Nucleation and Growth Process of Chunky Graphite in Heavy-Section Ductile Cast Irons

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Abstract: In this paper, the nucleation and growth process of chunky graphite in heavy section ductile cast irons was studied. The specimens were quenched at the selected points during the long solidification of Mg-treated irons, in which chunky graphite would finally form. The microstructure in the quenched specimen was observed using optical microscopy. Spheroidal graphite was only observed as the initial form of graphite at the early stage of the solidification. The number of graphite nodule was quite smaller and the size was much bigger than the similar stage of iron with the full spheroidal graphite structure. When the graphite nodule stopped its growth during the solidification, chunky graphite newly nucleated and grew at the interfacial sites between inclusions and solidification front of austenite. Chunky graphite continuously grew at the residual liquid iron until the eutectic solidification finished. Spheroidal graphite has no direct relations with the nucleation and growth of chunky graphite. The phenomena, which were found in this study, could be understood under the site theory.

Key Words: Chunky Graphite, Ductile Cast Iron

INTRODUCTION

The formation of chunky graphite at the thermal center in heavy section is the most incomprehensible phenomenon on the production of ductile iron castings. It has been already obvious that the elements such as Ce[1-5], Si[6,7], Ca[3,8], Ni[6,7,9] and Cu[7] promote the formation of chunky graphite when they exceed a certain amount of their content. On the other hand, it has been also known that the existence of the elements such as Pb[10-12], Sb[3,11,13,14], As[15], Bi[11] Sn[6, 16] and B[7] suppresses the formation of such graphite. Actually, Sb is added to avoid chunky graphite as the most effective countermeasure in practice. This, still, is not the stable countermeasure at present. This might be the reason why the solidification process of iron with chunky graphite has not been understood yet although many researchers tried to make the formation mechanism clear. The objectives of this paper are; to make the solidification process of iron with chunky graphite clear and to propose the formation mechanism of such graphite shape. The mechanism was considered to be explained with a common theory which was already proposed for spheroidal and compacted/vermicular graphite in irons[17,18].

EXPERIMENTAL PROCEDURE

The experimental apparatus is shown in Fig.1. The base metal was melted by 10ton low frequency induction furnace and spheroidized and inoculated with Fe-Si-5.5%Mg and Fe-75%Si by sandwich method. After Mg reaction finished, liquid iron of about 1.2Kg was taken from ladle by preheated graphite spoon, and poured into graphite crucible preheated at 1250°C in SiC furnace. The rest of liquid iron was poured into mold in practice. To adjust the chemical composition of liquid iron for the easy precipitation of chunky graphite, 50%Ce mish metal and Fe-75%Si were set in the preheated graphite crucible just before pouring. After pouring, the liquid in austenite shell. The nodule was already isolated from the residual liquid iron; the thin liquid channel was already closed. A large amount of austenite dendrite was observed in residual liquid iron. Sphere-like graphite was also observed around the growth front of those austenites. On the other hand, the precipitation of chunky graphite began to be observed in the specimen at this point. The precipitation patterns were divided into two. One was that chunky graphite precpitated between austenite shell with large graphite nodule and austenite dendrite. Another was that chunky graphite precipitated among such austenite shells. The microstructures at point 3 are shown in Fig.6.

Liquid iron 4 was kept for two hours at 1150°C in the furnace and quenched into water bath. The microstructures in specimen 4 are shown in Fig.7. In specimen 4, the growth of chunky graphite was dominant. It, however, seemed that large graphite nodule hardly changed on its morphology from specimen 3. At this stage, sphere-like graphite was not observed any longer around the growth front of the austenite shell and the dendrite. The additional precipitation pattern of chunky graphite was newly observed among austenite dendrite arms (Fig.7-b) in this specimen.

During the growth, the growth end of chunky graphite contacted with the residual liquid iron through the liquid channel (Fig.8). N.Yingyi[1] and J.Zhou[7] also mentioned this.

Fig.9 shows the microstructure of the specimen completely solidified in the furnace. The morphology and the number of large graphite nodule observed in specimens 3, 4 and 5 were almost the same each other. This means that the nucleation and the growth of graphite nodule almost saturated when chunky graphite began to nucleate and grow.

Through the whole observation, no chunky graphite connecting directly to large graphite nodule was observed. They had no direct relationship each other on the formation process. Chunky graphite newly nucleated after the growth of large graphite nodule almost stopped, as verified above.

(2) Nucleation Site

The areas around the growth front of austenite shell with large graphite nodule and austenite dendrite were observed in detail to find the nucleation site of chunky graphite, since the precipitation of chunky graphite began to start at those areas, as shown in Fig.6. As the result, the precipitation of sphere-like graphite at the austenite-inclusion interface was frequently observed at the following areas;

1) among austenite shell
2) between austenite shell and austenite dendrite
3) around austenite dendrite
4) between austenite dendrite arms

The growth end directly contacted with the residual liquid iron, the same as the growth end shown in Fig.8. The example is shown in Fig.10.

