Process of Graphite Precipitation in Calcium Graphite Steel

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Synopsis

The effect of calcium on the graphite precipitation from the γ phase of a hypereutectoid steel has been examined with an apparatus newly designed for the measurement of solidifying contraction. It was ascertained that the graphite precipitation in the solidifying process occurred over the range from the vicinity of the saturation curve E'S' of the γ phase (Agr point) to the A_1 point, and that the graphitization took place most remarkably near the A_1 point. The addition of a large amount of metallic calcium or of Fe-Ca-Si alloy greatly affected the solidifying contraction curve, leading to a considerable expansion due to ferrite formation near the A_1 point. In this case the rise of the A_1 point was not observed, although Si content increased. The addition of Fe-Ca-Si alloy as the graphitizing agent increased the amount of residual calcium more than that in the case of the addition of metallic calcium.

I. Introduction

Previously, the temperature range of graphite precipitation was examined by means of thermal analysis and dilatometric measurement to obtain an information on the graphite precipitation in the solidifying process. However, the thermal analysis was not a proper method because it was difficult to know exactly the range of temperature in question. On the other hand, considering that the graphite precipitation is accompanied by dilatation, some dilatometric measurements were carried out over the range of temperature at which graphite would precipitate, by reheating hypereutectoid Fe-C alloys quenched from γ region immediately after solidification. Strictly speaking, however, this was not also suitable to see the real phenomenon of graphite precipitation during solidification, showing merely the process of reheating the quenched specimen and the graphite precipitation in the process of cooling; that is, the Fe-C alloy water-quenched from a high temperature is not the one consisting only of γ phase, but with some martensite. The lattice of this martensite has a large strain, and carbon atoms are in the state in which they can easily precipitate as a heterogeneous phase. Such being the case, in the present experiment an apparatus was newly constructed to observe the graphite precipitation directly from γ region during solidification and to examine

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the effect of calcium on the graphite precipitation.

II. Experimental method and specimens

Of a number of methods of magnifying contraction or dilatation of a specimen, a lever-operated self-recording system was adopted, taking into account the vibration caused by the fluctuation of molten steel at the time of casting and avoiding a method which calls for a precise setting. The lever method has a defect of small magnification so that it is usual to increase the number of levers to enlarge dilatation, but, in the present case, in view of the above-mentioned vibration, a single lever was used and the defect of the small magnification was overcome by making the specimen longer. The bearing of the lever was made like a knife edge, and the distance between the point, at which the change in the length of the specimen was transmitted to the lever, and the bearing was made adjustable and the magnification could be changed over the range of 20 to 80 times. In the following measurements, the magnification ratio was set at 40 times. The molten steel was cast in a CO_2 sand mould and the change in length of the specimen in the process of solidification was recorded and the temperature was measured simultaneously. Fig. 1 shows

(1) Paper reel
(2) Roller
(3) Recording pen
(4) Time recorder
(5) Synchromotor
(6) Mould support
(7) Pouring gate
(8) CO_2 sand mould
(9) Electric furnace
(10) Thermocouple inlet
(11) Specimen
(12) Silica rod
(13) Switch
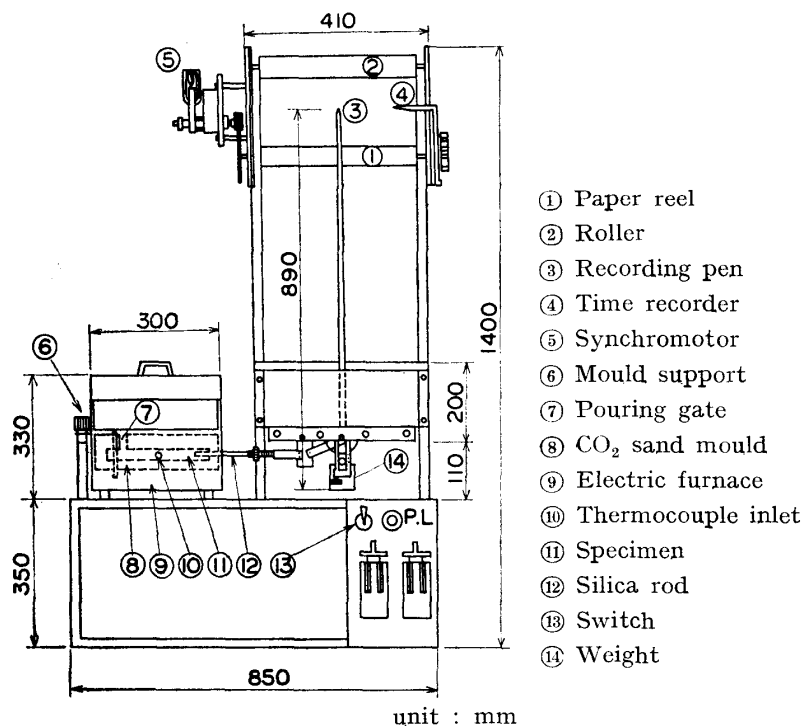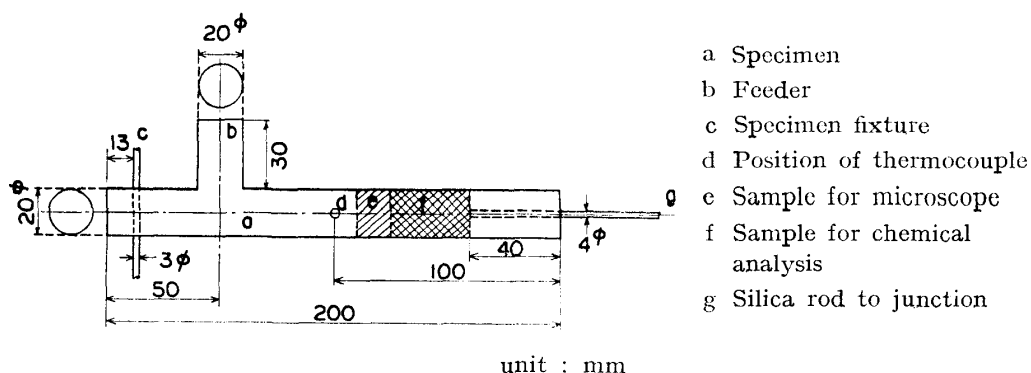(14) Weight

