

論 文

# Effect of Te on Graphite Morphology in the Directional Solidification of Fe-C-Si Alloys

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Fe-C-Si 합금의 일방향응고시 흑연의 형상에 미치는 Te의 영향

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## 초 록

일방향 응고법을 이용하여 텔루리움(Te)이 Fe-C-Si 합금 즉 주철의 응고시 흑연의 형상에 미치는 영향을 관찰하였다. Te이 산소와의 반응성향이 크을 감안하여 수소 및 아르곤으로 응고분위기를 조절함으로써 각각의 분위기에서 나타나는 Te의 영향을 비교 분석하였다. 그 결과 아르곤 분위기에 비하여 수소 분위기에서 Te의 효과가 현저하였으며, 이것은 수소가 산소의 영향력을 억제하여 Te의 산화를 방지함에 기인하는 것으로 판단되었다. 수소 분위기 하에서 Te의 효과가 극대화되었을 경우 회주철 조직은 응고속도가 극히 낮은 때에만 얻어졌으며, 미세한 片狀흑연이 평면형 응고선단을 형성하며 열전달이 일어나는 반대 방향을 따라 성장함으로써 지금까지 볼 수 없었던 독특한 조직이 관찰되었다.

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## 1. Introduction

Te is well-known for its carbide-promoting effect in the solidification of Fe-C-Si alloys. It has been reported that an increase in hydrogen content increases the effect produced by the addition of Te. When the hydrogen content is low enough to avoid the formation of white iron, Te is known to produce gray irons with abnormal graphite morphologies which tend to weaken castings severely[1~3]. It is, therefore, important to examine the effect of Te on the control of graphite morphology in cast iron solidification. Most previous studies on the Te effect have been carried out in air in conventional casting experiments. And there has been conflict concerning the graphite morphologies produced by the Te addition.

This study performed directional solidification experiments on the high purity synthetic cast iron alloys with and without the addition of Te. Considering the tendency for Te to react with oxygen, it seemed advisable to run the experiments with the O-activity strictly controlled and thereby the Te effect maximized. The O-activity was suppressed by using H<sub>2</sub> to control the solidification atmosphere. The main emphasis of the present study is placed on the graphite morphology as affected by Te under different solidification atmospheres in terms of the O-activity.

## 2. Experimental

Cast iron alloys were synthesized to a composition of Fe-3.4 wt.% C-2.0 wt.% Si with and

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without the addition of 0.05wt.% Te, using Glidden electrolytic iron, specified 99.95% Fe, a semiconductor grade Si and spectrographic grade C rod. Te doping additions utilized reagent grade ferric telluride ( $\text{FeTe}_2$ ).

Solidification was taken place in alumina containment tubes of 5mm inside diameter, and the solidification atmosphere could be easily controlled by evacuating the tube and then introducing gases of interest. High purity Ar and 10volume %  $\text{H}_2$  plus balance Ar were used to backfill the tube containing the alloys in an attempt to make two kinds of solidification atmospheres different in O-activity. When the furnace was stabilized at  $1450^\circ\text{C}$ , experiments were started at about  $100\mu\text{m/s}$  and then decelerated in steps down to  $1\mu\text{m/s}$ . The containment tube was quenched into water at the termination of the experiments while the solidification reaction was still in progress. The rapid quench proved useful in preserving the growth front, allowing evaluation of the morphology of the solid/liquid interface. Other features of the directional solidification experiments have been detailed elsewhere[4].

### 3. Experimental Results

Solidification experiments were first run under pure Ar atmosphere with the high purity Fe-C-Si alloys. Coral graphite was found to grow initially at the high solidification rate,  $100\mu\text{m/s}$ , which, in deceleration, was replaced by coarse type A flake graphite. The transition in graphite morphology from coral to flake was quite abrupt and consistently occurred at  $2.5\mu\text{m/s}$  in repeated experiments.

