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Partition of nitrogen in solidifying iron–carbon–silicon alloys

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The partition of nitrogen between austenite and liquid iron was examined from the measurement of solubilities of nitrogen in these phases. On primary austenite crystallization, nitrogen was rejected into liquid iron at high temperatures and the partition behaviour was reversed at low temperatures. Silicon lowered the critical temperature where the partition behaviour of nitrogen changed. The partition of nitrogen between cementite and austenite was investigated by analysis of nitrogen in iron–carbon–silicon alloys, which were quenched in ice-water from an equilibrium state at subeutectic temperatures, and in the cementite extracted from them. Nitrogen was enriched in cementite for Fe–C–0.5 wt% Si alloy, similar to the case of pure Fe–C alloy. However, silicon reduced the degree of enrichment of nitrogen in cementite. By the use of the partition coefficients, the variations of nitrogen concentrations in the coexisting phases were evaluated during the solidification of cast irons. In the irons with lower carbon concentrations, the supersaturation of nitrogen in liquid iron attained during solidification increased with increasing silicon content, and silicon had a detrimental effect to promote the formation of nitrogen gas blowholes in low-carbon cast irons.

1. Introduction

Gaseous elements in cast-iron melt are well known to cause casting defects such as blowholes and pinholes in the castings. Davison *et al.* [1] have indicated that the generation of "wormy" defects in large-sized grey cast irons is attributable to nitrogen. The critical nitrogen content to prevent the generation of "wormy" defects is 110 p.p.m. [1, 2] and that for "fissure" defects is 140 p.p.m. [3]. At the critical nitrogen content, nitrogen should be supersaturated in the melt and the nucleation and growth of these defects may need a certain degree of supersaturation of nitrogen. There is, however, little information on the critical degree of supersaturation of gaseous elements. For the comprehension of the causes of blowhole formation, it is of fundamental importance to know the partition behaviour of gaseous elements in freezing cast irons. Two of the present authors [4] have demonstrated that the partition of nitrogen between liquid iron and primary austenite solidifying from it strongly depends on the carbon content. Alloying elements affect the partition behaviour of nitrogen by interactions with nitrogen and carbon. Some nitride-forming elements, such as silicon and aluminium, influence the partition of nitrogen indirectly by forming nitrides. Consequently, silicon in cast iron is expected to have both these effects.

In the present work, the effects of silicon on the partition of nitrogen in freezing cast irons were investigated by determining the partition coefficients of nitrogen among coexisting phases on primary austenite crystallization and subsequent eutectic solidification of iron–carbon–silicon alloys. Using the partition coefficients obtained, the variations of nitrogen concentration in the coexisting phases during solidification were computed, and the possibility of the formation of nitrogen gas bubbles was investigated in terms of the degree of supersaturation of nitrogen in liquid iron.

2. Experimental procedure

2.1. Partition of nitrogen between austenite and liquid iron

The coefficient for partition of nitrogen between austenite and liquid iron was determined from the solubilities of nitrogen in these phases. Each iron–carbon–silicon alloy with the compositions given in Table I, of about 10 g weight, was held a little above the liquidus temperature or a little beneath the solidus temperature for a period given in the table under a purified nitrogen atmosphere of 1 atm, and then was quenched into ice-water. The details of the apparatus for rapid quenching have been described elsewhere [5]. After the surfaces of the quenched specimens were

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TABLE I Chemical compositions and equilibration conditions of alloys for the measurement of solubilities of nitrogen in austenite and liquid iron

Alloy	Chemical composition		Equilibration conditions	
	C (wt %)	Si (wt %)	Temperature (K)	Period (min)
A1	0.62	0.88	1643	80
A2	1.29	0.92	1523	180
A3	1.93	0.92	1413	360
A4	0.74	1.94	1598	80
A5	1.27	1.96	1503	180
A6	1.69	1.90	1420	360
L1	2.18	0.5*	1643	40
L2	2.92	0.5*	1573	90
L3	3.75	0.5*	1483	180
L4	2.04	1.0*	1643	40
L5	2.78	1.0*	1573	90
L6	3.56	1.0*	1483	180

*Nominal composition.

ground, they were washed with acetone and water in succession and were pulverized by crushing or drilling for the analysis of nitrogen.