unit : mm

Fig. 1. Schematic diagram of the apparatus for the measurement of solidifying contraction.

the schematic diagram of this new apparatus and the sizes of the specimens are shown in Fig. 2. The sand mould was made of silica sand and sand set, and formed in a metal frame 80 mm×80 mm×250 mm. After hardening with CO_2, it was used several hours later and within a day. The sand mould thus formed 8

a Specimen
b Feeder
c Specimen fixture
d Position of thermocouple
e Sample for microscope
f Sample for chemical
   analysis
g Silica rod to junction

unit : mm
Fig. 2. Size of the specimen.

was put in the electric furnace 9 without turning on the current and fixed on to the pillar 6 with a rod penetrating the upper and lower parts of the mould so that the specimen might not move. Then the molten steel ran from the pouring gate 7 into the mould. As soon as the flow of molten steel was over, the switch 13 was on, which set in motion the synchro-motor 5. The change in length of the specimen with lowering temperature was conducted to the lever by the quartz rod 12. The micro-movement of the lever was magnified 40 times and conducted by the pen 3 to be recorded on a paper. The specimen was 600 g in weight and the contraction was measured from the start of solidification down to 550°C, and the time

Table 1. Chemical composition of specimens (%)

Mark		Additional amount of graphitizing agent		T.C	Si	Mn	P	S	Ca
I	B-32	Ca	0.15	1.40	1.26	0.099	0.010	0.014	0.006
	B-33	//	0.35	1.59	1.23	0.041	0.014	0.012	0.006
	B-34	//	0.65	1.59	1.27	0.048	0.012	0.010	0.007
	B-40		—	1.53	1.30	0.044	0.012	0.015	—
II	A-32		—	1.34	0.43	0.019	0.008	0.010	—
	A-33	Ca	0.21	1.30	0.42	0.034	0.008	0.007	0.004
	A-34	//	//	1.31	0.75	0.030	0.007	0.006	0.004
	A-35	//	//	1.39	0.72	0.022	0.008	0.006	0.004
	A-36	//	//	1.40	1.12	0.032	0.007	0.005	0.005
	A-37	//	//	1.31	1.45	0.022	0.008	0.005	0.006
	A-38	//	//	1.32	1.88	0.039	0.008	0.004	00.06
	A-39	//	0.63	1.32	0.44	0.029	0.008	0.004	0.005
	A-40	//	//	1.41	0.72	0.035	0.008	0.004	0.006
	A-41	//	//	1.46	1.10	0.030	0.005	0.004	0.005
	A-42	//	//	1.35	1.47	0.041	0.006	0.004	0.005
III	SD- 1		—	1.55	0.95	0.20	0.018	0.012	—
	SD- 4	Ca	0.8	1.46	1.37	0.20	0.018	0.018	0.007
	SD- 6	Mg	0.8	1.53	1.33	0.23	0.018	0.018	0.044Mg
	SD- 8	Fe-Ca-Si	0.5	1.49	0.81	0.21	0.020	0.016	0.007
	SD- 9	//	1.0	1.37	1.00	0.19	0.018	0.019	0.009
	SD-10	//	1.5	1.48	1.32	0.21	0.018	0.013	0.010
	SD-11	//	2.0	1.59	1.53	0.22	0.018	0.013	0.020

required for cooling was less than 13 minutes. At the same time the temperature was measured by inserting the thermocouple in 10.

