CHAPTER VI

DISCUSSION

6.1 INTRODUCTION

In this Chapter the results of the accretion investigation in Chapter 5 are discussed. Phase equilibrium diagrams are used to identify the accretion phases using the thermal history such as liquid temperature, and the temperature range between solidus and liquidus. The effect of oxygen partial pressure is of interest because the amount of oxygen influences the oxidation of the elements in the dust samples which are used to create the laboratory accretions. The structure of the Kalgoorlie accretions and laboratory accretions are correlated with formation conditions and thermal properties in this Chapter.

6.2 THE ACCRETION COMPOSITION FROM KALGOORLIE NICKEL FLASH SMELTING FURNACE.

The SEM examination indicated that, in most burner port accretions, the dominant phase (dark phase) contained a high content of oxides of silica and iron. The dark phase has a composition near

A in Figure 6.1, which should be fayalite and silica (SiO_2). In the FeO-SiO_2-MgO system (Osborn and Muan, 1960), a small amount of magnesium can enter into fayalite ($2FeO.SiO_2$) which has a silica content over about 30 percent, forming an olivine, $2(Mg,Fe)O.SiO_2$. Thus, the dark phase in burner port samples which have 4 percent magnesium should be an olivine.

Segnit (1976) suggested that the olivine which has a high nickel content and contained a little magnesium could be represented as a $(Ni,Fe)_2SiO_4$ solid solution. Figure 6.2 shows the effect of addition of nickel on the FeO-Fe_2O_3-SiO_2 system. The area a-b-c-d is the fayalite region in the FeO-Fe_2O_3-SiO_2 phase diagram. The boundary will become extended into the quaternary tetrahedron when the nickel content in the system is increased. The addition of nickel causes the line c-d to become shorter up to point g, which is an invariant point of four phases; of Fe-Ni alloy, wustite, and spinel phases. It is not clear how temperature and oxygen pressure affect the amount of nickel which can enter into olivine forming a solid solution of $(Ni,Fe)_2SiO_4$.

The fine dendritic structure in Figure 5.6 could be a ternary eutectic (composition: 22 wt pct SiO_2, 14.2 wt pct Fe_2O_3, 63.8 wt pct FeO, T = 1150°C, Osborn and Muan, 1965). The chemical composition of fine dendrites in Table 5.3 are 40.6 wt pct Si and 38.4

wt pct Fe which is different from the ternary eutectic composition. The reason for this is that the size of the fine dendritic structure is smaller than the spot size of the SEM used for measuring the composition in the structure. Thus, the composition of the fine dendrites in Table 5.3 is actually the combined composition of the fine dendritic structure and the background phase (dark phases in Figure 5.6).