2.2. Partition of nitrogen between cementite and austenite

Iron–carbon–silicon alloys were prepared by induction-melting electrolytic iron, electrode graphite and metallic silicon in alumina crucibles under an argon atmosphere. The melts were degassed in a vacuum and potassium ferricyanide of about 0.1 wt % was added to the melts, followed by casting them in air into a steel mould with the inner dimensions of 8 mm diameter and 250 mm length. The chemical compositions of the round bar castings are given in Table II. The round bar castings were cut into small discs 3 mm thick, after their surface oxide film was removed by grinding. Each of the discs was sealed into a quartz tube with a given nitrogen gas pressure and was subjected to heat treatment for 1000 min at 1073 K, for 600 min at 1123 K, for 120 min at 1173 K, or for 25 min at 1073 K, followed by quenching into ice-water. In a preliminary experiment, the period of the heat treatment to attain equilibrium concentrations of nitrogen in cementite and austenite was examined for Fe–C–0.5 Si and Fe–C–1.0 Si alloys in relation to the period for graphitization. The former was shorter than the latter at the above-mentioned heat-treating temperatures for iron–carbon–silicon alloys with silicon content less than 1 wt %. After it was established that the quenched specimens were not graphitized, the surfaces of the specimens were ground, and the specimens were washed with acetone and water in succession and were crushed into 100 to 200 mesh powder to serve for the extraction of cementite. The extraction was performed by the method given in earlier work [6] and the nitrogen concentrations in the quenched specimens and the extracted cementite were analysed by the neutralization–titration method (JIS G1288-1969).

TABLE II Chemical compositions of as-cast alloys for the measurement of the coefficient for partition of nitrogen between cementite and austenite

Alloy	Chemical composition			
	C (wt %)	Si (wt %)	Al (wt %)	N (p.p.m.)
Fe–C–0.5 Si	3.94	0.48	0.026	63
Fe–C–1.0 Si	3.82	0.93	0.047	57

3. Results

3.1. Partition of nitrogen between austenite and liquid iron

It is indicated from the thermodynamic data on the solubility products of the nitrides, Si_3N_4 and AlN [7], and the interaction coefficients between nitrogen and carbon or solute elements [8, 9] that these nitrides cannot be formed in liquid iron and austenite within the composition range of the alloys used in this work. The solubilities of nitrogen in these phases are, therefore, given by the total nitrogen concentration N_T. In Fig. 1, the values of N_T for liquid iron and austenite are plotted against the carbon content of the alloys. The solubilities of nitrogen in liquid iron and austenite were lowered with increases in both carbon and silicon contents of the alloys. The decrease in the solubility with silicon is remarkable for austenite, while the dependence on carbon content is larger in liquid iron than in austenite, similar to the case of the pure Fe–C alloy [4]. The coefficient for partition of nitrogen between austenite and liquid iron was computed as a ratio of the solubility of nitrogen in austenite to that in liquid iron, which should be in equilibrium with the austenite. The result is given for alloys with different silicon contents in Fig. 2. In the calculation, the carbon concentrations of the liquidus and the solidus were evaluated as functions of silicon concentration and temperature, by use of the coefficient for partition of silicon between austenite and liquid iron [10]. In Fig. 2, the solid curve for Fe–C alloy is based on the result of regression analysis of the nitrogen solubility data for the Fe–C alloys [4] and the Fe–C–Si alloys in Fig. 1. The partition coefficient of nitrogen is smaller than unity at high temperatures and is larger than unity at low temperatures, indicating that the partition behaviour of nitrogen changes at a critical temperature. With increasing silicon content, the critical temperature is lowered and, for alloys with silicon content higher than about 1.5 wt %, the partition coefficient of nitrogen remains less than unity at temperatures above the eutectic temperature.