Inclusions connecting to graphite at the growth front of austenite shell and dendrite could be divided into two kinds by their color and morphologies. Each kind was analyzed by Energy Dispersive X-ray Spectrography (EDS). The results showed that one was light brown and Fe-Mg-Si-P-S-Ca-RE system, and that another was gray and Fe-Mg-Al-Si-tr.(S, Ca, RE) system.

J.Zhou[7] reported that chunky graphite nucleated near austenite dendrite but not in liquid iron. N.Yingyi[1] reported that chunky graphite formed at liquid iron-austenite interface and RE, Mg, S and O were enriched at the interface. Both did not, however, describe the details of the nucleation and growth sites.

DISCUSSION

(1) Role Of Magnesium For The Nucleation And Growth

For the nucleation and growth of spheroidal, CV and chunky graphite, spheroidizer element supplies primarily gas bubble and secondarily the morphology of austenite shell. The spheroidizer element does not directly influence the fundamental growth behavior of the hexagonal graphite crystal structure.

The nucleation and growth mechanism of spheroidal, CV and chunky graphite during the solidification can be schematically illustrated as shown in Fig.11. This illustration indicates that spheroidal, CV and chunky graphite partly have the common process on their nucleation and growth, and that their mechanism can be explained by a single theory. Graphite fills up a gas bubble and forms tiny graphite nodule less than 10μm (sphere graphite) in liquid iron[17]. The sphere graphite is then surrounded with austenite shell. Spheroidal and CV graphite start to grow from sphere graphite in the austenite shell. Chunky graphite has no direct relationship with the graphite nodule on its nucleation and growth. The first site for the nucleation and growth of chunky graphite is the interface around the growth front of austenite. Inclusion favorably makes the interfacial site but does not act as the nucleus substrate. The second is the thin liquid channel in austenite. Mg gas bubble for chunky graphite can be said as the potential site.

(2) Cause Of Chunky Graphite Formation

Even if the condition of liquid iron after spheroidizing treatment was suitable to form good spheroidal graphite structure, the final graphite morphology would not be always spheroidal. If the time duration from the magnesium treatment to the solidification start and the solidification time itself were too long, the number of graphite nodule would extreamly reduce and chunky graphite would form instead of that. This is because the effective number of Mg gas bubble lacks in liquid iron. The following reasons are considered as the factor;

1) Mg gas bubble floats out from liquid iron by the stoke's law.
2) Mg gas bubble becomes inclusion reacting with other suspended elements such as Ce, Ca, Al, etc. or their inclusions. The Brownian movement promotes this.
3) Mg gas becomes the liquid state[19] by the eutectic expansion pressure (maximum ≒60atm[20]).
4) Graphite preferentially precipitates into Mg gas bubble in the Si-rich region. The effective number, however, reduce by the homogenization of Si[22].

Under a small number of the sphere graphite nucleation, the growth of graphite nodule stops when the austenite shell become too thick. And then, the chunky graphite newly nucleates at some interfacial sites around the growth front of the austenite shell and dendrite. This is because the diffusion of iron atom becomes easier at new interfacial sites around the growth front of those austenites than the preexisted site of the graphite-austenite interface in thick austenite shell.

The elements such as Si, Ni, Cu, etc., which lead γ-graphite eutectic temperature to higher[21], are considered to promote long solidification.

(3) Relationship To The Precipitation Of Austenite Dendrite

Even if the chemical composition of liquid iron before the solidification is hyper eutectic, austenite dendrite precipitates in the residual liquid iron under the condition of the chunky graphite formation. The reasons are considered that;

1) The floating-off of graphite dross leads residual liquid iron to the eutectic composition.
2) There might be the micro-area of hypo eutectic composition by the negative segregation of Si in residual liquid iron.

CONCLUSIONS

1) At the early stage of the solidification, only small graphite nodule under 10μm (sphere graphite) directly precipitates in liquid iron.
2) Sphere graphite grows into spheroidal graphite in austenite shell but its number is quite a small compared with full nodule irons.
3) After the growth of spheroidal graphite stops on the way of the solidification, chunky graphite nucleates at the interfacial site around the growth front of austenite.
4) There is no direct relationship between spheroidal and chunky graphite on their nucleation and growth.
5) Chunky graphite grows along liquid channel in austenite and the growth end contacts with residual liquid iron.
6) The longer time duration from the spheroidizing treatment to the solidification start and the longer solidification promote the nucleation of chunky graphite, reducing the nodule number.

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Table 1 Temperature Change of Each Liquid Iron from Tapping to Quenching during Experiment (°C).

