The Control of the Morphology of MnS Inclusions in Steel during Solidification

Katsunari OIKAWA, Hiroshi OHTANI,¹⁾ Kiyohito ISHIDA¹⁾ and Taiji NISHIZAWA²⁾

Graduate School, Tohoku University, Aramaki, Aoba-ku, Sendai, Miyagi-ken, 980-77 Japan.

1) Department of Materials Science, Faculty of Engineering, Tohoku University, Aramaki, Aoba-ku, Sendai, Miyagi-ken, 980-77 Japan.

2) Formerly Department of Materials Science, Faculty of Engineering, Tohoku University. Now at Sumitomo Metal Industries, Ltd., Research & Development Center, Fuso-cho, Amagasaki, Hyogo-ken, 660 Japan.

(Received on November 15, 1994; accepted in final form on December 16, 1994)

The morphology of MnS inclusions in steel formed during solidification and the modification of this morphology by additions of alloying elements Al, Si, C and Ti have been investigated using optical and electron microscopy techniques.

In sulfur-lean melts the morphology of the secondary MnS inclusion formed after the primary crystallization of the Fe phase during solidification can be classified under the following categories: i) Globular or droplet shaped MnS resulting from a monotectic reaction, ii) Rod like MnS formed through an eutectic reaction and iii) a fish-bone type MnS formed as a result of an irregular eutectic reaction. In sulfur-rich melts the primary crystallization phase is MnS and depending on the nature of additional elements present in the melt and the melt atmosphere, the morphology of these primary MnS inclusions can be classified as iv) spherical, v) dendritic or vi) angular.

The formation mechanism of the different MnS morphologies is discussed on the basis of phase diagram information. It is shown that the spherical morphology of the primary and secondary MnS inclusions is a result of metastable reactions, while the eutectic, dendritic and angular morphologies are the products of stable reactions, with the high melting dispersed particles like TiN and Al_2O_3 acting as nucleants for the MnS crystals. It is also shown that the addition of C and Si increases the probability of stable reactions by increasing the temperature interval between the eutectic and the monotectic points.

KEY WORDS: manganese sulfide; inclusion; morphology; solidification; phase diagram; metastable reaction.

1. Introduction

Because non-metallic inclusions in steels are generally detrimental to their material properties, considerable efforts have been directed towards the development of alloys and processes to reduce their presence in steels to a minimum. However, of late, the utilization of inclusions for the control of microstructures is becoming a subject of considerable interest for improving the mechanical properties of steels.¹⁾

The beneficial effects of manganese sulfide inclusions in improving machinability and retarding grain growth in steels are well known. Since the morphology of these sulfide inclusions has a significant effect on the various properties of steels, numerous studies focusing on establishing the relation between solidification conditions and the morphology of the MnS inclusions have been conducted over the years.^{2–8)} According to the classical work by Sims and Dahle,²⁾ the morphology of MnS can be broadly classified into three types: *i.e.*, (1) randomly dispersed globular sulfides (Type I), (2) rod-like fine sulfides (Type II), and (3) angular sulfides (Type III). In addition to these types, dendritic sulfides have also been detected and the effect of alloying elements, such as Al,

C, and Si on the morphology of MnS has also been reported.^{2–8)} However the mechanism of the evolution of the different morphologies and their modification by various additions is still uncertain.

In view of these facts, the present study has been undertaken with a view to identifying and elucidating the role of the principal factors that control the morphological evolution of MnS in cast steels, using both experimental techniques and theoretical thermodynamic analysis.

2. Experimental Procedure

Firstly, 40 mm diameter and 30 mm long cylindrical alloy castings weighing 300 g were prepared by taking electrolytic iron, electrolytic manganese and iron sulfide, each of 99.9% purity, and high purity ferroalloys of Si, Al, Ti or C as and when required, and melting them in magnesia crucibles in an induction furnace, under an Ar atmosphere. Only in case of alloys where the role of TiN was to be studied, the melting atmosphere in the induction furnace was chosen to be N_2 . After melting, the alloys were kept at around 1600°C in the molten state for several minutes, and then allowed to solidify in

the crucibles themselves. The measured cooling rate in the solidification range was about 30°C/min.

