THE INFLUENCE OF TELLURIUM ON THE GRAPHITE FORMATION OF CAST IRON DURING SOLIDIFICATION

By Nobuhisa TSUTSUMI, Masato INAMURA, and Masayuki NAKADA

SYNOPSIS

The morphological change of graphite in gray cast iron during solidification when the melt was alloyed with pure tellurium was studied in this paper by using scanning electron microscope. It is seemed that the adsorption of tellurium on the prism plane of graphite crystal suppressed the crystal growth on the plane so that accelerated the growth of graphite crystal on c-plane in c-axis direction. Subsequently, a hexagonal structure or step-like structure of graphite crystal is observed in a deep etched alloy having higher content of tellurium in the case of slow cooling but not so remarkably observed in fast cooling. The same results on morphological change of graphite during solidification are obtained both in a nickel-carbon hypereutectic alloy and an iron-carbon-silicon hypereutectic alloy. Moreover, it can be assumed that in eutectic reaction of hypoeutectic iron, some extent of suppression of crystal growth of graphite in c-axis direction depending upon the cooperative growth of d-dendrite by tellurium addition causes the super-cooling of the melt then leads it to an eutectic reaction in metastable system.

1. Introduction

For the purpose of preventing molting formation of white cast iron as cast, bismuth and tellurium is used to be added to the melt in blackheart malleable iron production. The mechanism of suppression of molting with alloying element, however, has not been clarified yet. Several studies on the retarding behavior of the graphitization during solidification of cast iron has been reported in our laboratory. Consequently, it has been proposed that bismuth and tellurium may be adsorbed at the prism plane of graphite preventing its growth, then the melt may be undercooled so that the eutectic solidification behaviour changes from stable to metastable system.

With a view of investigating the effect of tellurium which is several order of magnitudes stronger than bismuth on the retardation of graphitization during solidification, Ni-C alloy are utilized in this experiment, because in a Ni-C alloy the metastable phase is difficult to obtain under normal condition, while in Fe-C alloy ledeburite structure as a product of metastable reaction is easy to obtain during eutectic solidification. Moreover the growth of eutectic graphite is influenced by the crystallization of eutectic during coupled growth, but that of primary graphite is not. Primary graphite which is precipitated and suspended in the melt during solidification has a tendency to be affected by the addition of alloying element remarkably. Therefore the influence of tellurium on the formation of primary graphite in hypereutectic melt has been studied in Ni-C alloy and then in Fe-C-Si alloy in this paper.

2. The Effect of Tellurium on the Graphite Formation

In cast iron tellurium is a powerful element to suppress the molting tendency in white iron castings. Besides, tellurium is also used to the treatment of melts of gray iron and spheroidal cast iron etc. Tellurium increases carbon activity in carbon saturated iron melt. It is seemed that this element improves the precipitation of graphite. However tellurium is used to suppress the molting in malleable foundries. These phenomena show the conflict results. In view of the stabili-
zation of cementite, tellurium may be replaced with carbon then stabilizes Fe₃C.¹⁰⁸-¹⁰⁹ Tellurium pick up in Fe₃C, however, has not been reported yet. The study of radiography and radiometry shows that radioisotope ¹²³Te has a tendency to settle in the boundaries of austenite dendrite and within graphite.⁶¹-⁶⁴ From these studies it seems that the effect of tellurium is different from that of normal carbide stabilizing element as chromium, vanadium, manganese, titanium, etc. in the case of retardation of graphite formation in cast iron.