For melting materials, Fe-C alloy (1.81% of carbon, 0.17% of silicon, 0.02% of manganese, 0.009% of phosphorus and 0.007% of sulphur) prepared with electrolytic iron and gas carbon in 50 KVA high frequency induction furnace with magnesium-lining was used. Fe-C alloy of 600 g in weight was charged in a graphite crucible with alumina lining and remelted in 35KVA high frequency induction furnace. After adjusting silicon content a fixed amount of metallic calcium or of Fe-Ca-Si alloy (20.9% of calcium, 50.3% of silicon, Bal. iron) was added to the molten steel at 1580°C. It was then poured into the mould equipped with the above-mentioned apparatus for measuring solidifying contraction. Metallic silicon was used for adjusting silicon content. The metallic calcium was wrapped in pure iron foil and tied fast to a stirring rod before it was inserted in the molten steel. As shown in Table 1, the chemical compositions of the specimens to be measured were as follows: (1) a system in which 0.15, 0.35 and 0.65% each of the metallic calcium was added to the melt containing 1.2% of silicon, (2) a system in which 0.21 and 0.63% each of the metallic calcium was added to the melt containing 0.4 to 1.8% of silicon, and (3) a system in which Fe-Ca-Si alloy was added.

III.   Experimental results and consideration

1.   Process of graphite precipitation due to metallic calcium

In Fig. 3 are shown the results obtained for the above-mentioned system (1), and that for the specimen B-40 containing no metallic calcium is also shown for comparison. As seen in the figure, little difference is observable in the contraction curves when the amount of calcium added is below 0.35%, but when it is as large as 0.65%, the contraction begins to decrease at about Agr. point, and a gradual decrease continues down to about A_1 point. This decrease in the contrac-
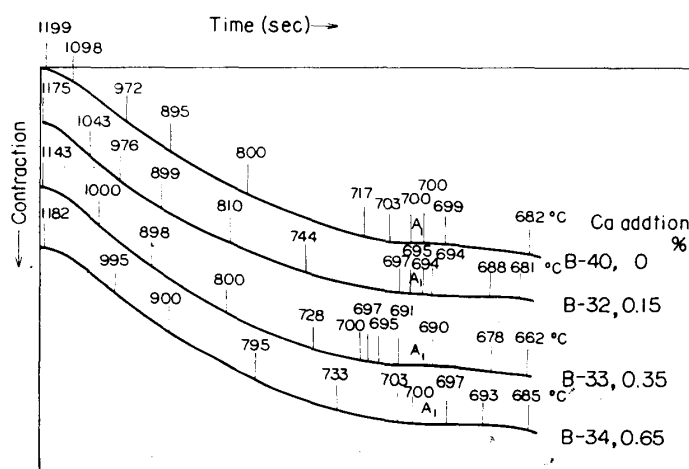

Fig. 3.   Solidifying contraction curves depending upon additional amount of metallic calcium (1.2% Si addition)
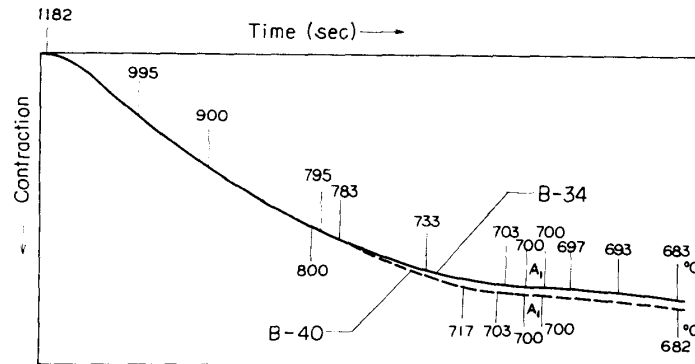
Fig. 4. Comparison of the solidifying contraction curves between calcium treated specimen B-34 and untreated specimen B-40.

tion was more remarkable in the specimens with a larger amount of graphite precipitate, and it could be anticipated that the decrease in the contraction during the cooling was due to the dilatation caused by graphite precipitation.   In Fig. 4, a comparison is made of the contraction curves between the specimen treated with 0.65% of calcium and the untreated one by placing one upon the other.   As shown, the curves separated from each other below 783°C, showing clearly the difference in the contraction.   It can be seen, therefore, that this difference in contraction is caused by graphite precipitation.   As to the specimen B-34 treated with calcium, the graphite precipitation begins at about 783°C and as it approaches the A_1 point, the dilatation caused by graphite precipitation becomes larger, in response to the contraction as a whole being more decreased in this case than in the untreated specimen.