Two series of alloys were prepared: (1) A sulfur-lean, Fe-1mass%Mn-0.3mass%S series in which MnS was formed as the secondary phase during solidification, and (2) a sulfur-rich, Fe-2.5mass%Mn-(1.0-1.7)mass%S series in which MnS was formed as the primary phase during solidification. Typical examples of oxygen and nitrogen contents in selected alloy specimens are shown in Table 1.

Microstructural examination of the specimens was carried out using an optical microscope (OM) and a scanning electron microscope (SEM). Specimens for microstructural examination were taken from a region 10 mm away from the bottom of the ingots. The sections to be examined by SEM were mechanically polished and then etched electrolytically in 1% tetramethylammonium chloride-10%acetylacetone-methanol.

3. Experimental Results

3.1. Morphology of the Secondary MnS Phase

The morphology of the secondary MnS phase that evolves during the solidification of the alloys of the Fe-1Mn-0.3S series is classified under three types as follows.

3.1.1. Monotectic MnS

Typical micrographs of this type of MnS are shown in Fig. 1. These sulfide phases have a droplet shape of

Table 1. Content of oxygen and nitrogen in typical specimens. (mass%)

Mn	S	X	O	N	Atmosphere
(2.5)	(1.3)	—	0.0135	0.0005	Ar
(1.0)	(0.3)	Si(1.0)	0.0048	0.0004	Ar
(1.0)	(0.3)	Al(0.1)	0.0017	0.0011	Ar
(1.0)	(0.3)	Al(0.2)	0.0004	0.0008	Ar
(2.5)	(1.0)	Ti(0.1)	0.0014	0.0396	N ₂

() charged value

about 10 μm in diameter, which seems to correspond to the Type I globular morphology in Sims' classification.²⁾ As will be discussed in a later section, since these sulfide phases are expected to be formed through the metastable monotectic reaction ($L_1 \rightarrow Fe(s) + L_2$), they shall be termed the monotectic MnS hereafter.

3.1.2. Eutectic MnS

Typical micrographs of MnS of the eutectic morphology which seem to correspond to the Type II morphology in Sims' classification,²⁾ are shown in Fig. 2. This type is characterized by an assembly of fine rod-like sulfides and has been variously considered to be the result of either the eutectic reaction ($L_1 \rightarrow Fe(s) + MnS$)³⁾ or the monotectic reaction ($L_1 \rightarrow Fe(s) + L_2$).⁵⁻⁷⁾ Fredriksson and Hillert^{5,6)} were of the opinion that these sulfides formed through the cooperative monotectic reaction, citing as evidence the fact that most of the tips of rod-like MnS are rounded as seen in Fig. 2(b). However, there exists a possibility that the rounded tips can also be the result of a possible local rise in temperature due to

Fig. 2. Rod-like eutectic MnS in Fe-1%Mn-0.3%S-0.1%Ti, melted under N₂. (a) optical micrograph and (b) scanning electron micrograph

Fig. 1. Monotectic MnS.

(a) optical micrograph (Fe-1%Mn-0.3%S-0.1%Ti)
(b) scanning electron micrograph (Fe-1%Mn-0.3%S)

Fig. 3. Irregular eutectic MnS.

(a) optical micrograph (Fe-1%Mn-0.3%S-1%C)
(b) scanning electron micrograph (Fe-1%Mn-0.3%S-5%Si)

Fig. 4. Morphology of MnS in hypo-eutectic (or -monotectic) specimens containing C, Si, Al and Ti.