Fig. 1 is an optical micrograph showing the graphite morphology grown at  $20\mu\text{m/s}$  from the Te-doped alloys under pure Ar atmosphere. It is typical of the type D graphite which appears in commercial purity cast irons. Fig. 1 was taken from the longitudinal section of a rod where the

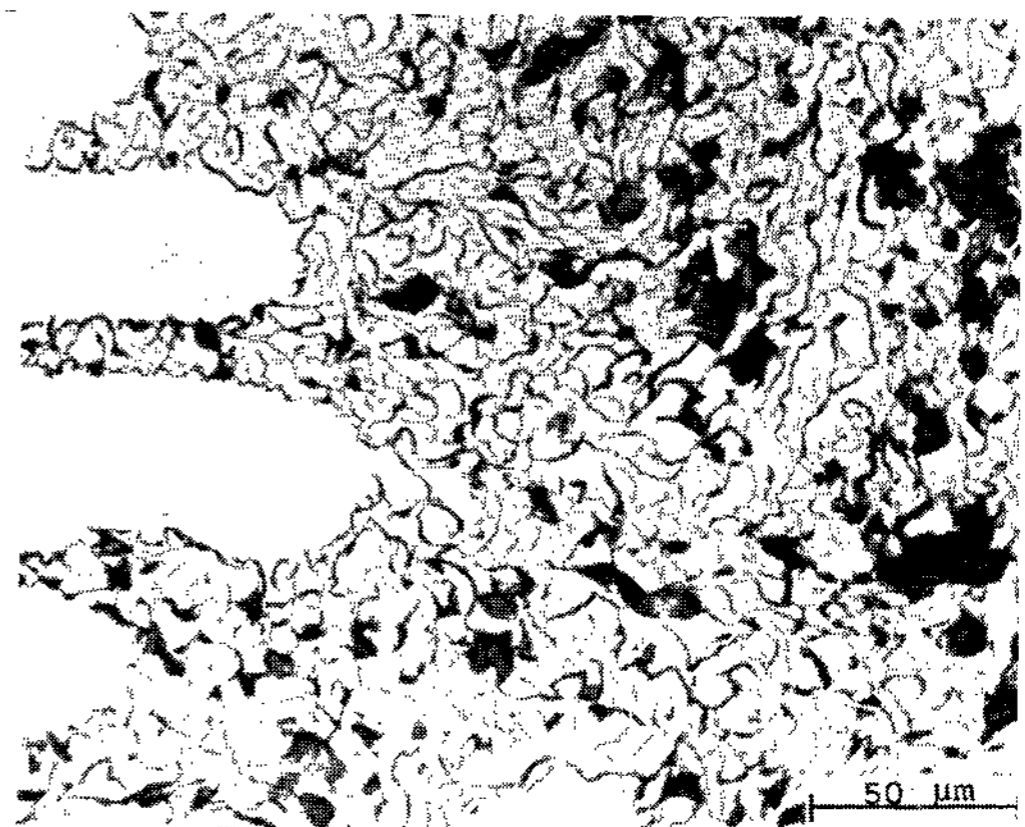


Fig. 1. Optical micrograph of type D flake graphite in a longitudinal section. Solidified from the Te-doped alloys at  $20\mu\text{m/s}$  under pure Ar atmosphere. Solidification direction upward.

solidification direction is upward. No difference in the graphite shape was observed in the transverse section of the same rod. It is apparent that the thin graphite flakes divide the interdendritic matrix iron phase into regions equiaxed in three dimensions. Formation of the type D graphite dominated all over the Te-doped samples solidified under pure Ar atmosphere except at the  $1\mu\text{m/s}$  region where both type A and D grew together as shown in Fig. 2. It is interesting to note that the growth of proeutectic dendrite is not so apparent at this low rate  $1\mu\text{m/s}$  as can be seen in Fig. 1. Fig. 2 presents the growth front quenched while solidifying at  $1\mu\text{m/s}$ , and it is seen that the coarse A graphite grows in advance of the fine type D structure. The maximum lead distance is about 1.5mm, which corresponds to a  $14^\circ\text{C}$  difference, the temperature gradient being measured here to be approximately  $90^\circ\text{C/cm}$ . Therefore, it is concluded that the type A structure grows at  $14^\circ\text{C}$  hotter than the type D structure at  $1\mu\text{m/s}$  in the present alloys. It is also to be noted that the A graphite starts to solidify from the molten iron in contact with the inner surface of the alumina containment tube.