Goel *et al.* (1980) have studied the Fe-O-Si system. The most noticeable difference between the diagrams developed by Goel *et al.* and Osborn and Muan (1965) is that according to Osborn and Muan, there is a ternary eutectic but the diagram of Goel *et al.* shows a ternary peritectic (composition: 25 wt pct SiO_2, 11.5 wt pct Fe_2O_3, 63.5 wt pct FeO, T = 1163° C). The reason is Muan and Osborn located the invariant point between wustite, fayalite, magnetite, and melt just within the subtriangle $FeO-Fe_2SiO_4-Fe_2O_3$, which makes it a ternary eutectic, but Goel *et al.* place the point just outside of $FeO-Fe_2SiO_4-Fe_3O_4$ subtriangle.
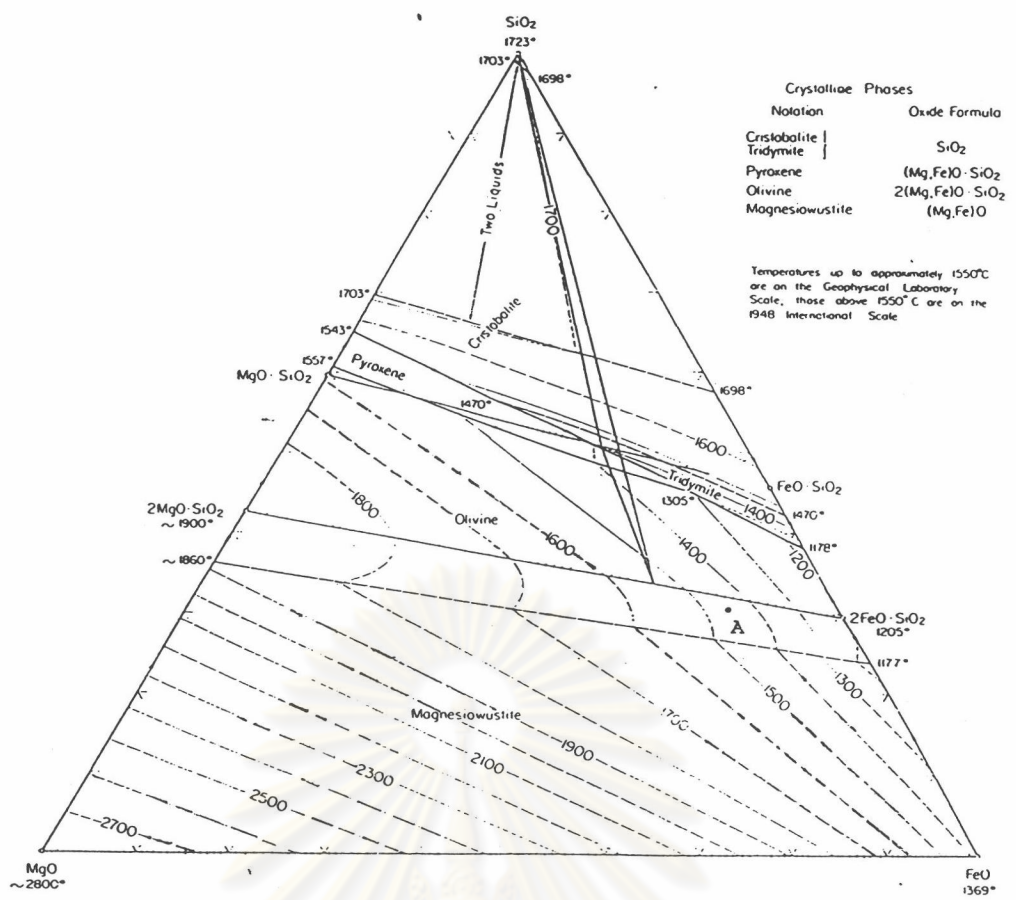
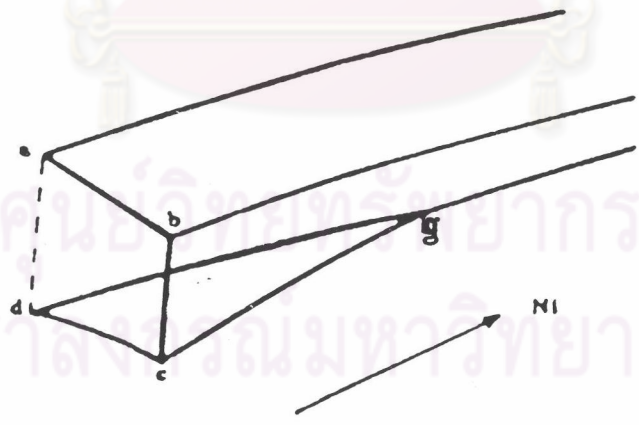**Figure 6.1   System FeO-MgO-SiO$_2$ (Osborn and Muan, 1960).**

Figure 6.2   The effect of nickel addition to the

FeO-Fe$_2$O$_3$-SiO$_2$ system.

The minor phases (light phases) of burner port accretion contained high-iron and nickel. According to Pelton *et al.* (1979), the phase formed with this composition and oxygen pressure between 10^{-9} to 10^{-3} atmosphere will be a spinel solid solution of Fe-Ni-O.

Referring to the composition of the dark band of the lamellar structure in Table 5.2, the dark band has composition near 'B' in Figure 6.3 which should be a wollastonite and a silica rich pseudowollastonite. In the system $FeO-Al_2O_3-SiO_2$ (Figure 6.4), the composition of the light band of lamellar structure lies close to the boundary between cristobalite and mullite, point C. According to the $FeO-Al_2O_3-SiO_2$ system, aluminium can enter into solid solution with SiO_2 forming mullite. Therefore, the light band of the lamellar structure should be a mullite with some iron and calcium solid in solution.

In the presence of silica content above about 60 wt pct. in the $CaO-SiO_2-Al_2O_3$ system, Figure 6.5, Pseudowollastonite, and anorthite ($CaO.Al_2O_3.SiO_2$) can exist in equilibrium together and give a ternary eutectic structure at 1170 C. The mechanism of formation of the lamellar structure will be discussed in section 6.4.

Most inclusions occurred as small spherical particles of nickel sulphide both in olivine and mixed spinel solid solution. Small sulphide particles had a high nickel content and contained a little silica. Some sulphide particles contained high contents of both iron and nickel. Large sulphide grains also occurred as isolated spheres, occasionally having nickel metal and copper sulphide. Sulphide particles could be expected to be non-oxidized or partially oxidized concentrate particles which enter into the accretions before it is solid. On slow cooling, sulphides were removed from olivine and spinel of Fe-Ni-O system forming large sulphide grains. Further slow cooling to room temperature causes the copper content in nickel sulphide to segregate and form Cu_2S. This is because Cu_2S and Ni_3S_2 are almost completely immiscible at room temperature while they are miscible in the all proportions in the liquid state (Figure 6.6). Figure 5.13 shows Cu_2S formed adjacent to nickel sulphide phase.