Fig. 5. Primary spherical MnS in Fe-2.5%Mn-1.3%S-0.3%C.
(a) optical micrograph and (b) scanning electron micrograph

Fig. 6. Primary dendritic MnS.
(a) optical micrograph (Fe-4%Mn-2%S-0.5%Al-0.3%C)
(b) scanning electron micrograph (Fe-2.5%Mn-1.3%S-0.5%Al)

recalescence in the last stages of the eutectic reaction. Since it is felt that there exists a sound thermodynamic basis for this assertion, as will be explained later, the fine rod-like sulfides are classified as the eutectic MnS.

3.1.3. Irregular Eutectic MnS

The micrographs showing the irregular eutectic morphology of MnS are shown in Fig. 3. These sulfides exhibit a complex structure composed of a branch-like part growing along characteristic directions and a plate-like part connecting the branches. Fredriksson and Hillert have termed these as fish-bone sulfides.⁵⁾ Since this type of sulfide is considered to be formed through the non-cooperative eutectic reaction, they are called the irregular eutectic MnS in the present paper.

The sulfides forming in the ternary alloy, Fe-1Mn-0.3S, are of the monotectic MnS type as shown in Fig. 1(b), whereas the sulfides forming in the specimens containing additional alloying elements are converted into the eutectic or irregular eutectic types depending on the content of alloying elements, as summarized in Fig. 4. The sulfides forming in the specimens containing the additional alloying element C or Si change from the monotectic to the irregular eutectic MnS through the eutectic one, as the alloying content is increased,

Fig. 7. Primary angular MnS.
(a) optical micrograph (Fe-2.5%Mn-1.3%S-1%Al)
(b) scanning electron micrograph (Fe-2.5%Mn-1.3%S-0.5%Al-0.1Ti, melted under N₂)

whereas the addition of Al or Ti (under N₂) causes a morphological change from the monotectic to the eutectic. The specimens alloyed with Ti (under Ar) exhibit

Fig. 8.

Morphology of primary MnS in hyper-eutectic (or -monotectic) specimens containing C, Si, Al and Ti.

only the monotectic MnS, though the eutectic TiS coexists with MnS in the specimens containing more than 0.3 % Ti.

3.2. Morphology of the Primary MnS Phase

In the alloy specimens of the sulfur-rich Fe-2.5Mn-(1.5-1.7)S series, the sulfides are formed as the primary phase occurring in three morphological types as follows.

3.2.1. Spherical MnS

Typical micrographs of the spherical MnS are shown in Fig. 5. Since this type of sulfides has a spherical shape with a diameter of 30-50 μm , it is obvious that both the matrix Fe phase and the dispersed MnS phase are in the molten state at the instant of separation, and the spherical MnS is formed through the two-phase separation of liquid.

3.2.2. Dendritic MnS

The micrographs of the dendritic MnS are shown in Fig. 6. This type of sulfides seems to be formed by primary crystallization in a highly supersaturated liquid.

3.2.3. Angular MnS

This type of MnS shows an octahedral or tetra-kaidecahedral shape as shown in Fig. 7. This seems to correspond to the Type III morphology in Sims' classification,²⁾ formed by primary crystallization under a small degree of supersaturation.

The spherical MnS is the only primary sulfide observed in the ternary alloy (Fe-2.5Mn-1.3S). The others are observed in the specimens containing alloying elements as summarized in Fig. 8. Progressive additions of Si, Al and Ti (under N₂), alter the morphology of the primary MnS from the spherical to angular type through the dendritic type. Additions of carbon also result in a change from the spherical to the dendritic types, but no angular type MnS is formed. There is no morphological change with the addition of Ti (under Ar).

4. Discussion

4.1. Stable and Metastable Fe-Mn-S Systems

According to the equilibrium phase diagram of the Fe-Mn-S system,¹⁰⁻¹²⁾ any Fe-rich melt (L_1), on cooling from the liquid state, would be expected to follow a solidification path that would result in the solidification of the primary Fe phase first, followed by a eutectic solidification according to the eutectic reaction ($L_1 \rightarrow$

Fig. 9. Schematic diagrams for the Fe-MnS pseudo-binary in stable and metastable systems.