The addition of tellurium to the cast iron melt leads to remarkable undercooling and shifts the eutectic solidification to lower temperature.²⁸-³⁵, 4²-⁴⁷, ¹⁴², ¹⁴³, ¹⁴⁵, ¹⁴⁶, ¹⁴⁷, ¹⁴⁸, ¹⁴⁹, ¹⁵⁰, ¹⁵¹ so that the graphite which is formed by addition of tellurium to the iron melt may be classified as follows: 1) Nodular, Spheroidal or Globular Graphite; ³⁶-³⁷, ³⁸-³⁹, ⁴⁰-⁴¹, ⁴²-⁴⁷, ⁴⁸-⁴⁹, ⁵⁰-⁵¹, ⁵²-⁵³, ⁵⁴-⁵⁵, ⁵⁶-⁵⁷, ⁵⁸-⁵⁹, ⁶⁰-⁶¹, ¹⁴², ¹⁴³, ¹⁴⁴-¹⁴⁷ This type graphite is precipitated during both the primary and eutectic solidification. In the eutectic solidification this graphite is formed besides primary γ-dendrite in ahead of the precipitation of eutectic-type or at the end of stable eutectic solidification. In general graphite may be formed directly from the melts,³⁶-³⁹, ⁴²-⁴⁷ or by the decomposition of supersaturated γ structure.⁴² It has been also reported Mn-S-Te and various oxide,⁴⁵-⁴⁸-⁵⁴ can be act as heterogeneous nucleus during the precipitation of graphite. 2) Mesh-like, Spiky or Fiber Graphite,⁴², ⁴⁷-⁴⁸, ⁵⁴-⁵⁵, ⁵⁹-⁶⁰, ⁶¹ This type graphite is formed in a certain area between eutectic-type graphite and ledeburite in high silicon iron. This is similar to eutectic-type at low magnification while it shows mesh-like structure at high magnification. This structure may be formed by decomposition of Fe₃C just after solidification. 3) Shell-type Graphite.⁴² This type graphite is precipitated in ahead of the precipitation of eutectic graphite as halo graphite surrounding γ-dendrite. Fig. ¹⁴¹ shows shell-type graphite by deep etching in our study. 4) Widmannstätten or Sooty Graphite,⁴², ⁶⁰-⁶¹ This type graphite is precipitated in rapid cooling from supersaturated γ in the form of semi-conformity. In many cases a lot of small, local cluster of fine graphite plate are arranged parallel to each other in several directions. The combination of these above mentioned graphite may be shown as rosette pattern.⁴²

3. Experimental Procedure¹³¹

A electrode graphite crucible charged with low cobalt electrolytic nickel is heated to 1500°C then...
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held at this temperature with graphite carbon covering for 40 min for obtaining the saturation with carbon in high frequency induction furnace. After holding the melt is poured to the iron mould.\(^{30-31}\) In the melting of cast iron Fe-C-Si alloy is melted in the same crucible and furnace with electrolytic iron and metallic silicon in the same process. The chemical composition of these materials are shown in Tables 1 and 2. The phase diagrams of Ni-C\(^{33-36}\) and Fe-C system\(^{32-35}\) are shown Figs. 2 and 3.

The molten metal of Ni-C alloy in alumina crucible held at 1550°C for 5 min in Tamman resistance furnace are cooled in furnace at 15, 30 and 60°C/min respectively in argon atmosphere.

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**Fig. 2.** Ni-C equilibrium diagram.

**Fig. 3.** Fe-C phase diagram.

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![Graphite formation diagram](image)

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**Fig. 4.** Variation of primary graphite with temperature of tellurium addition in nickel-carbon alloy.

Experimental condition: cooling rate, 15°C/min; added tellurium, 0.3 at %.
0.3 at% Te, i.e., 0.65 wt% Te are added at 1550, 1500, 1450, and 1400 °C respectively using a quartz plunger. A molten nickel with saturated carbon added with 0.3 at% Te at 1550 °C is cooled in furnace showing automatically its cooling curve by using Pt-65%Rh/Pt-30%Rh thermocouple. Tellurium used in this experiment is in the form of pellet having 99.99% Te.