6.3 COMPOSITION OF DUST FROM KALGOORLIE FLASH FURNACE

Referring to the composition of flash furnace dust in Table 5.5, the light phase (number 1) has composition near 'A' in Figure 6.1 which should be a magnesioferrite, $(Mg,Fe)Fe_2O_4$. The dark phase (number 2) is a high magnesium olivine. The phases corresponding to

number 3 and 4 in Table 5.5 are nickel oxide and particles of nickel metal. The main difference between the flash furnace accretions and dust is the lower olivine content in the flash furnace dust. The lower olivine content of flash furnace dust is probably because the silica flux does not have sufficient time to react with the oxidized particles of concentrate in the reaction shaft. Most of the reaction between oxidized concentrate and silica flux particles occurred near the slag layer in the hearth before they collected in the settler. However, some small oxidized particles or dust which have reacted with silica flux were carried over by the gas, which flows over the slag surface with high velocities, and then passed to the uptake shaft (Figure 6.7).

Optical microscope examination indicated that magnesioferrite can occur in many forms depending on the magnesium content in this phase. Magnesioferrite (light phase), which occurred as solid particles (Figure 5.14), contained higher magnesium levels than the magnesioferrite which occurred as dendrite growths (Figure 5.11) and dendrite intergrowths (Figure 5.12). The effect of the addition of magnesium to fayalite can be seen by considering the system Fe_2SiO_4-Mg_2SiO_4 (Figure 6.8). The liquidus temperature of fayalite is increased with increasing magnesium content. The addition of 5 percent magnesium increased the liquidus temperature of fayalite about 50° C (George-Kennedy).
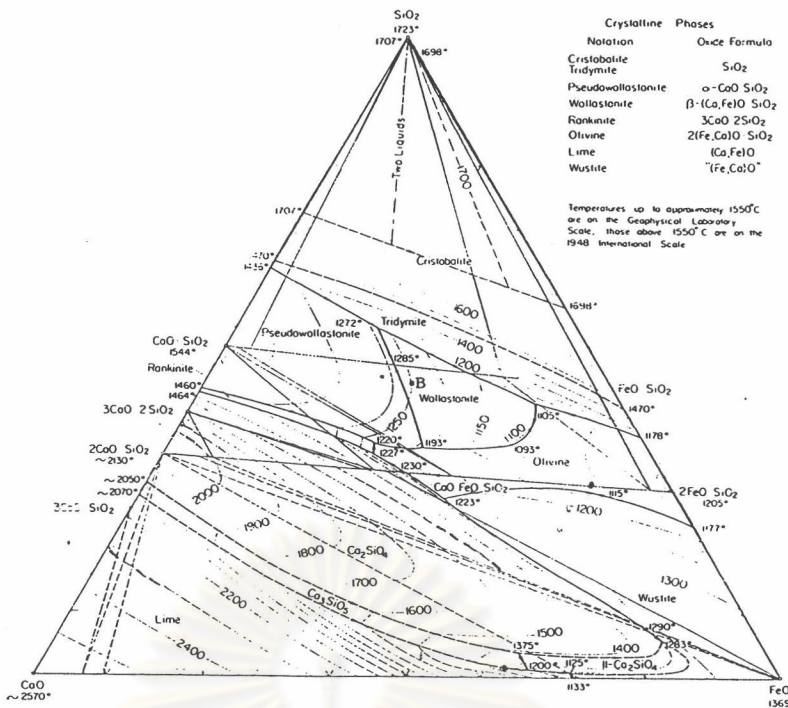
Figure 6.3   System CaO-FeO-SiO$_2$,   Point "B" shows the
composition of dark band of lamellar structure in burner
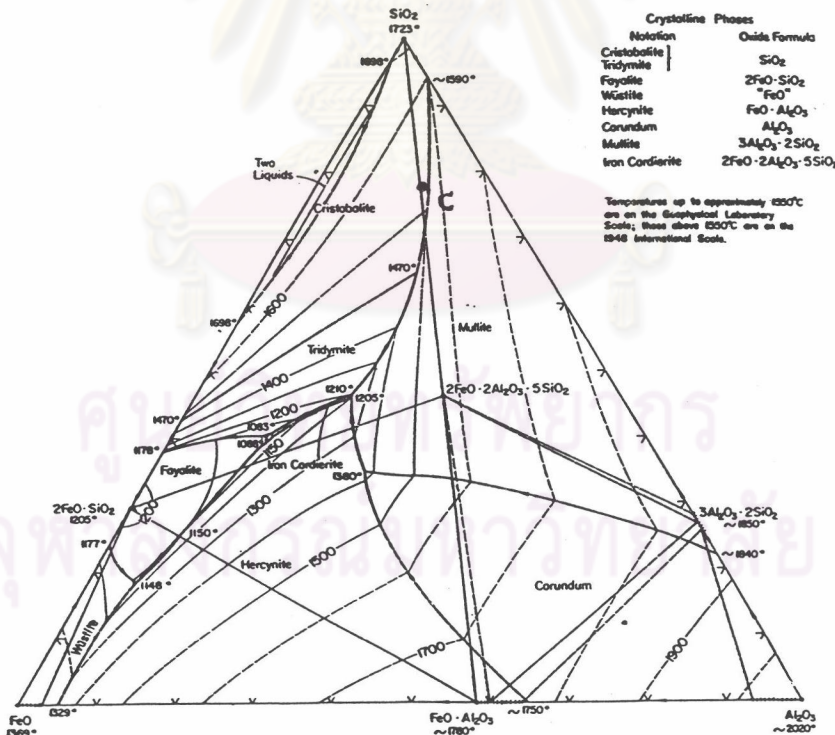port accretions, Osborn and Muan (1960).