(a) phase diagram and (b) free energy diagram at T_1

Fe(s) + MnS(s)). This would preclude the formation of any globular or droplet type MnS because the droplet type MnS would result only when the solidification path involves the monotectic reaction ($L_1 \rightarrow \text{Fe(s)} + L_2$). However the globular or the droplet type MnS has always been observed in Fe-Mn-S ternary alloys cooled from the liquid state in a normal way. Some previous studies²⁻⁸⁾ have been tried to explain the formation of this type of sulfide as arising from the lowering of the melting temperature of MnS to below the eutectic temperature because of oxygen contamination. This explanation is not valid because, according to the MnS-MnO phase diagram,⁹⁾ such a possibility would arise only when the oxygen content of the L_2 liquid exceeds 25%. Furthermore the monotectic MnS has been observed even in the presence of strong deoxidisers like Ti, C and Si as shown in Fig. 4.

In order to explain the occurrence of the globular type

MnS in Fe–Mn–S alloys the existence of a metastable phase diagram is invoked here. The schematic outline of the stable and metastable phase equilibria in the Fe–MnS pseudo-binary system is drawn in Fig. 9, where the solid and broken lines represent the stable and metastable equilibria respectively. The actual calculated stable and metastable phase equilibria in the Fe-rich portion are also shown in Fig. 10. The calculated difference between the eutectic point (*e*) and the monotectic point (*m*) is so small (only 3°C) that a metastable monotectic reaction leading to the formation of the globular MnS becomes a distinct possibility.

The method by which the metastable diagram in Fig. 10 is obtained, is described below. The solubility product of MnS(s) in liquid Fe is estimated from the experimental data¹¹⁾ as follows.

$$\log [\% \text{Mn}] \cdot [\% \text{S}] = -\frac{9200}{T} + 5.3 \quad \text{.....(1)}$$

The solubility curve for MnS(s) (*z*; line a, b in Fig. 10) in the Fe–MnS pseudo-binary system can be derived from Eq. (1) as the next equation.

$$z \approx \exp \left[\frac{-88080 + 25.0T}{RT} \right] \quad \text{.....(2)}$$

The Gibbs energy difference between MnS(s) and MnS(L₂) has been given by Hillert and Staffansson¹²⁾ as follows.

$$\Delta G_{\text{MnS}}^{s \rightarrow L_2} = 13054 - 6.625T \quad \text{J/g} \cdot \text{atom} \quad \text{.....(3)}$$

Since the numerator value in the square bracket of Eq. (2) corresponds to the Gibbs energy of formation of MnS(s), the solubility curve for MnS(L₂) (*z'*; line c, d in Fig. 10) is derived from Eqs. (2) and (3) as follows.

$$z' \approx \exp \left[\frac{-75030 + 18.4T}{RT} \right] \quad \text{.....(4)}$$

The liquidus line in Fig. 10 (line f, g) is estimated from

Fig. 10. Phase equilibria in the Fe-rich region of Fe–MnS pseudo-binary system, estimated from the data on solubility of MnS in molten iron.

the Fe–S binary system.¹³⁾

4.2. Driving Force for the Nucleation of MnS

ΔG^m and ΔG^e shown by thin arrows in Fig. 9(b) denote the steady state driving forces for the metastable monotectic and stable eutectic reactions respectively. In order to determine which of these reactions would be preferred during solidification, it would be necessary to examine the free energy differences $\Delta G^{L_1 \rightarrow L_2}$ and $\Delta G^{L_1 \rightarrow \text{MnS}}$ denoted by the thick lines in Fig. 9(b), which would induce the nucleation of L₂ or MnS(s) from L₁.