These specimen sectioned vertically through the center are polished for metallographic examination. By using image analyzing computer QTM 720 graphite from all specimen are classified as shape factor $s/A$. Summarized classification of

Table I. Chemical composition of Ni-C alloys, wt% (\%)

<table>
<thead>
<tr>
<th>Series</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 C min</td>
<td>2.35</td>
<td>0.03</td>
<td>Trace</td>
<td>Trace</td>
<td>0.004</td>
</tr>
<tr>
<td>30 C min</td>
<td>2.32</td>
<td>0.04</td>
<td>Trace</td>
<td>Trace</td>
<td>0.003</td>
</tr>
<tr>
<td>60 C min</td>
<td>2.29</td>
<td>0.09</td>
<td>Trace</td>
<td>Trace</td>
<td>0.007</td>
</tr>
<tr>
<td>Thermal analysis</td>
<td>2.35</td>
<td>0.07</td>
<td>Trace</td>
<td>0.003</td>
<td>0.003</td>
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</tbody>
</table>

Table II. Chemical composition of Fe-C-Si alloy, wt%

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.28</td>
<td>2.89</td>
<td>Trace</td>
<td>0.034</td>
<td>0.006</td>
</tr>
</tbody>
</table>

Table III. Number and shape factor of graphite

<table>
<thead>
<tr>
<th>Number</th>
<th>Shape Factor</th>
<th>Shape of Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 ~ 0.005</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.005 ~ 0.010</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.010 ~ 0.015</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.015 ~ 0.020</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.020 ~ 0.025</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.025 ~ 0.030</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.030 ~ 0.035</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>0.035 ~ 0.040</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.040 ~ 0.045</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.045 ~ 0.050</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0.050 ~ 1/4π</td>
<td></td>
</tr>
</tbody>
</table>

S : Area
I : Perimeter

Fig. 5. Variation of primary graphite with temperature of tellurium addition in nickel-carbon alloy.

Experimental conditions: cooling rate, 30 C/min; added tellurium, 0.3 at% Te.
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Fig. 6. Variation of primary graphite with temperature of tellurium addition in nickel-carbon alloy.
Experimental condition: cooling rate, 60°C/min; added tellurium, 0.3 at%.

Fig. 7. Variation of primary graphite in no addition specimen with cooling rate.

Fig. 8. Variation of primary graphite in specimen added tellurium with addition temperature: cooling rate, 15°C/min; added tellurium, 0.3 at%.
graphite form is shown in Table 3. As it is important to observe primary graphite only, the melt which is cooling at the rate of 15°C/min from 1550°C is cooled rapidly in atmosphere from 1450°C to obtain extremely fine eutectic graphite. Subsequently shape factors (s²/δ) are measured in each specimen on 90 flakes of primary graphite having over 1.75 × 10⁻² mm².

In general in Fe-C-Si alloy exist a different carbon solubility comparing with in Ni-C alloy. Therefore a different cooling rate (15°C/min) and temperature of tellurium addition (1400°C) are taken for Fe-C-Si alloy series. In this case amounts of tellurium addition are determined as 0.042 at % (0.10 wt%), 0.84 at % (0.20 wt%), and 3.36 at % Te (8.0 wt% Te).

4. Results Obtained and Discussion

The graphite structure cooled at 15, 30 and 60°C/min are shown in Fig. 4, 5 and 6, respectively. It is clarified that the higher temperature of addition increases the width of graphite and changes the form of graphite from flake to spherical. First of all, the form of primary graphite in tellurium-free specimen cooled at various cooling rate are classified by shape factor (s²/δ) then compared with the distribution of shape factor in Fig. 7. It is obvious that graphite in specimen cooled at lowest cooling rate is the longest flake among these three specimens. As the temperature of tellurium addition becomes high, graphite in the specimen has a tendency to be changed to spherical form. Fig. 8 which illustrate this factor is obvious in the distribution of morphological change of graphite and the variation of the peak of shape factor.

For the explain of these phenomena in graphite formation mentioned above a following reaction can be proposed. If the temperature of tellurium addition is higher than the temperature of primary graphite precipitation, i.e., 1500°C. In other words, if the melt is cooled under the condition of having tellurium suspension during the primary graphite precipitation, globular graphite is formed in general (Fig. 9-11). But if the temperature of addition is lower than the temperature of primary graphite precipitation (Fig. 9-21), i.e., if tellurium is added after primary flake graphite is precipitated and suspended in the melt already, thicker flake graphite coexisted with globular graphite is formed. The growth of this thicker flake graphite is improved with spheroidizing effect, i.e., the promotion of growth in e-axis direction, of tellurium. Perfect globular graphite, however, is hard to growth and remains as flake form. Besides, globular graphite is formed below the determined temperature of tellurium addition.