Phot. 1-a shows the microstructure of the untreated specimen B-40, containing needle-like primary cementite in the matrix.   In this case, the chemical analysis revealed graphite precipitate to be 0.038%, being extremely small in amount. Phot. 1-b is for the specimen B-34 treated with 0.65% of metallic calcium, showing that the matrix consists of fine pearlite, and that graphite precipitate
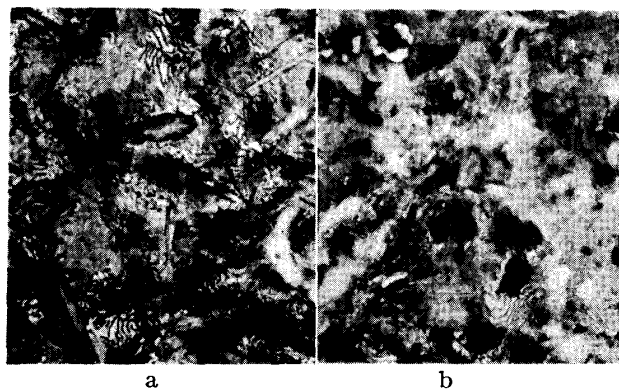
a   b
Specimen B-40 untreated   Specimen B-34 treated with 0.65%Ca
Phot. 1. Microstructures after contraction measurement, etchant, 5% nital ×160

is partially of bull's eye structure. The amount of graphite was 0.27%. Consequently it was seen that in the case of the calcium treating, graphite began to precipitate above the A_1 point, in the vicinity of which graphite precipitation was maximum. Fig. 5 shows the results of thermal analyses of the tested specimens in the solidifying process. In the specimen treated with calcium, the A_1 point becomes lower in some degree than in the untreated specimen B-40, and a supercooled phenomenon appears. As seen in Phot. 1-b, the pearlite structure of the specimen treated with calcium is very fine, which is considered to be due to the fall of the A_1 point.

2. Effect of silicon on graphite precipitation in the calcium treated steel

In Fig. 6 are shown the contraction curves in the process of solidification of the specimens in which the amount of metallic calcium to be added was fixed at
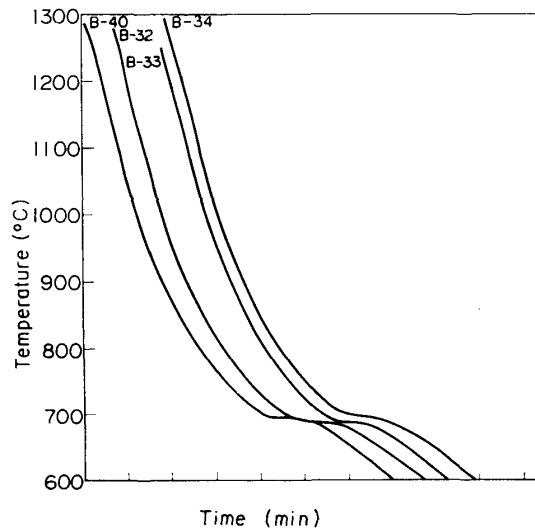