Figure 6.4   System FeO-Al$_2$O$_3$-SiO$_2$,   Point C shows the composition of
the light band of lamellar structure of burner port accretions.
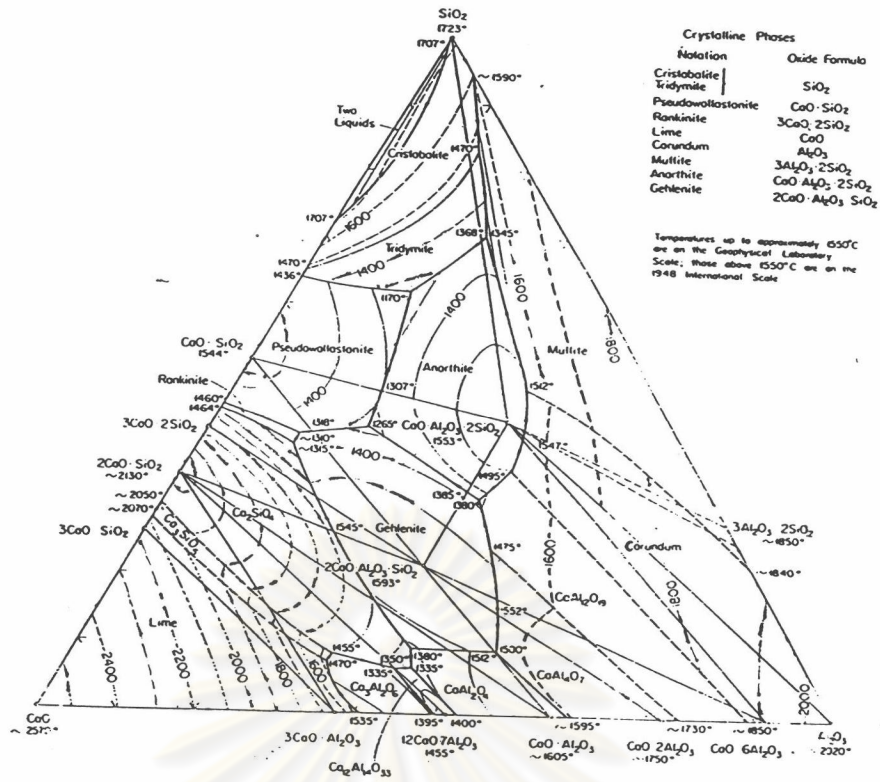(Osborn and Muan , 1960)

Figure 6.5   System CaO-Al$_2$O$_3$-SiO$_2$ shows a ternary eutectic of silicate,   anorthite and pseudowallastonite at 1170° C (Osborn and Muan, 1960).
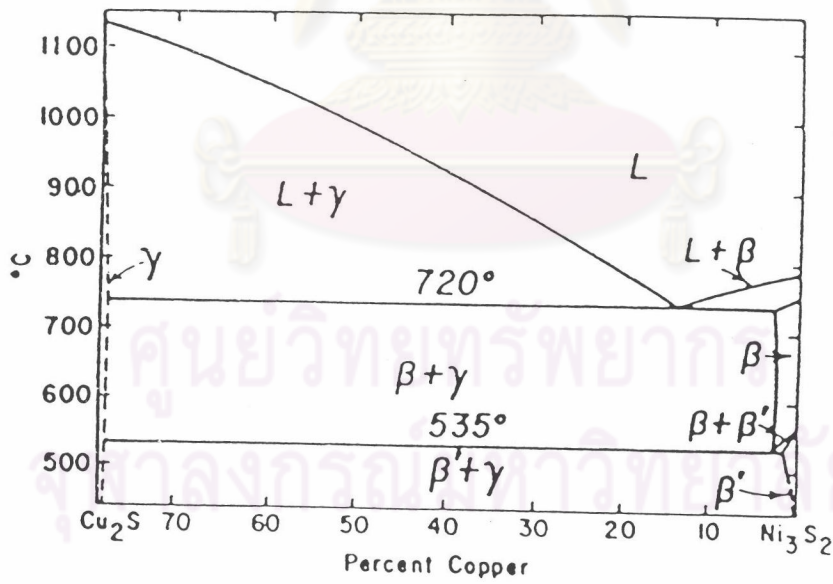

Figure 6.6   The Cu$_2$S-Ni$_3$S$_2$ Phase Diagram.