Specimen	Induction furnace	Ladle	Graphite crucible					
			Initial	Primary reaction	Eutectic reaction		Recalescence ΔT	Quenching
					Min.	Max.		
1	1461	1406	1272	1177	—	—	—	1165
2	1457	1396	1256	1170	1157	—	—	1158
3	1448	1392	1230	1180	1150	1154	4	1153
4	1468	1405	1260	1189	1150	1154	4	1153
5	1550	1516	1310	1183	1154	1158	4	As cast

Table 2 Chemical Composition of Each Quenched Specimen with Chunky Graphite Structure.

Specimen	Chemical composition (Wt%)								
	C	Si	Mn	P	S	Ca	Ce	Mg	CE
1	3.42	2.94	0.30	0.046	0.005	0.0037	0.047	0.035	4.40
2	3.42	2.88	0.15	0.048	0.005	0.0021	0.037	0.029	4.38
3	3.29	2.91	0.14	0.046	0.006	0.0012	0.022	0.035	4.26
4	3.30	2.78	0.22	0.036	0.009	0.0004	0.031	0.042	4.23
5	3.31	2.79	0.19	0.042	0.014	0.0053	0.020	0.026	4.24

CE=C+1/3Si

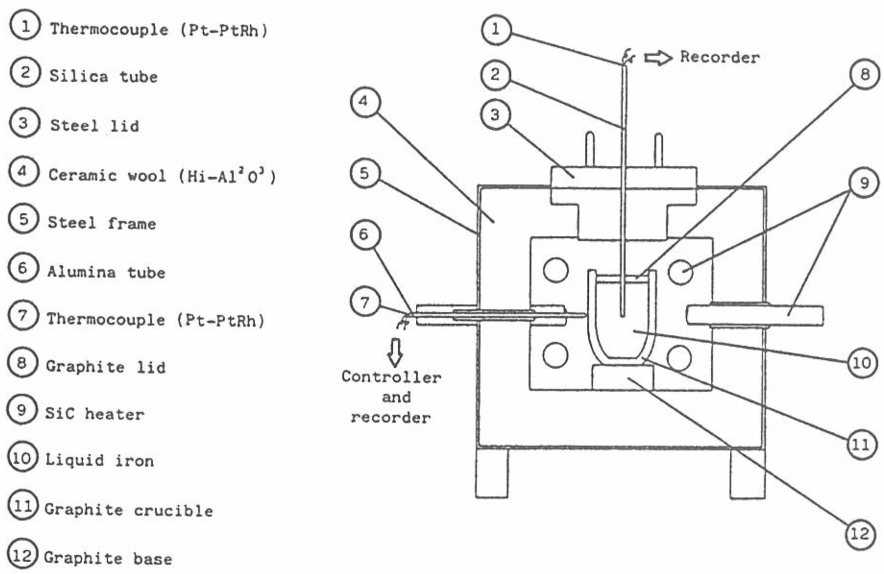


Fig.1 Experimental apparatus for simulative solidification (effective inside dimension = 150 x 150 x 180mm).

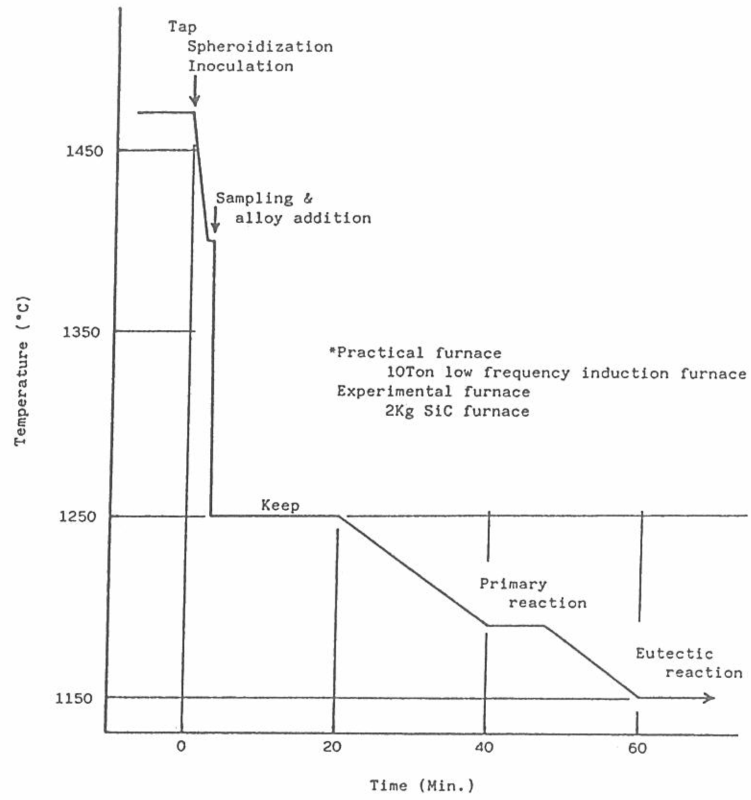


Fig. 2 Time and temperature schedule for chunky graphite precipitation during solidification.