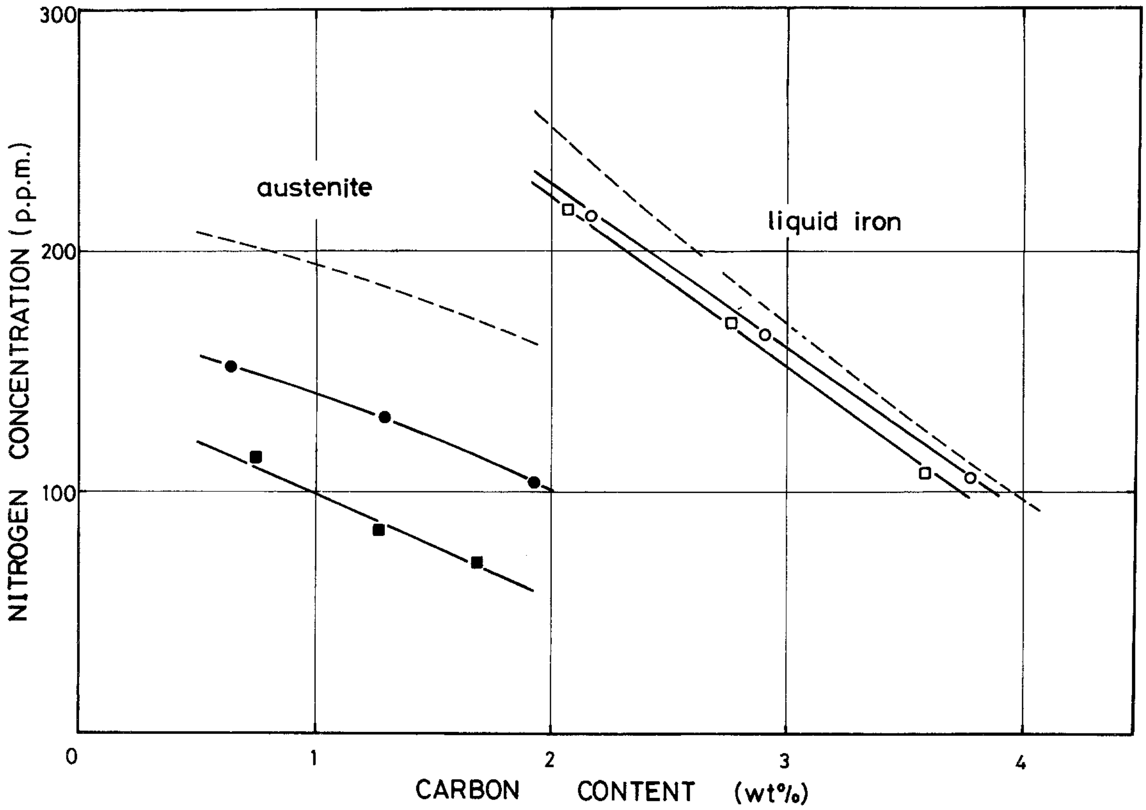

Figure 1 Solubilities of total nitrogen (N_T) in liquid iron and austenite under nitrogen atmospheric pressure of 1 atm. (- - -) Fe–C [4]; (○) Fe–C–0.5 Si; (●, □) Fe–C–1.0 Si; (■) Fe–C–2.0 Si.

3.2. Partition of nitrogen between cementite and austenite

Nitrogen concentrations of heat-treated Fe–C–0.5 Si alloys and the cementites extracted from them are shown in Fig. 3. The values of N_T in the alloys are the same level as those of the as-cast alloy. The values for acid-soluble nitrogen, N_S, and acid-insoluble nitrogen, N_I, in the cementites are higher than those in the alloys. The volume fraction of eutectic and proeutectoid cementities in the alloys were measured by the point-counting method. It is known from the small difference between the density of cementite [11] and that of pearlite estimated from the densities of pure iron and cementite that the weight fraction is identical with the volume fraction. From the results given in Fig. 3, the nitrogen concentration in austenite was evaluated from the lever rule. The values of N_S and N_I in austenite are lower than those in cementite, which means that the coefficient for partition of nitrogen between cementite and austenite, defined by the ratio of nitrogen concentration in cementite to that in austenite, is larger than unity in the Fe–C–0.5 Si alloy

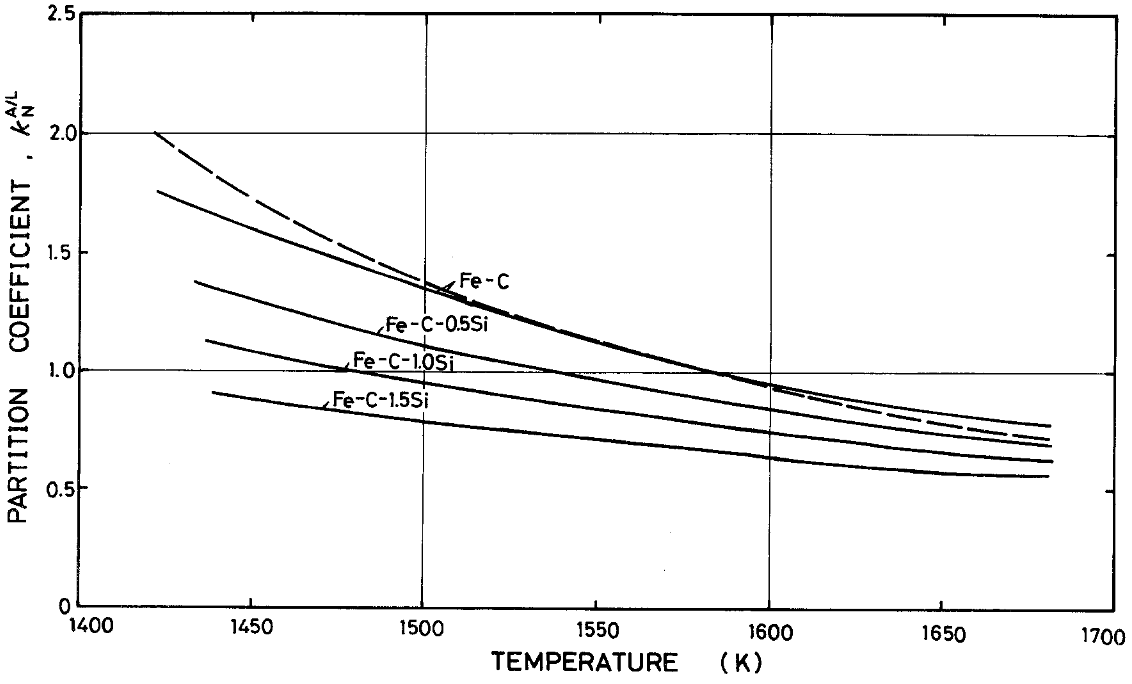

Figure 2 The coefficients for partition of nitrogen between austenite and liquid iron in Fe–C [4] and Fe–C–Si alloys.

