemical Co., Ltd., which offered us the pig iron willingly, and Ibigawa Electrical Industrial Co., Ltd. which gave us calcium cyanamide.

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2) N. Kameyama: *ibid.*, **13** (1923), 73-102.
3) R. Kusakawa: The Journal of Iron and Steel Institute of Japan. **37** (1952), 6, 16-22.