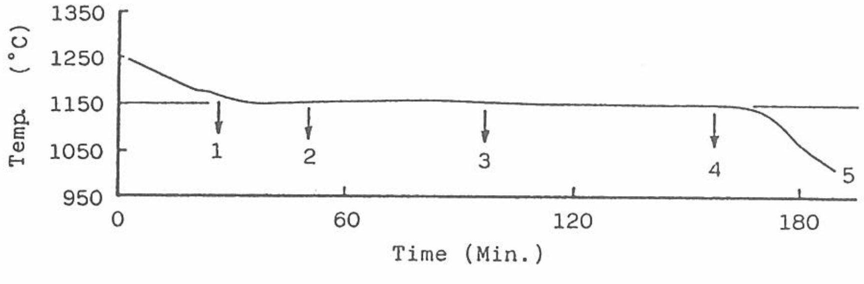


Fig. 3 Cooling curve of iron with chunky graphite and quenching points during solidification.

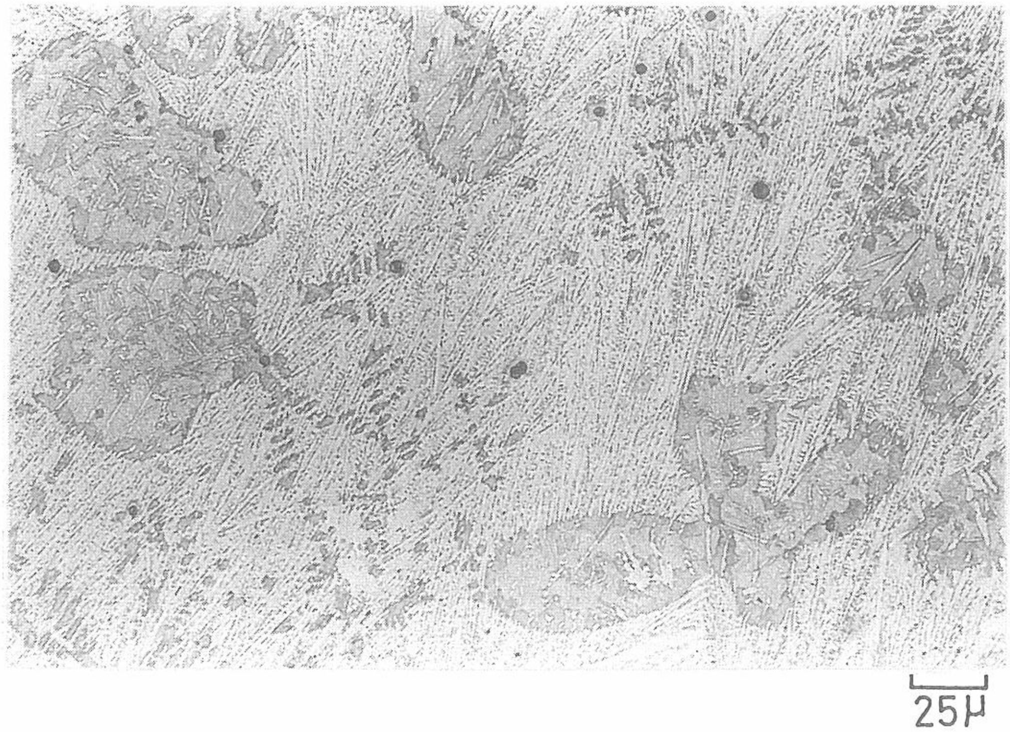


Fig. 4 Microstructure of specimen quenched at point 1 in Fig. 3.