The ratio of Fe/Mg in magnesioferrite in Figure 5.14 and dendrite growths structure in Figure 5.11 equal 8.73 and 41.23, respectively. SEM examination indicated that the magnesium content in the flash furnace dust is not consistent. The magnesium content in dust probably depends on the magnesium to silica ratio in the concentrate feed. Nickel often formed as a nickel oxide at the edge of dust particles. A small amount of nickel (less than 1 percent) in olivine indicated that Ni_2SiO_4 solid solution does not appear in the accretions. However, nickel can dissolve in olivine as nickel oxide (Wang *et al*, 1974) and nickel metal (Grimsey and Biswas, 1977). Sahoo and Reddy (1985) indicated that the presence of aluminium (9 to 13 percent) increases the solubility of nickel in olivine.

6.4. COMPOSITION OF LABORATORY ACCRETION.

6.4.1 Composition of Laboratory Accretion

The laboratory accretions contained small grains of Fe-Ni-O spinel and a solid solution series of $(Ni_yMg_{1-y})_2.SiO_2$. According to the pseudoternary diagram given by Mukhopadhyay and Jacob (1995), Figure 6.9, Ni_2SiO_4 will react with Mg_2SiO_4 to form a solid solution series of orthosilicates, $(Ni_yMg_{1-y})_2.SiO_4$. Campbell and Roeder (1986) have studied the solid solution series of $(Ni_yMg_{1-y})_2.SiO_2$ at

1673 K using CO_2/H_2 gas mixtures. They suggested that Ni_2SiO_4 solid solution does not exist for the nickel-deficient orthosilicate compositions, the orthosilicate will react with silica to form the metasilicate, which can be presented as follows;

$$(Ni,Mg)_2SiO_4 + SiO_2 \leftrightarrow (Ni,Mg)SiO_3 \qquad (6.1)$$

The Gibbs free energy of formation of Mg_2SiO_4 and Ni_2SiO_4 given by Jacob and Mukhopadhyay shows that the Gibbs energy of formation of Mg_2SiO_4 (-29.78 kJ/mol) is more negative than that of Ni_2SiO_4. This indicates that Ni_2SiO_4 is not stable in this system.

There is a structure which is believed to be fayalite, which has precipitated in the orthosilicate close to the iron rich orthosilicate band, found in the 1353-40 sample, Figure 6.10. This structure would occur if iron from the light phases of the dust sample reacts with the silica in the orthosilicate phases.
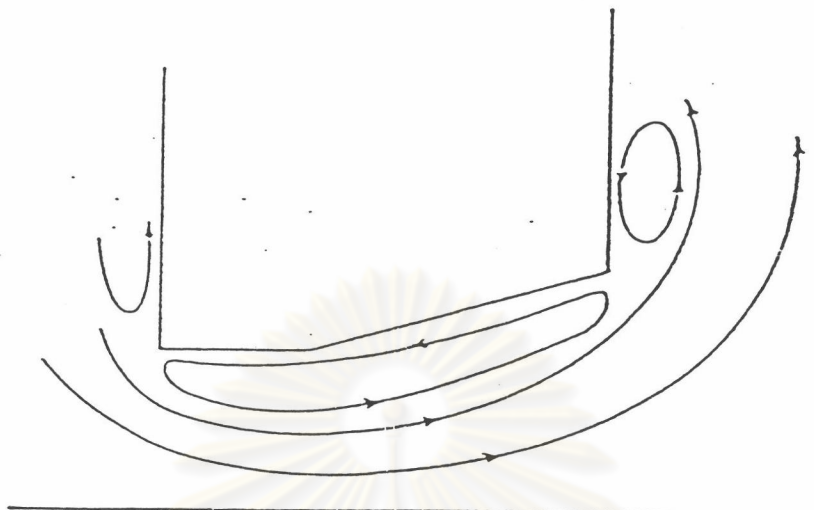
Figure 6.7 Path of Gas Flow in Kalgoorlie Flash Furnace
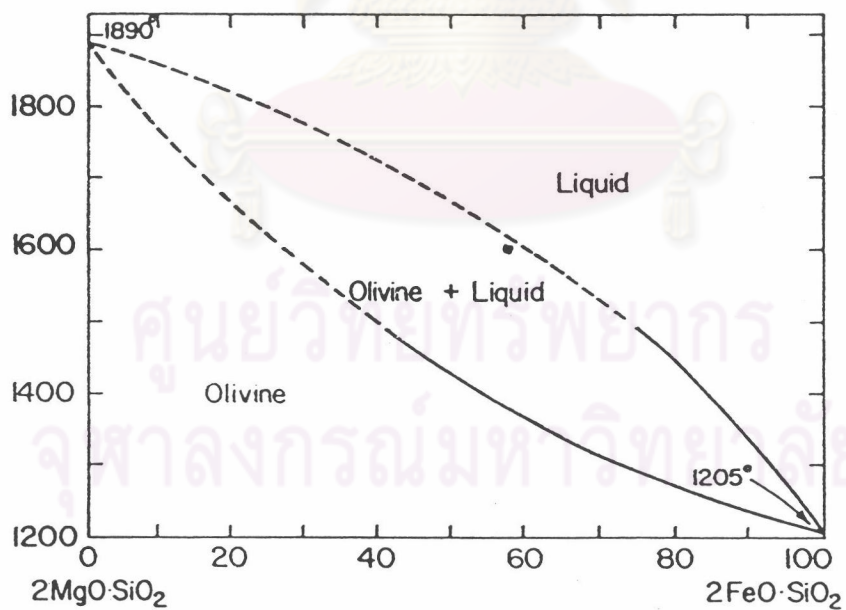
(Pleysier, 1985)