Fig. 5. Thermal analysis curves depending upon additional amount of metallic calcium (1.2%Si addition).
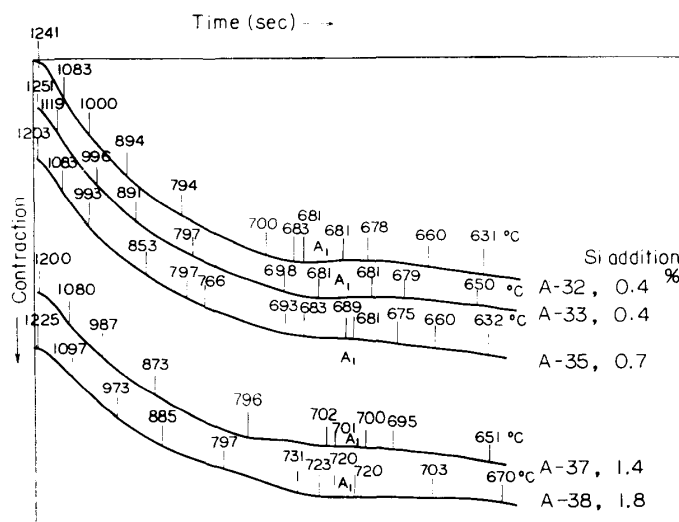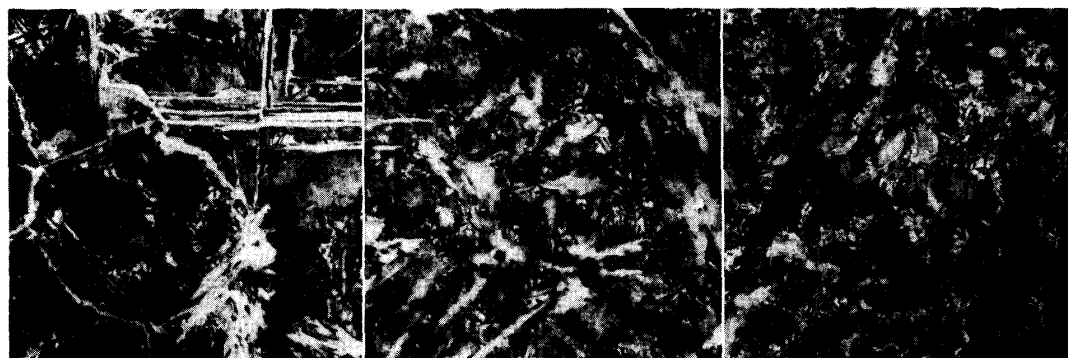

Fig. 6. Effect of silicon contents on the solidifying contraction curves (0.21% Ca addition), A-32: Ca untreated specimen.

a   b   c
Specimen A-32 treated with   Specimen A-36 treated with   Specimen A-38 treated with
0.4% Si only   1.1% Si and 0.21% Ca   1.8% Si and 0.21% Ca

Phot. 2.   Microstructures depending upon the additional amount of silicon, etchant,
5% nital × 160

0.21% and silicon contents were made variable, corresponding to the above-mentioned system (2). The specimen A-32 was prepared by adding 0.4% of silicon without calcium treatment, and when its curve is compared with that of the specimen A-33 treated with 0.21% of metallic calcium, little difference is seen between them. When calcium to be added was fixed at 0.21% and silicon content was increased, the solidifying contraction of Fe-C alloy tended to decrease in response to the silicon content. This was considered to be a phenomenon resulting mainly from silicon dissolved in the γ solid solution. However, even the silicon content was increased, much graphite would not precipitate because 0.21% of calcium added was too small an amount. In Phot. 2 are shown the microstructures representative of this series. The needle-like primary cementite decreased remarkably resulting in the appearance of fine cementite when silicon content was 1.1%. When silicon content increased to 1.8%, the needle-like primary cementite was no longer seen, and an imbricate structure, something like the primary cementite but much wider than it, appeared in the matrix pearlite. Such a structure was often observed in the case where the amount of metallic calcium added was small and graphite precipitation was insufficient. It was produced on the plane of cleavage of the γ solid solution, around which fine pearlite was observed to be growing. Fig. 7 shows the results of the thermal analysis during the solidification, in which it can be seen that the A_1 point rises due to the increase of silicon content. In Fig. 8 are shown the solidifying contraction curves of the specimens in which the amount of metallic calcium added was fixed at 0.63% and silicon content was varied over the range from 0.4% to 1.4%. When the silicon content was small, graphite hardly precipitated, and for most part, cementite precipitated. When the silicon content was 0.7%, the primary cementite decreased in amount, and graphite precipitated in the range from about 773°C to the A_1 point. When the silicon content was increased to 1.1% or more, graphite began to
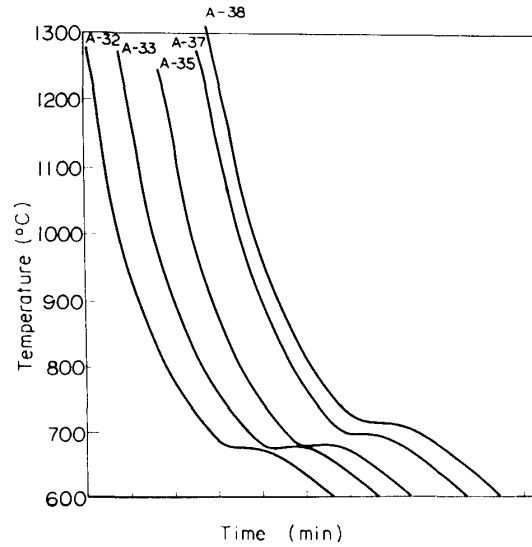
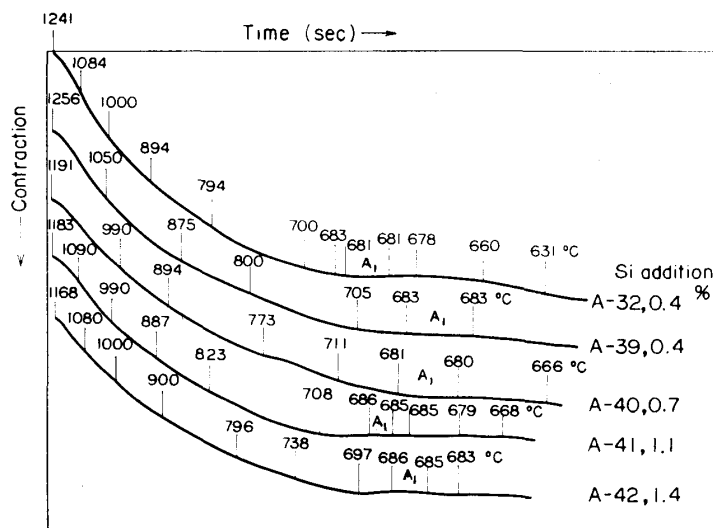Fig. 7. Thermal analysis curves depending upon silicon contents (0.21% Ca addition).