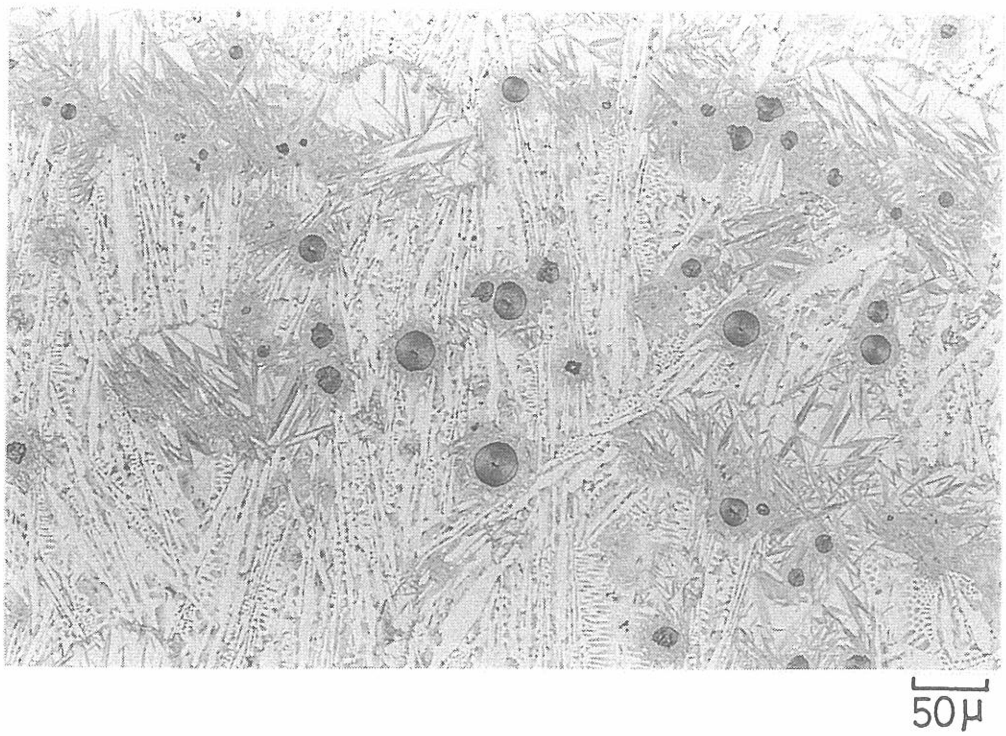
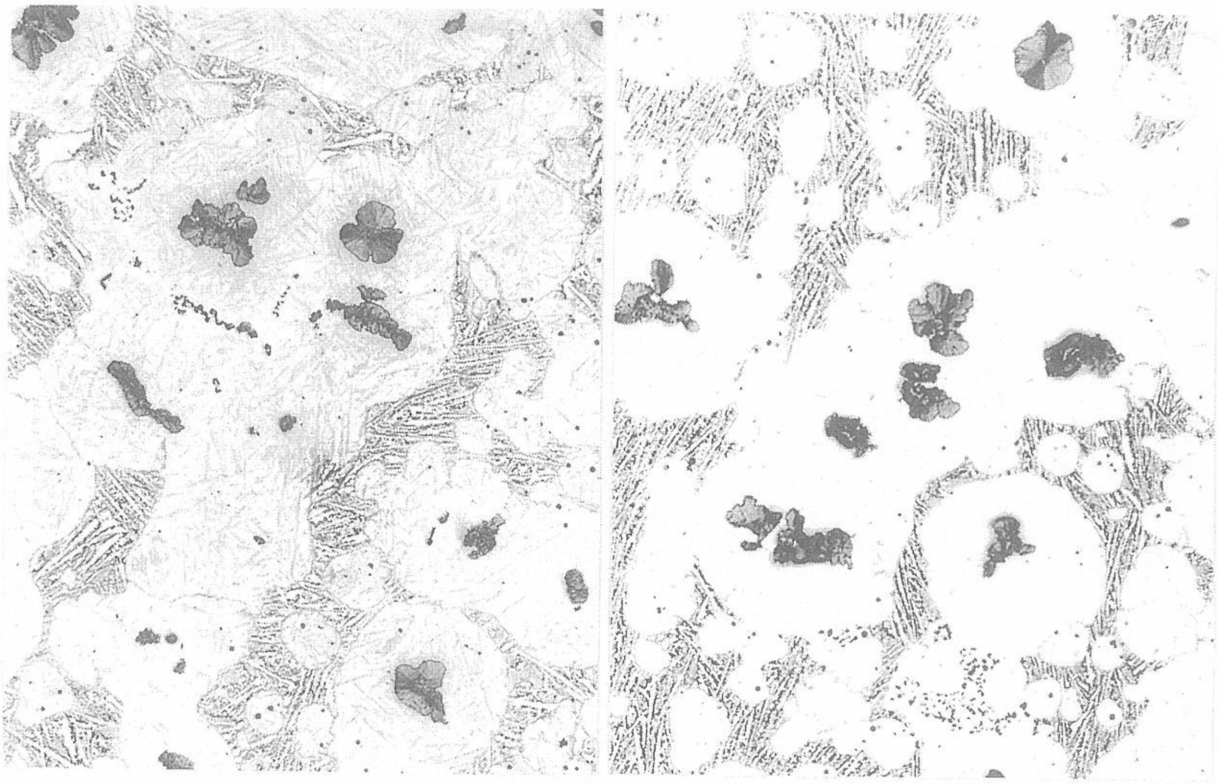