Figure 6.8 The system forsterite (Mg$_2$SiO$_4$)-fayalite
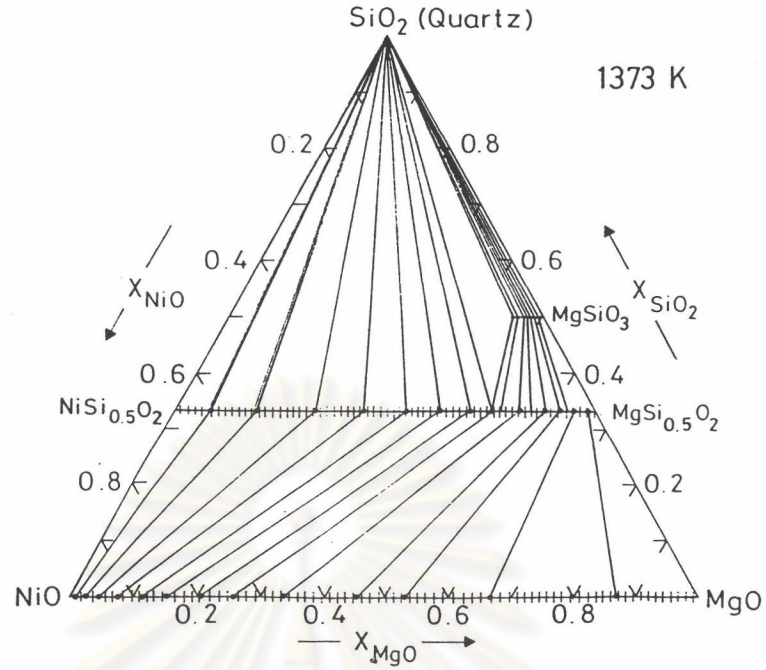
(Bowen and Schairer, 1935)

Figure 6.9   The Pseudoternary NiO-MgO-SiO₂ System at 1373 K

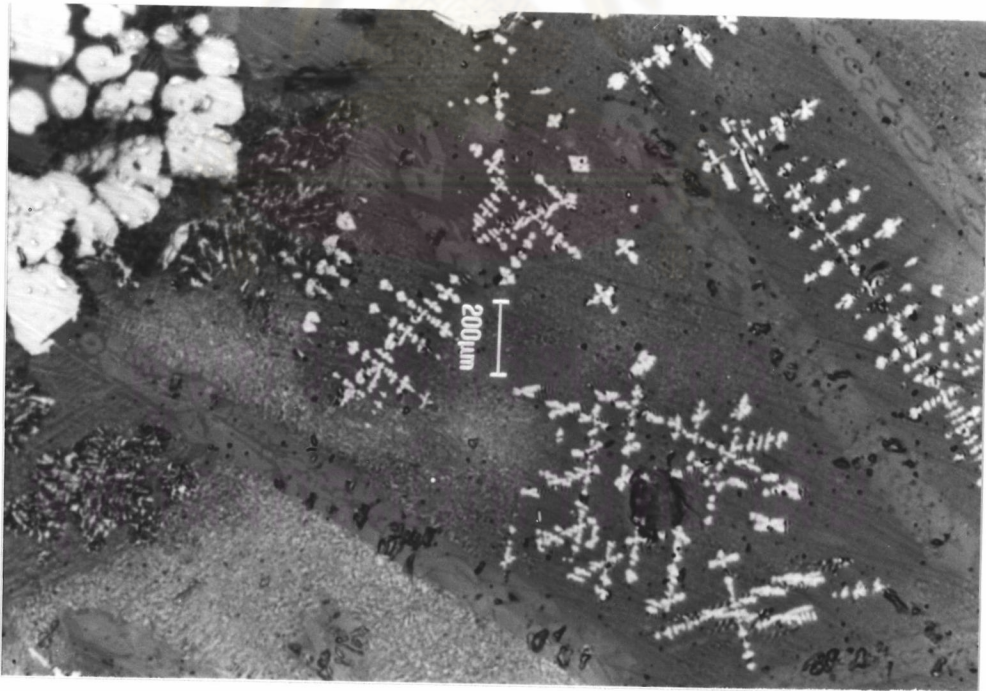(Mukhopadhyay and Jacob, 1995)

Figure 6.10 Structure, which is believed to be fayalite,

found in 1403-40 sample, Unetched, x500.