Fig. 10 shows EPMA observation result in the specimen cooled at 60°C/min and with following addition of 0.3 at % Te at 1450°C. In this case, almost of all tellurium is segregated locally within primary graphite or at the boundary between graphite and nickel matrix. Moreover, remains of tellurium exists as nickel solid solution with tellurium or tellurium compound as NiTe or Ni₂Te (7). From this result, it can be considered that tellurium are penetrated into graphite or adhered on graphite by diffusion through molten metal. As radiographic observation with using ¹²⁵Te by Lyubchenko shows that the existence of tellurium in graphite structure, the tellurium content under the detection limit of EPMA might be adsorbed within graphite of the specimen. Also the existence of free tellurium in the neighbor of eutectic graphite are observed in X-ray image as shown in Fig. 11.

Fig. 12 shows the typical cooling curves of both Ni-C alloys with no and 0.3 at % Te addition. The temperature of eutectic arrest in tellurium-free alloy is at 1318°C, but the eutectic arrest of alloy with 0.3 at % Te addition at 1550°C exists at 1305°C. However, when the specimen is cooled fast in upper position of furnace, no arrest or supercooling are observed during eutectic solidification in cooling curve.
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Figure 10. Primary graphite and X-ray image.
Experimental conditions: cooling rate, 60°C/min; addition temperature, 1450°C; added tellurium, 0.3 at%.
Fig. 11: Flake graphite and X-ray image.

Experimental condition: cooling rate, 60°C/min; addition temperature, 1450°C/min; added tellurium, 0.3 at%.
Fig. 13 shows the graphite structure as the mixture of coarse plate-like primary graphite and highly branched eutectic graphite in the tellurium-free alloy cooled in atmosphere. Also Fig. 14 shows the graphite structure in tellurium-free alloy cooled slowly at 15°C/min in furnace.

Moreover, Fig. 15 shows the graphite structure of alloy with 0.3 at% Te addition at 1450°C cooled slowly at 15°C/min. This graphite shows so-called hexagonal stacking structure which is much different from the structure in tellurium-free alloy. It is also observed in this figure that some graphite show twisting with c-axis on the central axis which may be considered as rotation twin. These stacking structure of graphite are formed as the result of two-dimensional nucleation upon graphite and hexagonal anisotropy of graphite is appeared as crystal habit. It shows that this hexagonal stacking structure of graphite forms as the result of remaining of the prism plane having the lowest ratio of growth during growth of graphite crystal. The typical hexagonal stacking structure of graphite having a reflection twin is shown in Fig. 16.

Globular graphite in tellurium added alloy shown in Fig. 17 has hexagonal stacking structure on its surface. It is considered that this type of hexagonal stacking structure forms as the result of growth in furnace.

Fig. 12. Cooling curves of Ni-C alloys.

Fig. 13. Graphite in rapid cooled alloy.
Experimental condition: rapid cooling in atmosphere; no addition.

Fig. 14. Graphite in slow cooled alloy.
Experimental condition: cooling rate, 15°C/min; no addition.

* This is the result of bunching and substructure is shown as spiral growth.
Fig. 15. Hexagonal structure in primary graphite.
Experimental condition: cooling rate, 15°C/min; addition temperature, 1450°C; added tellurium, 0.3 at%.

Fig. 16. Hexagonal structure with reflection twin.
Experimental condition: cooling rate, 15°C/min; addition temperature, 1450°C; added tellurium, 0.3 at%.

Fig. 17. Globular graphite among primary graphite.
Experimental condition: cooling rate, 15°C/min; addition temperature, 1450°C; added tellurium, 0.3 at%.
Fig. 18. Eutectic graphite and step.
Experimental condition: cooling rate, 15°C/min; addition temperature, 1450°C; added tellurium, 0.3 at%.

Fig. 19. Adhered tellurium on graphite during deep etching and washing.
Experimental condition: cooling rate, 15°C/min; addition temperature, 1450°C; added tellurium, 0.3 at%.