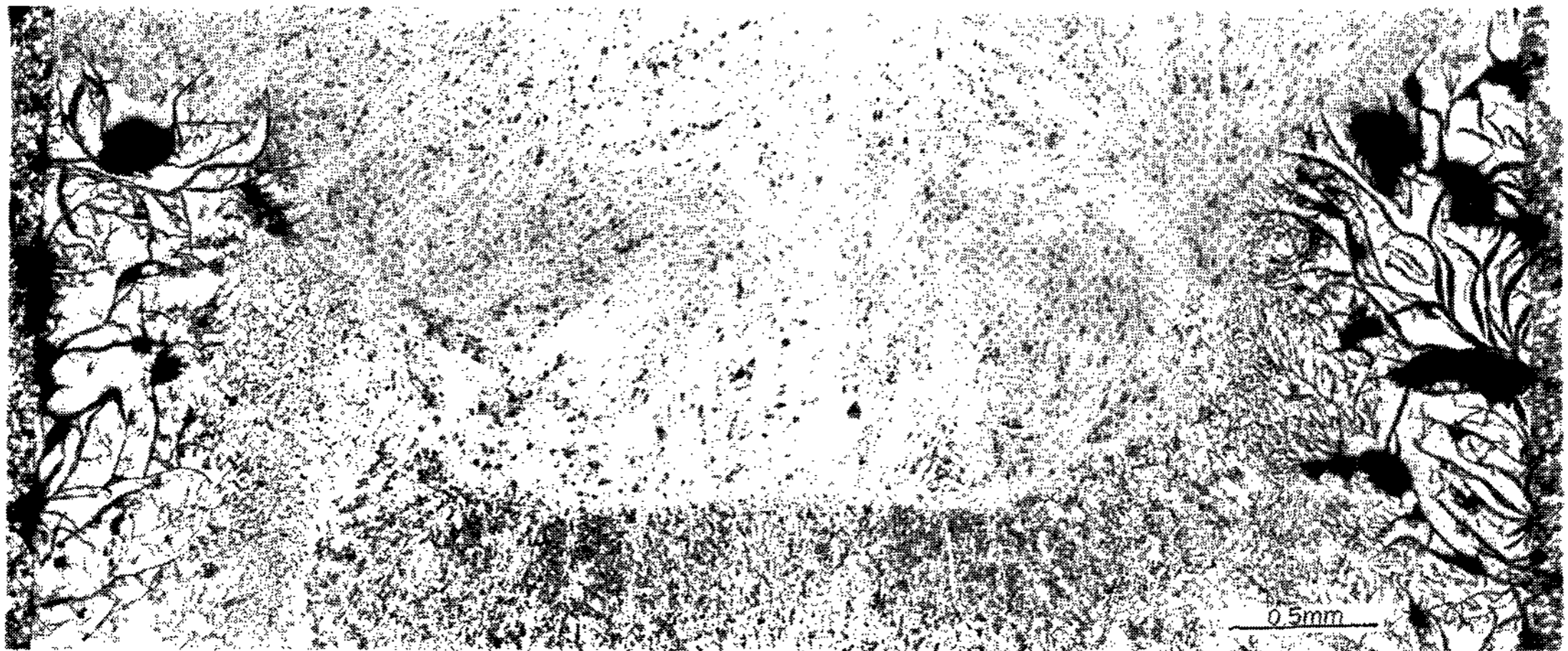


Fig. 2. Optical micrograph of a quenched interface. Solidified from the Te-doped alloys at  $1\mu\text{m/s}$  under pure Ar atmosphere. Solidification direction upward.