The structure which looks like a eutectoid structure in both 1353-40 and 1403-40 samples is made up of small lath like crystals of pseudowollastonite and mullite. The pseudowollastonite crystal contained 4 to 6 percent aluminium and it often appears adjacent to the free silica and iron rich orthosilicate region. On cooling, aluminium probably was rejected from pseudowollastonite crystals into the low melting point phases around them. Mullite, which formed around these lath-like crystals will prevent crystal growth along the minor axis. However, the crystal may grow along a major axis. This may explain the formation of the lamellar structure.

6.4.2. Effect of Oxygen Potential on Accretion Microstructure.

The effect of increasing oxygen pressure on composition and structure of accretions can be summarised as :

a. increased grain size of spinel of the Fe-Ni-O system;

b. decreased spinel content;

c. large dendritic structure of Fe-Ni-Si-O system was present;

From Figure 5.15 and 5.17 (microstructure of 1353-40 and 1353-55 samples), respectively, the grain size of spinel (light phase) of 1353-40 is larger than the 1353-55 sample. The increasing grain

size of spinel in the laboratory accretions with increase in oxygen pressure was probably because of the formation of magnetite and nickel oxide by the oxidation of spinel and wustite at higher oxygen pressure. This can be expressed by equation 6.2:

$$NiFe_2O_{4(spinel)} + FeO = Fe_3O_{4(spinel)} + NiO \qquad (6.2)$$

It was found that most light grains of sample 1535-60 contained wustite which occurred adjacent to the magnetite solid solution (spinel). The amount of wustite decreased in sample 1353-55 and remained small amount in sample 1353-40. The presence of wustite in spinel was described by Segnit (1976). The existence of wustite in the magnetite phase was due to nickel metal which forms partial rims around the magnetite grains preventing oxygen diffusion into the crystals. When the oxygen pressure is increased, nickel will oxidize to form nickel oxide dissolved in magnetite. Wustite will also oxidize to give a magnetite.

6.4.3 Effect of Temperature on Laboratory Accretions.

The effect of temperature on structure and composition can be summarised as:

a. more free silica phases at high temperature;

b. lower nickel content in spinel of Fe-Ni-O system at low temperature;

c. higher nickel content in orthosilicate at low temperature;

d. spinel grain size increased with increased temperature.

It is convenient to discuss the effect of temperature by the ratio of elements in spinel/orthosilicate as shown in Table 6.1, which are given by Tables 5.6 and 5.7. The values of $Fe_{(spinel)}/Fe_{(orthosilicate)}$ and $Ni_{(spinel)}/Ni_{(orthosilicate)}$ increased with increase in temperature, while the silica and magnesium ratios were reduced. The nickel behavior can be explained by the activity coefficient of nickel oxide $(\gamma°_{NiO})$ in the $FeO-NiO-Fe_{0.5}O-AlO_{1.5}-SiO_2$ slag, which increases with temperature. Therefore, the nickel content in slag will decrease with increasing temperature (Sahoo and Reddy, 1985). This indicates that nickel oxide will be removed from the orthosilicate and dissolve in magnetite. It can be expressed as;

$$Ni^{2+} \text{ (liquid, orthosilicate)} \rightarrow Ni^{2+} \text{(liquid, spinel)} \qquad (6.3)$$

At constant oxygen pressure, the free silica content increases with increasing temperature. This is similar to the effect of decreasing oxygen pressure at constant temperature. Decreasing oxygen pressure will result in the formation of metasilicate and metal
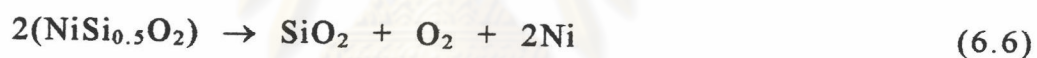
(Mukhopadhyay and Jacob, 1995). This reaction can be expressed by the precipitation of nickel metal from orthosilicate at high temperature and low oxygen pressure. It can be written as;

$$2(NiSi_{0.5}O_2) \rightarrow (NiSiO_3) + {}^1/_2 O_2 + Ni \qquad (6.4)$$
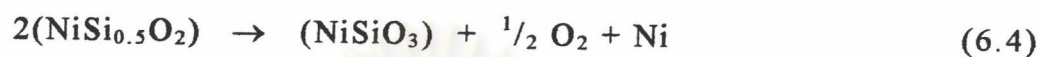
And when the oxygen pressure is reduced further, metasilicate will decompose to silica and nickel as equation (6.5);

$$(NiSiO_3) \rightarrow SiO_2 + Ni + {}^1/_2 O_2 \qquad (6.5)$$

or

$$2(NiSi_{0.5}O_2) \rightarrow SiO_2 + O_2 + 2Ni \qquad (6.6)$$
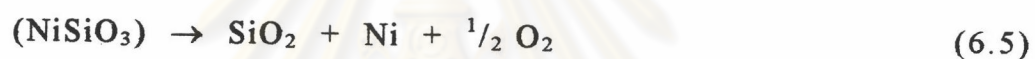
(when the mole fraction of magnesium in $(Ni_yMg_{1-y})Si_{0.5}O_2$ is higher than 0.243, (Mukhopadhyay and Jacob, 1995)).