Assuming that a spherical nucleus is formed in the supercooled L₁ phase at *T*₁, the Gibbs energy change due to the formation of the nucleus can be expressed by the next equation.

$$\Delta g = \frac{4}{3} \pi r^3 \frac{\Delta G}{V} + 4 \pi r^2 \sigma \quad \text{.....(5)}$$

where, ΔG is $\Delta G^{L_1 \rightarrow L_2}$ or $\Delta G^{L_1 \rightarrow \text{MnS}}$, *V* is the molar volume and σ is the interfacial energy between L₁ and MnS(L₂) or L₁ and MnS(s).

The maximum Gibbs energy change Δg_{max} and the critical radius *r_c* are given by

$$r_c = -\frac{2\sigma V}{\Delta G} \quad \text{.....(6)}$$

$$\Delta g_{\text{max}} = \frac{16}{3} \pi V^2 \frac{\sigma^3}{\Delta G^2} = \frac{4}{3} \pi r_c^2 \sigma \quad \text{.....(7)}$$

The driving force for the nucleation from a super-saturated liquid is generally approximated by $\Delta G \approx -RT(\Delta z/z)$, where *z* is the equilibrium solubility of MnS phase and Δz the degree of supersaturation. Δz itself is related to the undercooling ΔT by the expression $\Delta z/z \approx (Q/RT) \cdot \Delta T/T$ where $z = A \exp(-Q/RT)$. From these expressions it follows then that the driving force for nucleation at an undercooling level ΔT can be approximated by the next equation.

$$\Delta G \approx -Q \cdot \frac{\Delta T}{T} \quad \text{.....(8)}$$

From Eqs. (2) and (4) it is seen that the calculated values of *Q* for MnS(s) and MnS(L₂) are not likely to be very different. For example, *Q* is equal to 43.8 kJ/mol for MnS(s) and 42.4 kJ/mol for MnS(L₂) at 1500°C. From Eq. (8) it is obvious that when the degree of supercooling is the same, the difference between $\Delta G^{L_1 \rightarrow L_2}$ and $\Delta G^{L_1 \rightarrow \text{MnS}}$ is going to be quite small. This fact suggests that the interfacial energy σ in Eqs. (6) and (7) could play an important role in controlling the critical radius *r_c* and thereby the energy barrier Δg_{max} for the nucleation.

4.3. Interfacial Energy between Liquid Iron and MnS

The values of the interfacial energies between liquid iron and liquid MnS(L₂) or liquid and solid MnS(s) have not been determined experimentally. One can however, estimate the interfacial energy between Fe(L₁) and MnS(L₂) to be in the region of 0.2 N/m by extrapolation of the data¹⁴⁾ on the interfacial energy of Fe(L₁) and slag (MnO–SiO₂–CaO–MnS system) as shown in Fig.

Fig. 11. Estimation of interfacial energy between Fe(L₁) and MnS(L₂) from the data on interface between Fe(L₁) and slag (MnO–SiO₂–CaO–MnS).¹⁴⁾

Table 2. Estimation of interfacial energy between liquid Fe and MnS from the data on various interfaces.

Interface	Energy/N·m ⁻¹	Reference
liq. Fe/liq. MnS	0.2 (estimated)	14)
liq. Fe/liq MnO–SiO ₂ –CaO	0.7	14)
liq. Cu/liq. Cu ₂ S	0.1	16)
liq. Fe/sol. MnS	0.6 (estimated)	
liq. Fe/sol. Al ₂ O ₃	1.8	18)
liq. Cu ₂ S/sol. Fe	0.47	16)
liq. FeS/sol. Fe	0.4	17)
liq. Fe/sol. Fe	0.2	15)
sol. Fe/sol. MnS	1.0	17)
sol. Fe/sol. Fe (random grain boundary)	0.85	16)

11. This value seems reasonable when one compares it with the value of interfacial energy of 0.1 N/m reported for the Cu(L)/Cu₂S(L)¹⁶⁾ interface. As for the value of interfacial energy between Fe(L₁) and MnS(s) it is estimated to be 0.6 N/m by referring to the interfacial energies between Fe(s) and MnS(s), FeS(L) and Cu₂S(L) listed in Table 2.