Formation of white iron structures was observed to dominate the Te-doped samples solidified under 10 vol.%  $\text{H}_2$  plus Ar atmosphere down to  $2.5\mu\text{m/s}$ . And the gray iron growth is allowed only at  $1\mu\text{m/s}$ . The effect of Te on the promotion of white irons will be discussed in the subsequent paper. Fig. 3 presents optical micrographs taken from the longitudinal, Fig. 3 (a), and transverse section, Fig. 3 (b), of the  $1\mu\text{m/s}$  region solidified gray. The graphite morphology such as shown in Fig. 3 is quite unusual and has not been reported to the best of the author's knowledge. In view of the fine size of the graphite flakes, however, the present study will call it type D. The type D graphite is seen to undergo constant small scale fluctuations in growth direction, but grow, on the average, following the general direction imposed by the unidirectional heat flow. The D graphite seems to have little difficulty in changing growth direction but possess substantial flexibility. The structures shown in Fig. 3 can be regarded as subdivision of the iron matrix into longitudinal columns surrounded by thin flexible graphite flakes. This kind of structure is usually observed in the solidification of the regular eutectics where the component phases grow in close cooperation

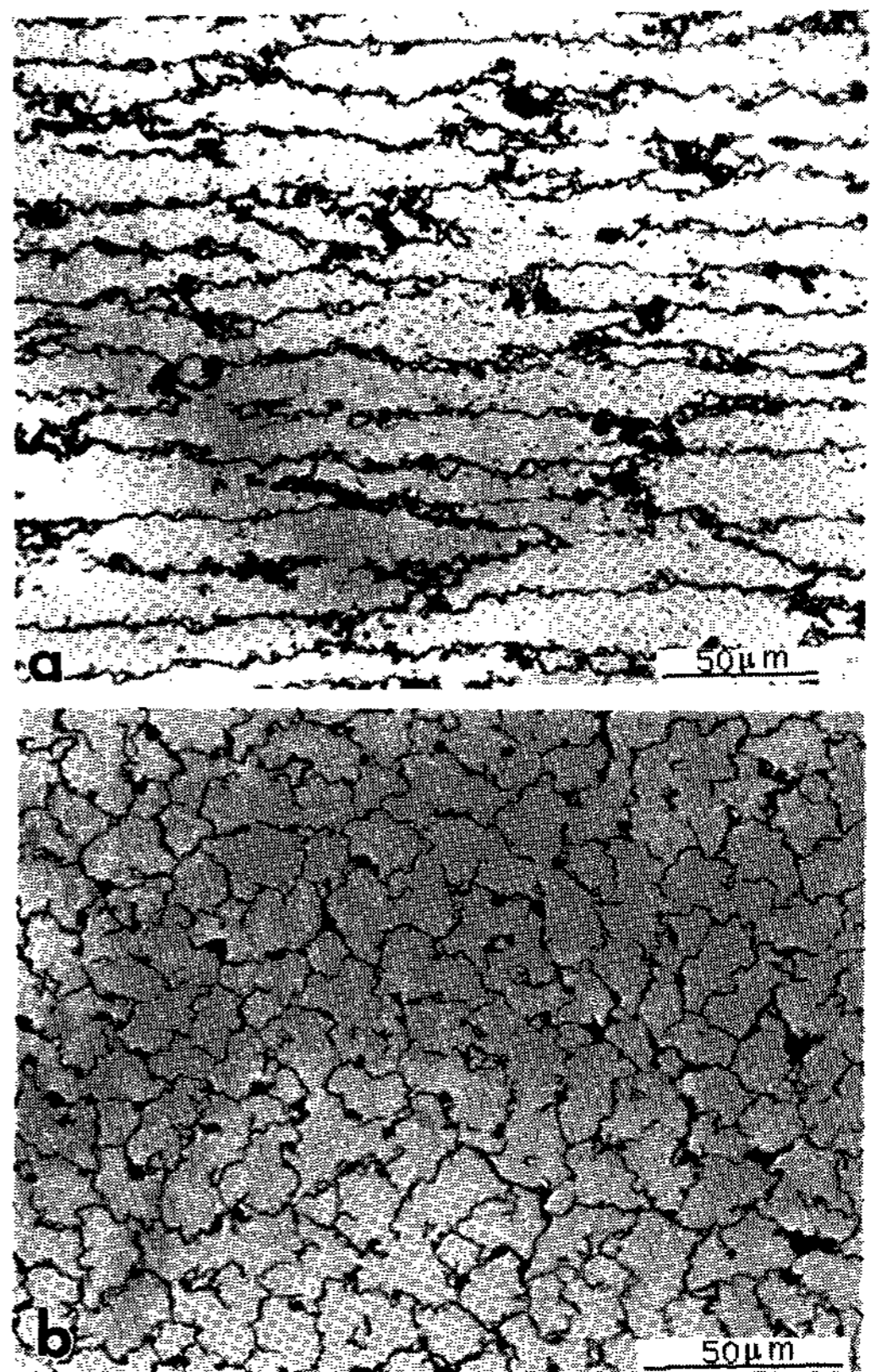


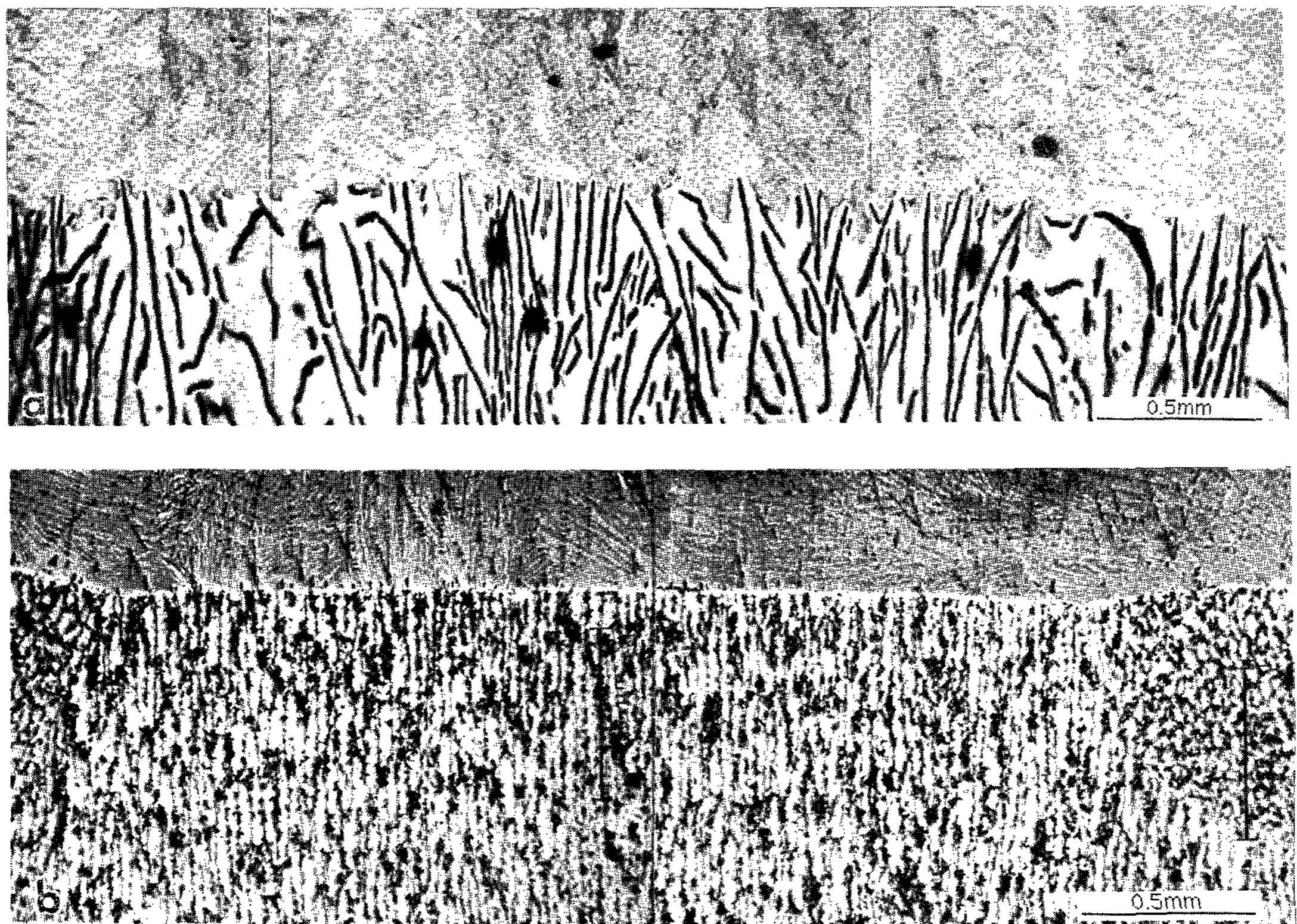
Fig. 3. Optical micrograph of type D flake graphite solidified from the Te-doped alloys at  $1\mu\text{m/s}$  under H-rich atmosphere. (a) Longitudinal section, solidification direction to the right, (b) Transverse section.