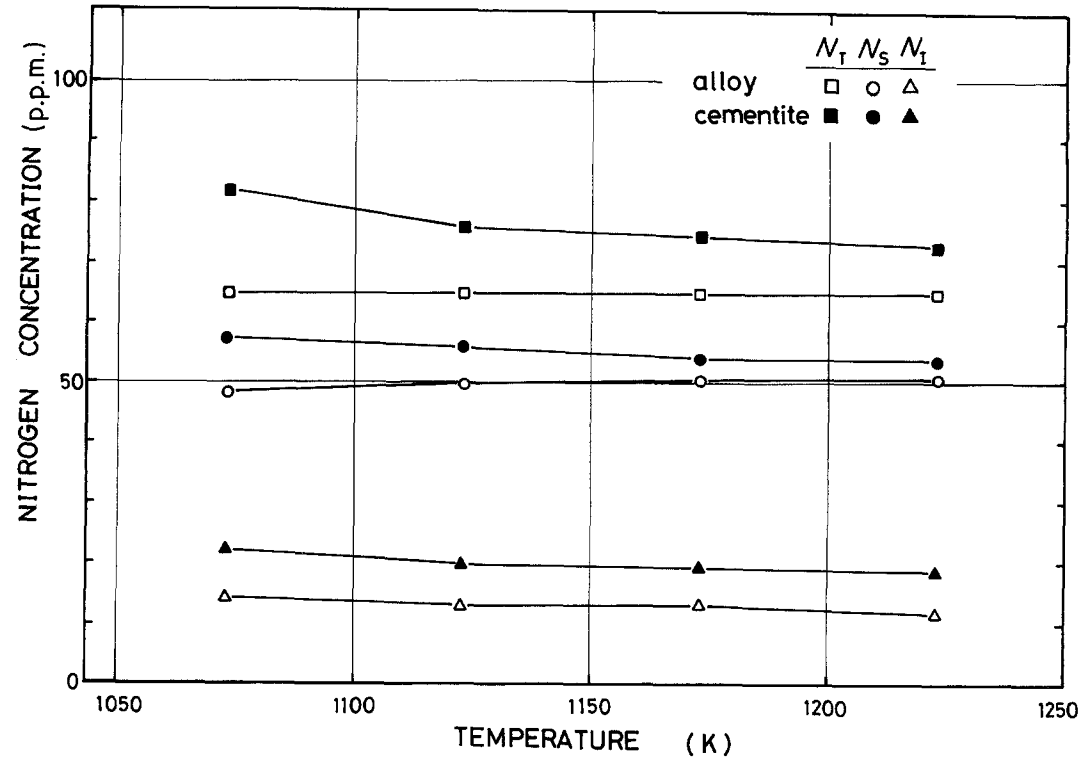

Figure 3 Nitrogen concentrations of heat-treated Fe–C–0.5 Si alloys and the extracted cementite. N_T = total nitrogen, N_S = acid-soluble nitrogen, N_I = acid-insoluble nitrogen.

and hence nitrogen tends to concentrate in cementite, as is the case in the pure Fe–C eutectic alloy [4]. The coefficients for partition of acid-soluble nitrogen and total nitrogen are given as a function of temperature in Fig. 4. The partition coefficient of total nitrogen is larger than that of acid-soluble nitrogen, and both the coefficients decrease exponentially with an increase in temperature. From the thermodynamic data described in the preceding section, it is known that the nitrides Si_3N_4 and AlN can be formed in austenite. In cementite, Si_3N_4 cannot be formed because of the negligible solubility of silicon in cementite [11]. Assuming that the thermodynamic data on AlN for austenite are applicable to cementite, it is indicated that AlN is possibly formed in cementite at temperatures concerned in the present experiment. Therefore, the partition coefficient of acid-soluble nitrogen is adopted in this work.