Fig. 8. Effect of silicon contents on the solidifying contraction curves (0.63% Ca addition), A-32 Ca untreated specimen.

precipitate gradually at about 823°C, the largest precipitation being observable at the A_1 point in the vicinity of 708°C, and continued to do so after passing the A_1 point. Fig. 9 shows the results of the thermal analysis, in which a rise of the A_1 point in response to the increase in silicon content observed in Fig. 7 could hardly be seen. This is because the tendency of the A_1 point to fall becomes stronger due to the effect of supercooling of calcium, and because that of the A_1 point to rise by silicon content is reduced as a result of the increase in the amount of metallic calcium added. Phot. 3 is the microstructure of the specimen A-41 containing 1.1 % of silicon. As seen in the photograph, it showed only the nodular graphite and pearlite structure, when 0.63% of metallic calcium was added and the silicon
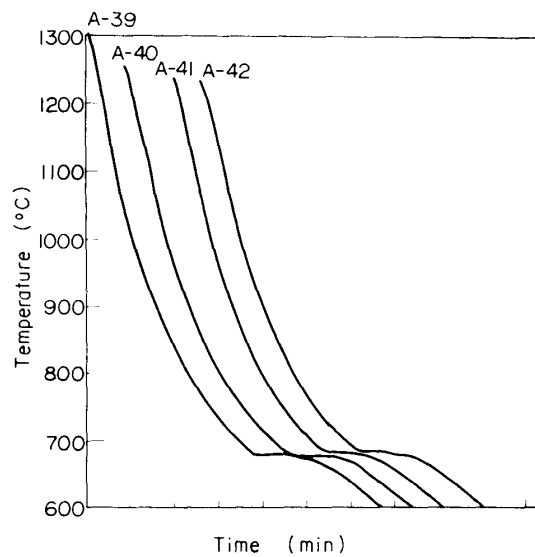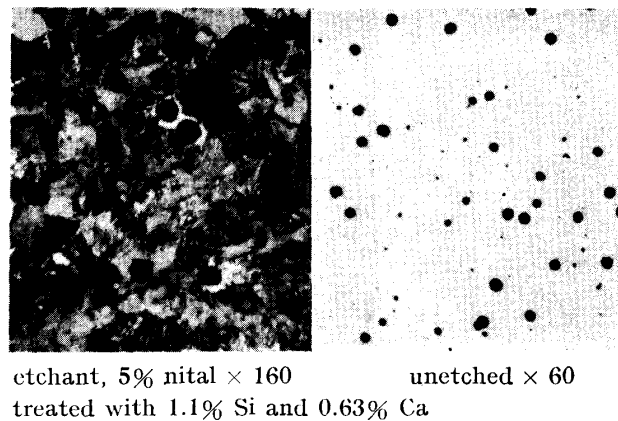
Fig. 9. Thermal analysis curves depending upon silicon contents
(0.63% Ca addition).

etchant, 5% nital × 160   unetched × 60
treated with 1.1% Si and 0.63% Ca

Phot. 3. Microstructures of the specimen A–41 after contraction measurement.

content was more than 1.1%. In this case the graphite precipitation was 0.25%.