with each other, having no such growth anisotropy as the graphite phase. The flexibility shown in Fig. 3 to be possessed by flake type graphite is unusual in irregular eutectics like the iron/graphite systems, especially at the extremely low rate  $1\mu\text{m/s}$ .

Fig. 4 (a) and 4 (b) present the quenched interface regions of type A and D graphite, respectively. The A graphite was grown from the alloys with no Te addition under pure Ar atmosphere and the D graphite from the Te-doped ones under  $\text{H}_2$  atmosphere, both at  $1\mu\text{m/s}$ . Fig. 4 (a) illustrates several characteristics typically expected in the solidification of irregular eutectics like cast irons, i.e., the irregular macroscopic interfaces and large average lamel-

lar spacings together with a very wide dispersion of local spacings. Apparently they result from the specific growth anisotropies of the faceted phase. The local growth direction of the faceted phase graphite is determined by its local crystal orientation, and graphite flakes tend to show a large resistance to small changes in growth direction. This makes each flake grow in its own direction without strict cooperation with the neighboring iron phase, thereby producing the irregularities in the interface morphology and the interphase spacings. In contrast to Fig. 4 (a), the component phases in Fig. 4 (b) are seen to be in close cooperation in growth and form a strictly planer interface, which explains how the columnar structures as



**Fig. 4.** Optical micrograph of (a) type A and (b) type D flake graphite at the quench interface. Type A solidified from the alloys without the Te-doping under pure Ar atmosphere and type D from the Te-doped alloys under H-rich atmosphere, both at  $1\mu\text{m/s}$ . Solidification direction upward.

in Fig. 3 (a) result. The strict cooperation in the growth of iron-graphite eutectic would be allowed only if the faceted graphite is provided with an effective means to overcome the growth anisotropies, and has freedom to change growth directions whenever required in adjusting the lamellar spacing. The author recently observed a frequent occurrence of rotational stacking faults from the transmission electron microscopy performed on the S- or Te-induced flake graphite specimens[5]. And it was concluded that S and Te control graphite morphology by being deeply involved in the fault-creating mechanism. Fig. 4 (b), showing a planar interface developed at right angles to the unidirectional heat flow direction, verifies that Te, when present in H<sub>2</sub> atmosphere, can make the graphite flake overcome its growth anisotropy and grow in complete cooperation with the metal phase.