4. Discussion

It has been demonstrated that the carbon concentration of pure cementite reduces from the stoichiometric composition with rising temperature above the eutectoid temperature, while in an Fe–C–Si alloy the

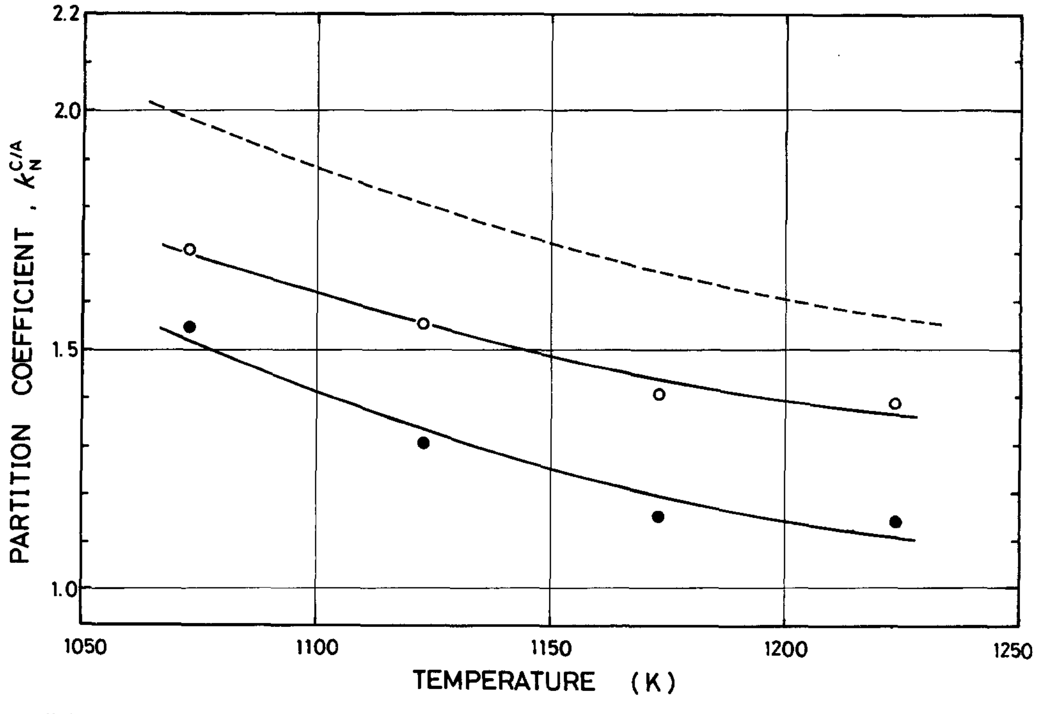

Figure 4 The coefficients for partition of (●) acid-soluble nitrogen N_S and (○) total nitrogen N_T between cementite and austenite. (– – –) Fe–C [4], (——) Fe–C–0.5 Si.

carbon concentration of the cementite increases, approaching the stoichiometric one [11]. When nitrogen atoms in cementite occupy the interstitial sites where carbon atoms should be situated in pure cementite, more nitrogen atoms can be accommodated in the vacant interstitial sites of pure cementite on eutectic solidification. In an alloy containing silicon, the number of vacant interstitial sites in cementite reduces and the accommodation of nitrogen atoms in cementite is limited on eutectic solidification, which results in a reduction in the enrichment of nitrogen in cementite on the partition of nitrogen between cementite and austenite. The effect of silicon on the partition coefficient of nitrogen given in Fig. 4 is very demanding of the above consideration.

Temperature dependences of the coefficients for partition of nitrogen given in Figs 2 and 4 were represented by the following equations:

For Fe–C–0.5 wt % Si alloy

$$k_N^{A/L} = 0.0153 \exp(6420/T) \qquad (1)$$

$$k_N^{C/A} = 0.11 \exp(2810/T) \qquad (2)$$

For Fe–C–1.0 wt % Si alloy

$$k_N^{A/L} = 0.0189 \exp(5870/T) \qquad (3)$$

where $k_N^{A/L}$ and $k_N^{C/A}$ denote the coefficient for partition of nitrogen between austenite and liquid iron and that between cementite and austenite, respectively, and T is the absolute temperature. The solid curves in Figs 2 and 4 represent the regression equations of Equations 1 to 3.

The variations of nitrogen concentration in liquid iron and austenite, N^L and N^A, respectively, during austenite crystallization were calculated from the equations