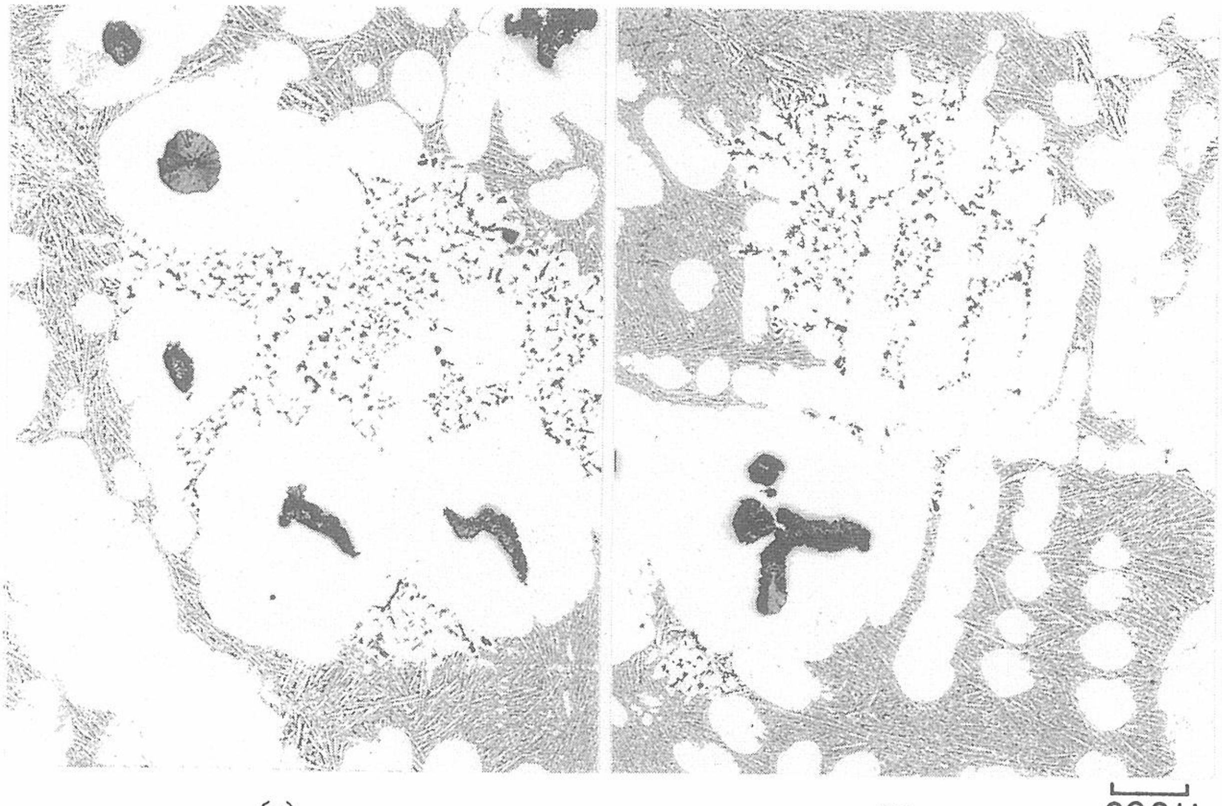
Fig. 5 Microstructure of specimen quenched at point 2 in Fig. 3.



(a) (b)

200μ

Fig. 6 Microstructure of specimen quenched at point 3 in Fig. 3.



(a) (b)

200μ

Fig. 7 Microstructure of specimen quenched at point 4 in Fig. 3.