It is immediately obvious from the above estimates of interfacial energies that MnS(s) nucleation would require three times large extent of the undercooling for a given critical radius (from Eq. (6)), and the energy barrier for its nucleation would also be three times larger (from Eq. (7)) when compared to the undercooling and energy barriers required for MnS(L₂) nucleation for the same critical radius. It is therefore concluded that, during the solidification of the Fe–Mn–S ternary melt, the nucleation of MnS(L₂) is energetically more favored than the nucleation of MnS(s), and the metastable monotectic reaction would predominate over the stable eutectic reaction.

4.4. Effect of Additional Elements

4.4.1. Effect on Nucleation of MnS

It has been mentioned in the preceding sections

Fig. 12. Rod-like eutectic MnS developed from (a) cubic TiN in Fe–1%Mn–0.3%S–0.1%Ti and (b) primary angular MnS in Fe–2.5%Mn–1.3%S–0.5%Al–0.1%Ti melted under N₂.

elsewhere, that while the angular, dendritic and rod-like MnS were observed in the specimens containing Al(melted under Ar) and Ti(melted under N₂), only monotectic MnS was observed in the alloys containing Ti melted under Ar. The difference in the morphologies observed in the two cases of melting atmosphere are explained as follows: In the case of alloys containing Ti(melted under N₂) and alloys containing Al(melted under Ar), TiN and Al₂O₃ crystallinities respectively, act as nucleation catalysts for MnS(s), promoting primary crystallization of the MnS(s) phase and the eutectic reaction of the stable system. Figure 12 shows the eutectic MnS developed from (a) a cubic TiN crystal and (b) an angular MnS which had also probably nucleated from TiN. The solid particles such as TiN and Al₂O₃ are more effective nucleants for MnS(s) than liquid particles because such solid particles with smaller solubilities and higher melting points are likely to be more favorable heterogeneous nucleating agents for MnS(s) phase. On comparing the melting points of oxides, nitrides and sulfides related to this study, it is seen that the compound with the highest melting point is TiN and the one next to it is Al₂O₃. It is therefore clear that in alloys melted under N₂ atmosphere TiN has acted as the nucleant for the MnS(s) phase forcing the solidification path to follow the stable reaction. In the case of alloys melted under an Ar atmosphere only oxides TiO₂ and SiO₂ are formed and they combine with MnO, forming compounds of lower melting temperature, although their

Fig. 13. Changes in phase equilibria in the Fe-MnS pseudo-binary system by alloying C or Si.

own melting temperatures are about 100°C higher than Fe.^{19,20)} As a result, in the alloys containing Ti melted under Ar, liquid oxide droplets are formed first, acting as nucleants for MnS(L₂), thereby favoring the metastable monotectic reaction leading to the monotectic morphology of MnS in these alloys.

4.4.2. Effect of C and Si

Figures 4 and 8 show the eutectic, dendritic, angular and irregular eutectic MnS observed in the specimens containing C or Si. The reason for these morphologies has sometimes been ascribed to the deoxidization of melt by these elements.³⁻⁸⁾ However, it has been pointed out earlier that the MnS morphology is not so sensitive to the oxygen content, so the reason must lie elsewhere. An explanation is given here based on the fact that C and Si lower the melting point of iron and raise the activity of sulfur. This would result in the expansion of the 2-liquid region and increase in the slope of the liquidus line for iron, leading to an increase in the temperature difference between the metastable monotectic and stable eutectic points as shown in Fig. 13. From a thermodynamic analysis, this difference in temperature is estimated to be about 10°C in the Fe-1%Mn-0.3%S-1%C alloy. This could explain why the stable eutectic reaction develops more easily in preference to the metastable monotectic reaction. When large amounts of C and Si are added, the eutectic point is moved closer to the iron side of the phase diagram. In such a case, it is known that a divorced eutectic reaction can often occur. This may be the reason for the formation of irregular eutectic MnS at higher concentrations of C and Si in these systems.