$$N^L = N_0/[1 - f^A(1 - k_N^{A/L})] \qquad (4)$$

$$N^A = N^L k_N^{A/L} \qquad (5)$$

$$C_{Si}^L = C_0(1 - f^A)^{(k_{Si}^{A/L} - 1)} \qquad (6)$$

$$C_{Si}^A = C_{Si}^L k_{Si}^{A/L} \qquad (7)$$

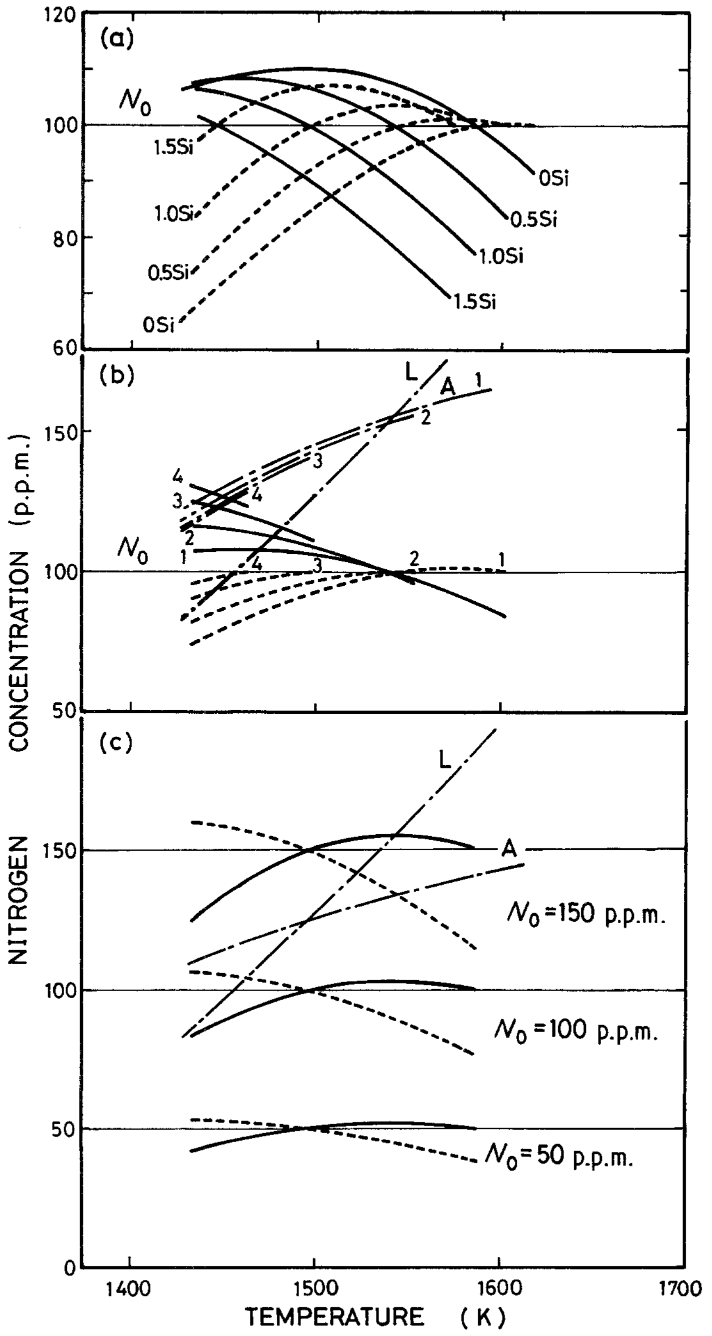

Figure 5 Effects of (a) silicon content, (b) carbon content and (c) initial nitrogen concentration on the variations of nitrogen concentrations in liquid iron and austenite during the solidification of Fe–C–Si alloys. (a) Fe–2.5 wt % C; (– – –) liquid iron, (——) austenite. (b) Fe–C–0.5 wt % Si with (1) 2.5, (2) 3.0, (3) 3.5 and (4) 3.8 wt % C; (–·–) solubility of nitrogen. (c) (– – –) liquid iron, (——) austenite.

where N_0, C_0, and f^A are the initial nitrogen concentration and silicon content of an alloy melt, and austenite weight fraction, respectively, C_{Si}^{v} (v = L or A) is the silicon concentration in liquid iron (L) or austenite (A), and $k_{Si}^{A/L}$ is the coefficient for partition of silicon between austenite and liquid iron.