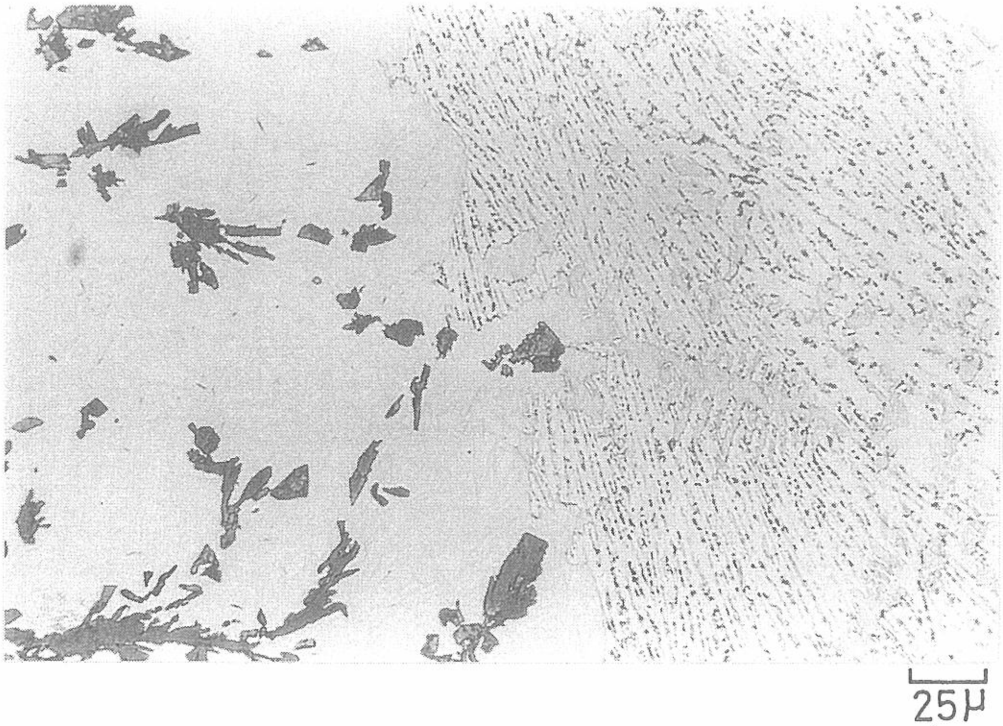


Fig. 8 Growth end of chunky graphite contacted with residual liquid iron through liquid channel. Specimen was quenched at point 4 in Fig. 3.

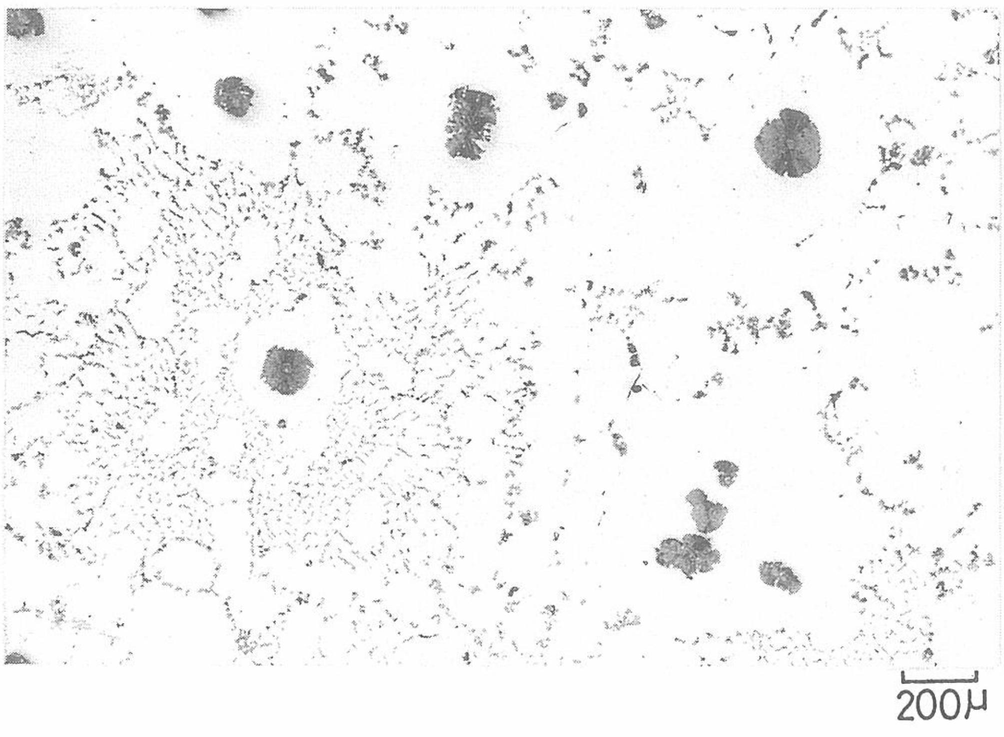
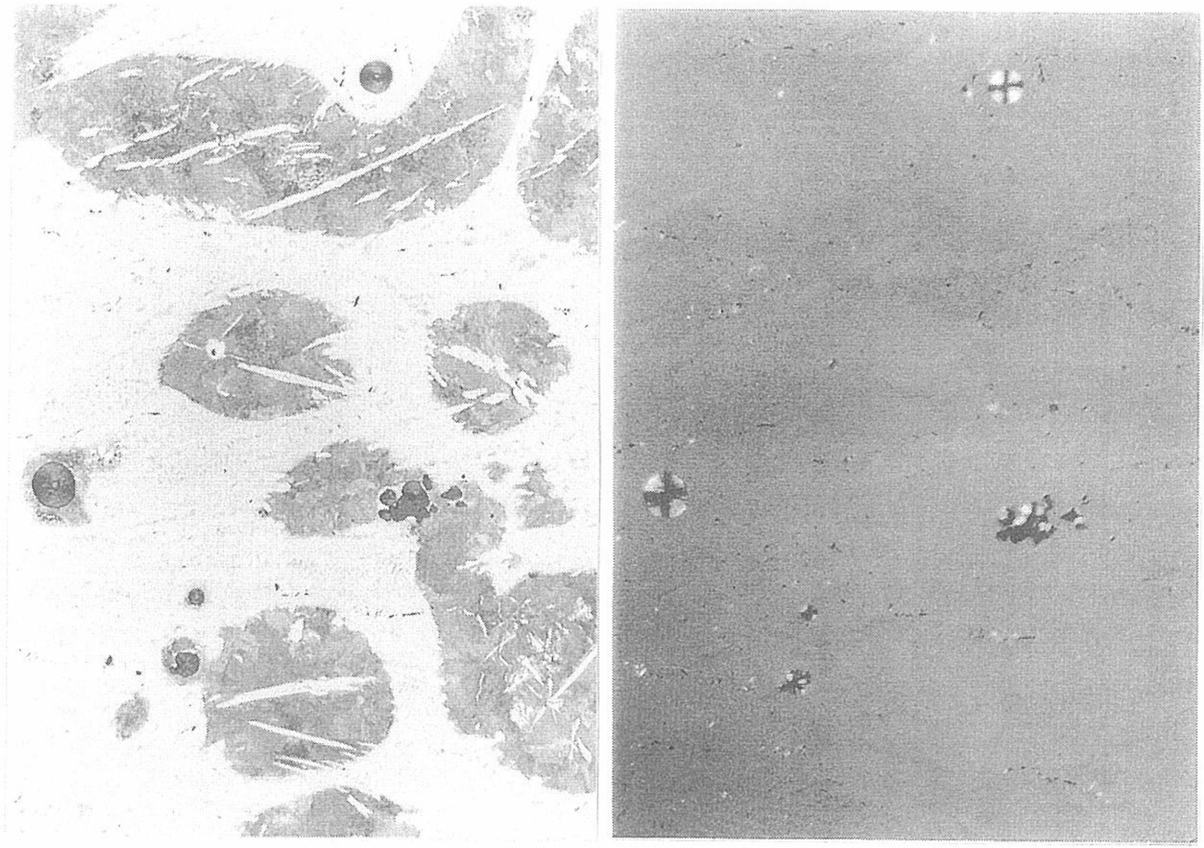