Fig. 20. Behaviour of tellurium compounds during deep etching and washing.
gonal stacking structure shows the retardation of 0-axis growth of poly-crystal graphite as globular graphite.

Moreover, eutectic graphite precipitated in the lower part of the specimen in Fig. 18 shows the hexagonal stacking structure with some step of hexagonal structure. In this case the c-axis growth of graphite is not so highly developed as in the case of primary graphite, because eutectic graphite is surrounded always with eutectic nickel during coupled growth in eutectic solidification.

Fig. 19 shows tellurium adhered on the surface of graphite which is originally contained in the specimen and may be formed by hydrolysis of dissolved tellurium during deep etching. The proposed mechanism of these phenomena is illustrated in Fig. 20. EPMIA observation shows that this adhered tellurium is pure but not oxide or

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Fig. 21. Primary and eutectic graphite in tellurium-free alloy (Fe-C-Si alloy).
Experimental condition: cooling rate, 15°C/min; no addition.

Fig. 22. Primary and eutectic graphite (Fe-C-Si alloy).
Experimental condition: cooling rate, 15°C/min; addition temperature, 1400°C; added tellurium, 0.10 wt%.

Fig. 23. Hexagonal structure in primary graphite (Fe-C-Si alloy).
Experimental condition: cooling rate, 15°C/min; addition temperature, 1400°C; added tellurium, 2.0 wt%.
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After nickel during solidification.

...t tellurium on the surface, a layer of tellurium is contained in the alloy, which is removed by hydrolysis during the etching. The presence of this phenomenon is illustrated. The formation shows that the compound is not oxide or

Fig. 24. Hexagonal structure in primary graphite (Fe-C-Si alloy).
Experimental condition: cooling rate, 15°C/min; addition temperature, 1400°C; added tellurium, 8.0 wt%.

Fig. 25. Eutectic graphite in tellurium-free alloy (Fe-C-Si alloy).
Experimental condition: cooling rate, 15°C/min; no addition.
chloride. It has been observed that considerably much amount of tellurium are adhered to the prism plane of each graphite, but few tellurium is adhered on the basal plane of it. Consequently it can be assumed that this aspect may simulate the adsorption of tellurium on the prism plane of graphite during solidification.

Subsequently, the morphological change of graphite in the tellurium added Fe-C-Si alloy is as follows. Fig. 21 shows primary graphite in tellurium-free Fe-C-Si alloy cooled slowly at 15°C/min in furnace. In this iron primary graphite observed by deep etching is the same coarse flake in tellurium-free Ni-C alloy. In the iron added with 0.1 wt% Te almost same primary graphite flake is precipitated (Fig. 22) in pro-eutectic solidification, whilst in the metal with 2 wt% Te same step like hexagonal structure are formed (Fig. 23). Moreover a lot of hexagonal stacking structure of graphite, shown in Fig. 24, are observed in the iron with 0.8 wt% Te.

As compared with eutectic graphite in tellurium-free iron (Fig. 25), in the iron with 0.1 wt% Te eutectic graphite is precipitated as undercooled or sooty type fine graphite. Each graphite flake has clearly hexagonal structure, which shown in Fig.

26. In the iron with higher addition of tellurium, the same type of graphite are also observed.

### 5. Summary

Morphological change of graphite in 0.30 to 3.36 at% (i.e., 0.65~8.0 wt%) of tellurium added Ni-C and Fe-C-Si alloys are observed and discussed as follows:

Tellurium may be adsorbed to the step of graphite crystal and decreases the edge energy of the step so that interruption of the further deposition of carbon atom on the graphite. Therefore the c-axis growth which is perpendicular to a-axis may be preferred by the interruption of a-axis growth of graphite.

It has been clarified in cast iron that the addition of tellurium or bismuth may retard the a-axis growth of graphite crystal during eutectic solidification. In the case of the addition of these metals the c-axis growth of graphite may be also retarded some degree with the precipitation of austenite during coupled growth in eutectic solidification so that the melt may be supercooled to the metastable eutectic. Consequently the melt solidifies as white iron having no precipitation of graphite flake.

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graphite flakes.

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