3. Effect of Fe-Ca-Si alloy on graphite precipitation

Measurements were made of the process of graphite precipitation during solidification of Fe-C alloy treated with Fe-Ca-Si alloy, and the results were compared with those treated with metallic calcium or with metallic magnesium. For this experiment, 2 kg of Fe-C alloy of hypereutectoid composition was prepared by melting together electrolytic iron and Swedish pig iron (HERRANG). After adding Fe-Ca-Si alloy as a graphitizing agent, the molten steel was cast in the already described apparatus. The amount of Fe-Ca-Si alloy added was 0.5, 1.0, 1.5 and 2% each, and for comparison, 0.8% each of metallic calcium and metallic magnesium was added. The compositions of specimens SD-1 to SD-11 shown in Table 1 were obtained by chemical analyses.

In Fig. 10 are shown the contraction curves of the graphite precipitation in the process of cooling of Fe-C alloys to which the above-mentioned each amount of Fe-Ca-Si alloy was added as a graphitizing agent. Because the amount of Fe-Ca-Si alloy added was small in the specimen SD-8, its contraction curve shows a comparatively steep gradient in the range from 932° to 716°C, and no remarkable change due to graphite precipitation was observed. . In the specimen SD-8, 0.094% of graphite precipitated, whereas in the specimen SD-9, 0.13% of graphite precipitated, and its contraction curve showed a slow gradient from about 835°C to the A_1 point. When the amount of Fe-Ca-Si alloy added was increased to 1.5%, 0.59% of graphite precipitated, and its curve became gentle at about 960°C and graphite precipitation continued to about 691°C near the A_1 point, at which the temperature, though slight, began to rise, showing a dilatation due to the appearance of ferrite. In the specimen SD-11 with the addition of 2% of Fe-Ca-Si alloy, 0.76% of graphite precipitated, and the contraction curve became very gentle. The dilatation due to graphite precipitation began at about 1,011°C, increasing in the vicinity of 748°C which is far above the A_1 point, and the dilatation due to the precipitation overcome the contraction due to cooling, proceeding horizontally to 694°C, at which the dilatation due to ferrite appeared. When the additional amount of Fe-Ca-Si alloy was over 1.5%, the graphite precipitation began at about Agr point in the phase diagram of Fe-C-Si ternary alloy, the precipitate increasing as it approaches the A_1 point, under the cooling condition in the present experiment.

Fig. 11 shows the results of comparison of the contraction curve in the case of Fe-Ca-Si alloy treatment with that in the case of metallic calcium or of magnesium treatment. In the specimen SD-4 with 0.8% cf metallic calcium added, the slope of the contraction curve became gentle at about 909°C, keeping nearly a constant slope from 870°C to the A_1 point, a. which it became horizontal. The graphite precipitation began at about 909°C and the precipitate increased immediately
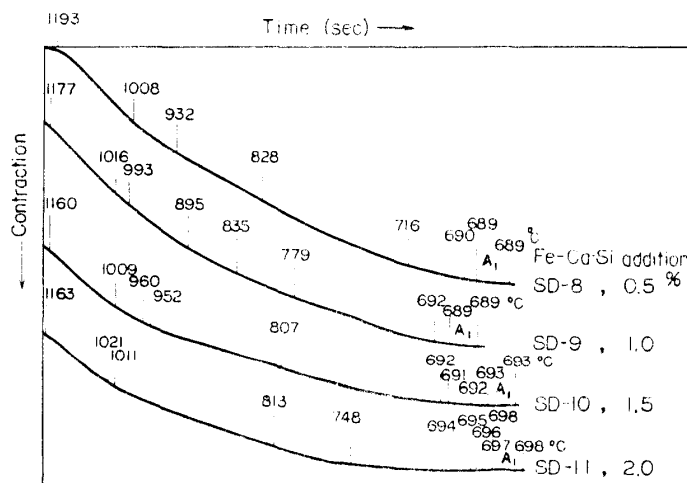

Fig. 10. Solidifying contraction curves depending upon additional amount of Fe-Ca-Si alloy.
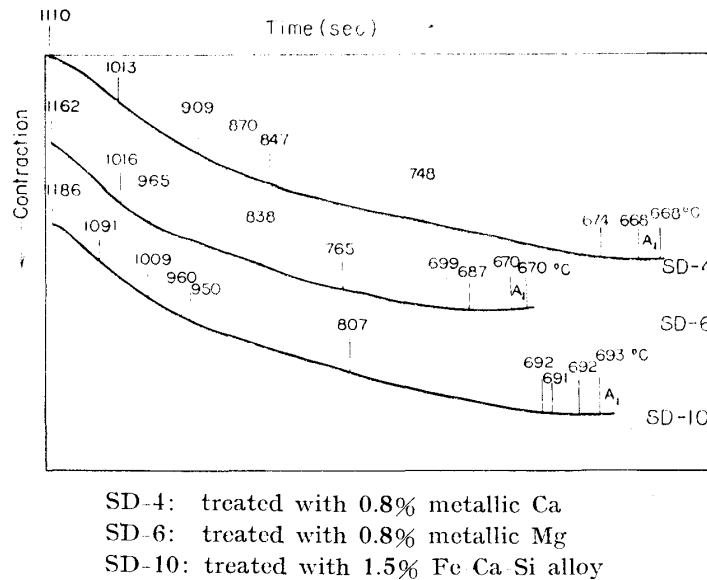
SD-4:   treated with 0.8% metallic Ca
SD-6:   treated with 0.8% metallic Mg
SD-10: treated with 1.5% Fe-Ca-Si alloy