In the calculation, it was postulated that nitrogen and carbon distributed uniformly in both the phases and that the silicon distribution during primary austenite solidification is represented by the Sheil equation [12]. In Fig. 5, the variations of nitrogen concentration in austenite and liquid iron during solidification of Fe–C–Si alloys are shown as functions of silicon content (Fig. 5a), carbon content (Fig. 5b) and initial nitrogen concentration (Fig. 5c) in the alloy melts. In Fig. 5a, the nitrogen concentrations in liquid iron given by broken curves increase and then decrease in the progress of austenite solidification, while the nitrogen concentrations in austenite of the alloys with higher silicon contents given by solid curves increase monotonously with lowering temperature. These nitrogen concentrations intersect at about 1540 K for a melt with 0.5 wt % Si, at about 1490 K for a melt with 1 wt % Si, and at about 1430 K for a melt with 1.5 wt % Si, where the partition coefficient $k_N^{A/L}$ become unity. The temperature of intersection of the concentration curves is reduced with the silicon content of alloy melts. The influences of carbon content and initial nitrogen concentration on the variations of nitrogen concentration in liquid iron and austenite are illustrated in Fig. 5b for alloy melts with an initial nitrogen concentration of 100 p.p.m. and 0.5 wt % Si, and in Fig. 5c for alloy melts with 2.5 wt % C and 1 wt % Si. The chain curves (–·–) in the figures show the solubilities of nitrogen in liquid iron and austenite equilibrated with nitrogen atmosphere of 1 atm. In the solidification of alloy melts with an initial nitrogen concentration of 100 p.p.m., both the nitrogen concentrations exceed the solubilities of nitrogen in these phases below the critical temperature T^* where the supersaturation of nitrogen given as a ratio of N^L to the solubility N^{L^*} at the same temperature is unity. The maximum supersaturation, $(N^L/N^{L^*})_{max}$, is attained at the eutectic temperature and this value becomes larger with increasing carbon content (Fig. 5b) and increasing initial nitrogen concentration (Fig. 5c). The maximum supersaturation attainable during the solidification of Fe–C–0.5 wt % Si alloy melts is shown as functions of initial nitrogen concentration and carbon content in Fig. 6. It is indicated that, if the initial nitrogen concentration in the melt is below the curve of $(N^L/N^{L^*})_{max} = 1.0$, nitrogen remains unsaturated in the melt. In the figure, the nitrogen solubility curve for liquid iron equilibrated with air of atmospheric pressure is shown as well. When Fe–C–0.5 wt % Si alloy is melted in air, the melt can contain nitrogen up to the solubility for liquid iron equilibrated with air. This is often encountered in Cupola charges prepared from steel scraps [3]. In such a case, the value of $(N^L/N^{L^*})_{max}$ attained during solidification is known from the contour curves of $(N^L/N^{L^*})_{max}$ in the figure. Similar curves of $(N^L/N^{L^*})_{max}$ for Fe–C–Si alloy melts with different silicon contents are summarized in Fig. 7. It is seen from these figures that the possibility of gas bubble formation increases with reducing carbon content of an Fe–C–Si alloy melt, and increasing silicon content of an alloy melt with a lower carbon content. From the critical nitrogen content to form nitrogen blowholes given by Davison *et al.* [1] and Caspers [2], the degree of supersaturation for the formation of nitrogen gas defects amounts to 1.4, which suggests that the critical degree of supersaturation to prevent the formation of nitrogen blowholes may be around 1.4.

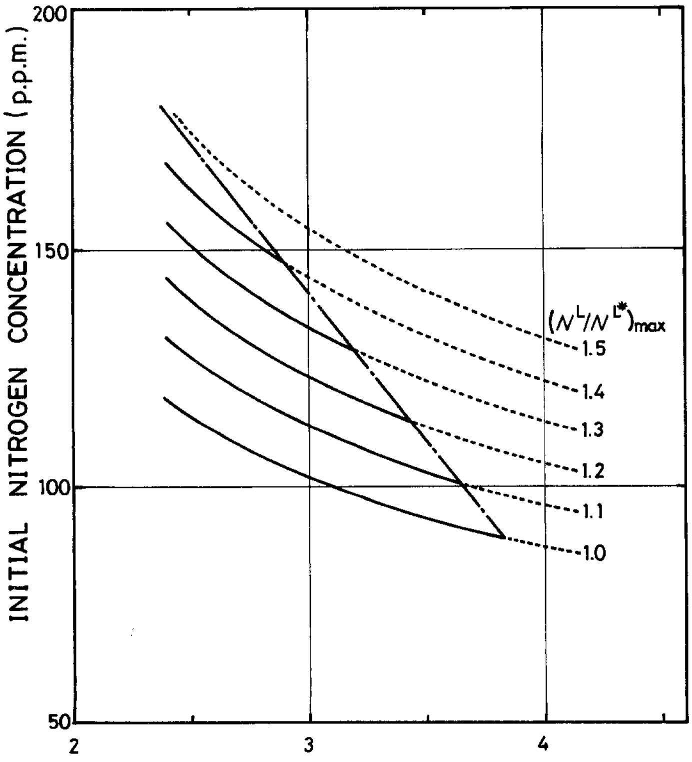

Figure 6 Effects of initial nitrogen concentration and carbon content in Fe–C–0.5 wt % Si alloy melts on the maximum degree of supersaturation of nitrogen, $(N^L/N^{L^*})_{max}$, attained during solidification. (–·–) Nitrogen solubility in liquid iron equilibrated with air.