5. Conclusions

The morphology of MnS found in cast Fe-Mn-S steels

is classified and their occurrence explained on the basis of stable and metastable phase diagrams.

(1) The morphology of MnS formed by primary crystallization in sulfur-rich alloys is classified under a first set of three types as; (i) spherical, (ii) dendritic, and (iii) angular, while the morphology of the secondary MnS formed in sulfur-lean alloys is classified under a different set of three types as; (i) monotectic, (ii) eutectic, (iii) irregular eutectic.

(2) The monotectic and spherical types of MnS are formed through metastable reactions, while the other types of MnS are formed by stable reactions.

(3) Solid particles like TiN and Al₂O₃ promote the stable eutectic reaction, dendritic and the angular morphology by acting as nucleants for the MnS crystalline phase. Molten oxide droplets such as the oxide of Ti-Mn-O system act as nucleants for the separation of liquid MnS and promote the metastable reaction leading to monotectic MnS morphology.

(4) C and Si raise the activity of sulfur in iron and lower the melting point of iron, enlarging the temperature difference between the eutectic and monotectic points, and thereby promoting the stable eutectic reaction.

Acknowledgment

The authors would like to thank Mr. Yoshio Kawashita for his help in carrying out this study.

REFERENCES

- 1) J. Takamura and S. Mizoguti: Proc. of 6th Int. Iron and Steel Cong., Vol. I, ISIJ, Tokyo (1990), 591.
- 2) C. E. Sims and F. B. Dahle: *Trans. Am. Foundrymen's Ass.*, **46** (1938), 65.
- 3) W. Dahl, H. Hengstenberg and G. Düren: *Stahl Eisen*, **86** (1966), 782.
- 4) P. P. Mohla and J. Beech: *J. Iron Steel Inst.*, **207** (1969), 177.
- 5) H. Fredriksson and M. Hillert: *J. Iron Steel Inst.*, **209** (1971), 109.
- 6) H. Fredriksson and M. Hillert: *Scand. J. Metall.*, **2** (1973), 125.
- 7) T. J. Baker and J. A. Charles: *J. Iron Steel Inst.*, **210** (1972), 702.
- 8) L. K. Bigelow and M. G. Flemings: *Metall. Trans.*, **6B** (1975), 275.
- 9) J. H. Andrew, W. R. Maddocks and E. A. Fowler: *J. Iron Steel Inst.*, **124** (1931), 295.
- 10) R. Vogel and W. Hotop: *Arch. Eisenhüttenwes.*, **11** (1937), 41.
- 11) N. Sano, M. Iwata, H. Hosoda and Y. Matsushita: *Tetsu-to-Hagane*, **57** (1971), 1984.
- 12) M. Hillert and L-I Staffansson: *Metall. Trans.*, **7B** (1976), 203.
- 13) H. Ohtani and T. Nishizawa: *Trans Iron Steel Inst. Jpn.*, **26** (1986), 655.
- 14) Sh. M. Mikrashvili and A. M. Samarin: "Fiziko-Khimicheskie Osnovy Proizvodstva Stali", Nauk., (1964), 42.
- 15) D. Turnbull: *J. Chem. Phys.*, **18** (1950), 769.
- 16) L. H. Van Vlack: *Trans. AIME*, **191** (1951), 251.
- 17) L. H. Van Vlack, O. K. Riegger, R. J. Warrick and J. M. Dahl: *Trans. Metall. Soc. AIME*, **221** (1961), 220.
- 18) K. Ogino, A. Adachi and K. Nogi: *Tetsu-to-Hagane*, **59** (1973), 1237.
- 19) J. White, D. D. Howatt and R. Hay: *J. Roy. Tech. Coll. (Glasgow)*, **3** (1933-36), 239.
- 20) J. Greive and J. White: *J. Roy. Tech. Coll. (Glasgow)*, **4** (1940), 661.

(Originally published in *Tetsu-to-Hagane*, **80** (1994), 623, in Japanese)