Fig. 11. Solidifying contraction curves of the specimens treated with various graphitizing agents.

above the A_1 point. In the specimen SD-6 to which 0.8% of metallic magnesium was added, the graphite precipitation began at about 965°C, which was a little higher than in the case of metallic calcium, and continued to 670°C, being maximum at 699°C. The comparison of the process of graphite precipitation by magnesium addition with that by calcium addition revealed that in the former the graphite precipitation began at a higher temperature than in the latter and the contraction during precipitation was smaller; consequently, the graphite precipitation was larger in amount in the case of magnesium addition. The chemical analysis showed that in the calcium treatment the graphite precipitation was 0.33%, whereas in the magnesium treatment it was 0.62%. As shown in Table 1, this seemed to be due to the fact that only 0.007% of calcium and 0.044% of magnesium remained in the steel. According to Flinn[1],[2], calcium differs much from magnesium in solubility in iron so that they should differ from each other in residue even if they are added in equal amount. The graphite precipitation in the specimen SD-10 with 1.5% of Fe-Ca-Si alloy addition has already been described, which, when compared with those in the specimens SD-4 (metallic calcium) and SD-6 (metallic magnesium), resembles the case of metallic magnesium addition rather than that of metallic calcium addition. About 0.3% of calcium is contained in 1.5% of Fe-Ca-Si alloy, which is about 1/2.7 of the amount of metallic calcium added to the specimen SD-4. This is considered to be due to the fact that the yield of calcium has been improved by the addition of calcium in the form of a ferroalloy. As is clear from the analytical results in Table 1, in the case of adding calcium in the form of Fe-Ca-Si alloy, the residue of calcium remarkably increases in amount.

(1)   D.L. Sponseller and R.A. Flinn, Trans. AIME, **230** (1964), 876.
(2)   P.K. Trojan and R.A. Flinn, Trans. ASM, **54** (1961), 549.

Similar to the case of the specimen SD-6, the graphite precipitate in the specimen SD-10 was 0.59%. In this case, the cooling rate was more rapid in the specimen with metallic magnesium addition than in the those with Fe-Ca-Si alloy or metallic calcium addition. Thus, it will be seen that in the case of magnesium treatment, the cooling rate is more rapid than in the case of calcium treatment. This is considered to be due to the fact that magnesium absorbs much more heat from the molten iron than calcium because the latent heat of evaporation of magnesium is 136 kcal/g, whereas that of calcium is 101 kcal/g[3], when they are heated up to 1,550°C, at which they become vapor of more than 1 atm, although they dissolve very slightly in iron.

Summary

The effect of calcium on the graphite precipitation from the γ phase has been investigated by means of solidifying contraction, thermal analysis and micro-structure with specimens prepared by adding metallic calcium, metallic magnesium and Fe-Ca-Si alloy to the melt of hypereutectoid Fe-C alloy and casting in CO_2 sand mould of 20 mm ϕ. The following results were obtained.

(1) Regardless of graphitizing agent used, it was observed directly with the newly designed apparatus of measuring solidifying contraction that the graphite precipitation would occur in the vicinity of Agr point of the ternary system Fe-C-Si, and continued most near the A_1 point.

(2) When silicon content was more than 0.7% with the addition of more than 0.63% of metallic calcium, the changes in the solidifying contraction curve due to graphitization could be observed clearly. The thermal analysis revealed that when metallic calcium was added in large amount, the rise of the A_1 point due to the increase in silicon content could no longer be observed, which was considered to be caused by supercooling of calcium.

(3) When calcium was added in the form of Fe-Ca-Si alloy, the amount of residual calcium increased remarkably. When more than 1.5% of Fe-Ca-Si alloy was added, the slope of the solidifying contraction curve became gentle, graphite precipitation continued to the A_1 point and the dilatation due to the formation of ferrite was also observed.

Acknowledgement

(3)   F.E. Fowle, Smithsonian Physical Tables, (1933), 295.