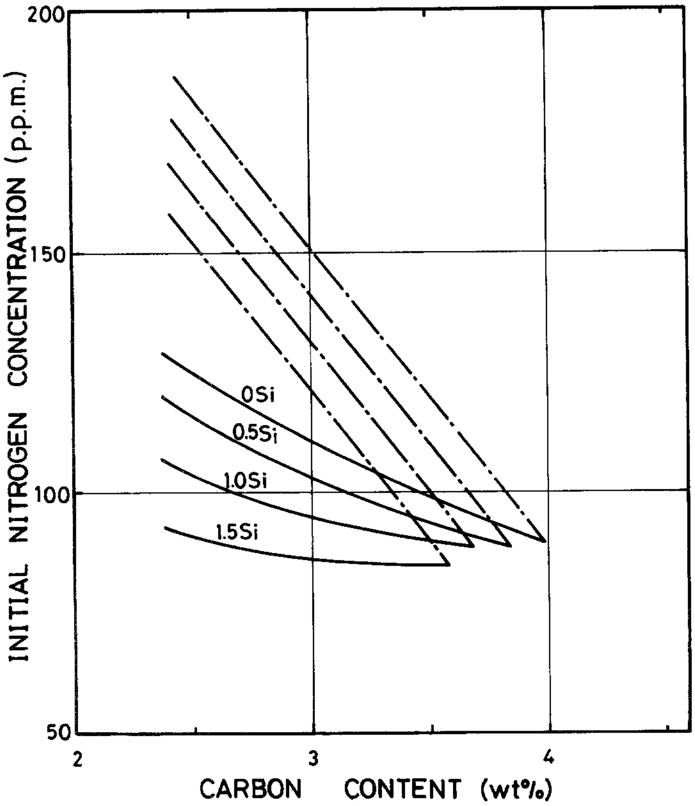

Figure 7 (——) Relation between carbon content of an Fe–C–Si alloy and initial nitrogen concentration in the melt with which the degree of supersaturation of nitrogen $(N^{L}/N^{L*})_{max}$ at the eutectic temperature becomes unity. (–·–) Nitrogen solubility in liquid iron equilibrated with air.

It should, however, be noted that, for the alloys with higher silicon content, the formation of silicon nitride may happen in austenite during solidification, which decreases both the silicon and nitrogen concentrations in liquid iron and reduces the formation of nitrogen gas bubbles.

On eutectic solidification, the possibility of the formation of nitrogen gas bubbles may be discussed in terms of the coefficient for partition of nitrogen between eutectic liquid and its solid. The partition coefficients on stable and metastable eutectic solidifications, K^{S} and K^{M}, respectively, are given by the equations

$$K^{S} = f^{A'} k_{N}^{A/L} \qquad (8)$$

$$K^{M} = [f^{A} + (1 - f^{A}) k_{N}^{C/A}] k_{N}^{A/L} \qquad (9)$$

where $f^{A'}$ and f^{A} are austenite weight fractions in the stable and metastable eutectic solids, respectively.

The values of $k_{N}^{A/L}$ and $k_{N}^{C/A}$ at the eutectic temperature are $k_{N}^{A/L} = 1.35$ at 1432 K and $k_{N}^{C/A} = 0.80$ at 1416 K for Fe–C–0.5 wt % Si alloy, $k_{N}^{A/L} = 1.13$ at 1435 K for Fe–C–1.0 wt % Si alloy, and $k_{N}^{A/L} = 0.89$ at 1435 K for Fe–C–1.5 wt % Si alloy. The partition coefficients on the eutectic solidifications are $K^{S} = 1.32$ and $K^{M} = 1.28$ for Fe–C–0.5 wt % Si alloy, $K^{S} = 1.10$ and $K^{M} = 0.79$ for Fe–C–1.0 wt % Si alloy and $K^{S} = 0.87$ for Fe–C–1.5 wt % Si alloy. On the eutectic solidification of Fe–C–0.5 wt % Si alloy melt, nitrogen is captured in solidifying eutectic solid, while nitrogen is rejected into eutectic liquid on the eutectic solidification of the alloy melts with higher silicon contents. The problem of the formation of nitrogen gas bubbles may arise in the latter case where the partition coefficient of nitrogen on eutectic solidification is less than unity.

5. Conclusion

The effect of silicon on the partition behaviour of nitrogen was investigated on primary austenite crystallization and subsequent eutectic solidification.

As for the partition of nitrogen between austenite and liquid iron, nitrogen is rejected into liquid iron at high temperatures and is conversely enriched in austenite at low temperatures. The critical temperature where the partition behaviour of nitrogen changes is lowered with increasing silicon content of the alloys. The variations of nitrogen concentrations in primary austenite and liquid iron were calculated by use of the coefficient for partition of nitrogen between these phases, and the degree of supersaturation of nitrogen was evaluated as functions of initial nitrogen concentration and the carbon and silicon contents in alloy melts. The results indicated that the possibility of gas bubble formation in liquid iron increased with decreasing carbon content and increasing silicon content and initial nitrogen concentration.

On the partition of nitrogen between cementite and austenite, nitrogen was enriched in cementite for Fe–C–0.5 wt % Si alloy as is the case for the pure Fe–C alloy. Silicon reduced the degree of enrichment of nitrogen in cementite, indicating that the partition behaviour of nitrogen possibly changes in the alloy with higher silicon content. The partition coefficients of nitrogen on stable and metastable eutectic solidification were evaluated from the temperature dependences of the partition coefficients between austenite and liquid iron and between cementite and austenite. It is suggested from these partition coefficients that the problem of nitrogen blowhole formation arises in eutectic alloy melts with higher silicon contents where the partition coefficient of nitrogen on eutectic solidification reduces to less than unity.

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