#### 4. Discussion

Comparison of the results obtained from the Fe-C-Si alloys with and without the Te addition shows that the major effect of Te in the gray solidification is to promote the formation of type D flake graphite. However, it is important to notice that the Te effect is greatly influenced by the control of solidification atmosphere with H<sub>2</sub> gases. In the absence of H<sub>2</sub>, i.e., under the pure Ar atmosphere, growth of the type D graphite produces the equiaxed microstructures as shown in Fig. 1 at the velocity ranges of 1 to 100  $\mu\text{m/s}$  and the transition in graphite morphology from D to A starts to occur at 1  $\mu\text{m/s}$  as in Fig. 2. The solidification run under the H-rich atmosphere was found to promote the white structures down to 2.5  $\mu\text{m/s}$  and thereby restrict the gray iron growth only at 1  $\mu\text{m/s}$ . The fine type D flakes, well aligned to produce the columnar structures as in Fig. 3, are the only graphite morphology that can grow

under the H-rich atmosphere.

The strong influence caused by H<sub>2</sub> on the Te effect may be understood by considering the fact that the experiments were run inside the alumina tubes with the furnace temperature set at the high temperature 1450°C. The element Te is very reactive that at the high temperature it would oxidize at relatively low O-activities in the iron melt, and once oxidized Te would not exert its maximum influence in the solidification. In this respect, introducing the H<sub>2</sub> gases into the solidification atmosphere is expected to lower the O-activity and suppress the oxidation of Te in solution in melt, enhancing the effectiveness of Te. As a matter of fact, it has been observed in the author's previous experiments that introduction of the H<sub>2</sub> gases into the solidification atmosphere counteracts the effects caused by oxygen, and that pure Ar atmosphere, without the introduction of H<sub>2</sub>, acts like O-rich atmosphere[4]. Evidence of the reduced effectiveness of Te through oxidation is also observed here in Fig. 2 where type A growth starts in the melt near the tube wall only under the pure Ar atmosphere. When the solidification atmosphere is not controlled by H<sub>2</sub>, the O-activity in the molten iron is expected to be relatively high. And oxidation may preferentially occur near the alumina tube wall by either a tendency for Te to reduce Al<sub>2</sub>O<sub>3</sub> at the high temperature or the easy penetration of oxygen from the upper molten surface.

It is also seen from the analysis of Fig. 2 that the growth front temperature of type D graphite is lower than that of type A by approximately 14°C. This is in agreement with the results of the cooling curve experiments done by Bates and Wallace[6]. Addition of Te to the commercial purity gray irons was found to change the graphite morphology from type A to D and increase the undercooling from 5 to 17°C, the difference of 12°C being reasonably close to the present results 14°C. Dawson[1-3] reports that

the Te addition changed the graphite morphology from type D to a coarse mesh-type graphite. This result is at variance with the present study as well as that of Bates and Wallace[6]. The present experimental results lead to the conclusion that the true Te effect in the gray solidification, when maximized in the H-rich atmosphere, is to promote the fine type D graphite at low solidification velocities by suppressing the type A formation.

The growth of well-aligned type D flakes forming a planar growth front as in Fig. 4 (b) indicates that Te, when its effect is enhanced under the H-rich atmosphere, somehow provides the faceted phase graphite with an effective means to change its growth direction whenever necessary in adjusting the eutectic phase spacing. This suggests that the mechanism by which Te produces such a dramatic effect on the structure of cast iron is closely related to the planar defect mechanism of graphite crystals. Accordingly, transmission electron microscopy was utilized to study the crystal defects in the Te-induced type D flake graphite and the results are soon to be published[5].

## 5. Conclusions

1. Directional solidification experiments with the Te-doped Fe-3.4wt.%C-2.0wt.%Si have established that the effect of Te on the graphite morphology of gray cast iron is greatly influenced by the control of solidification atmosphere with H<sub>2</sub> gases. Strong evidence has been produced that hydrogen enhances the Te effect by

suppressing the O-activity which may otherwise lead to the oxidation of Te in solution in melt.

2. The true Te effect in the gray solidification, observed only under the H-rich atmosphere, is to promote the fine type D graphite flakes forming a strictly planar interface in growth to produce the well-aligned structures along the heat flow direction. This suggests that Te makes the faceted graphite phase overcome the growth anisotropy by being deeply involved in the fault-creating mechanism of graphite crystals.

3. Quench interface experiments show that type D graphite experiences greater undercooling in growth than type A graphite by approximately 14°C.

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