Fig. 9 Microstructure of specimen solidified and cooled in SiC furnace.



(a) General light (b) Polar light 25μ

Fig.10 Nucleation of chunky graphite at austenite-inclusion interface around austenite dendrite in specimen 3.

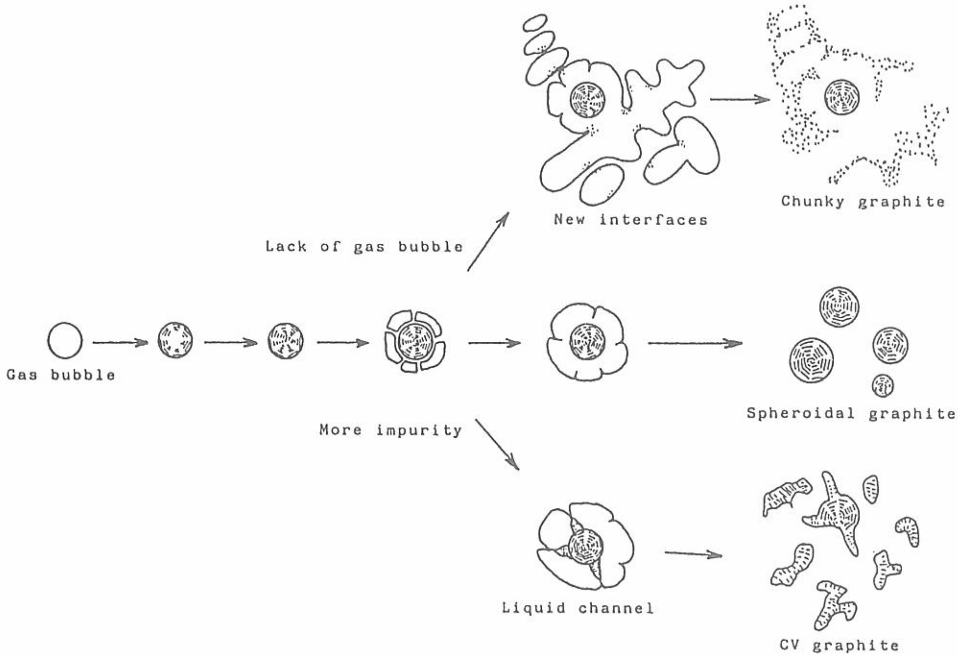


Fig.11 Schematic illustration of graphite formation in liquid iron treated with spheroidizer.