Table 6.1 Comparison Ratio of % in Spinel/ % in Orthosilicate as a Function of Temperature.

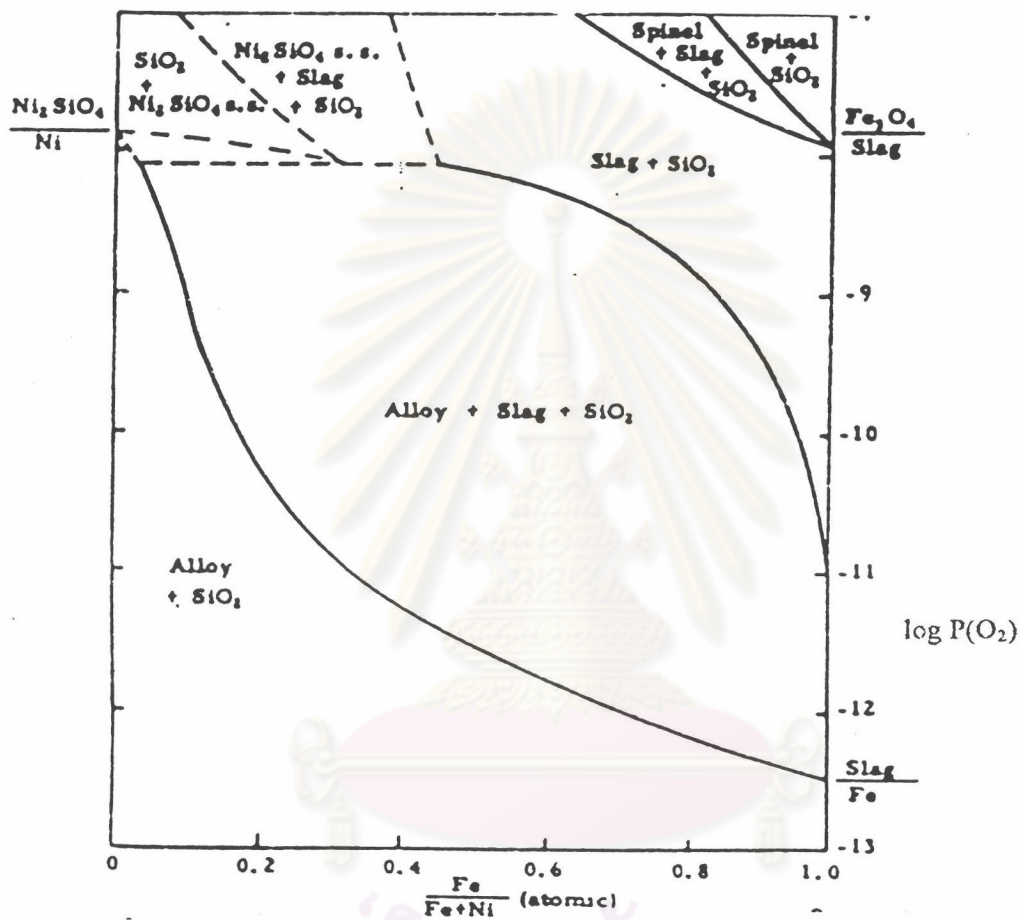| % in Spinel/% in Orth.	1350 K	1400 K
Iron	8.534	14.04
Silica	0.053	0.010
Nickel	0.715	1.174
Magnesium	0.163	0.114

Figure 6.12   The   Fe-Ni-Si-O   system   at   1200 C

(Shaw and Willis, 1975)

6.4.5 Correlating Structure Between Dust, Furnace and Laboratory Accretions.

Since the laboratory accretions were formed from dust particles which were heated at different oxygen partial pressures and temperatures, the variation of composition of the dust particles and laboratory accretions may provide indirect information for explaining the mechanism of formation of flash furnace accretions. A comparison of the composition of the light phases and dark phases of laboratory and furnace accretion, and dust particles as shown in Table 6.2 indicated that the differences between the composition of the laboratory accretions and dust were;

a. orthosilicate of laboratory accretion contained low iron content (3-6 percent) while olivine of dust contained iron content about 30-40 percent;

b. both spinel and orthosilicate of laboratory accretion had high nickel contents up to 25 percent, but spinel and olivine of dust particles had nickel content only 0.5 to 3 percents. Most of nickel in dust occurred as isolated nickel oxide and nickel alloy.

The presence of the high nickel content in the laboratory accretion is due to the isolated nickel metal phases (see Figures 5.11-12

and 5.14) diffusing into spinel and orthosilicate. According to the Fe-Ni-O diagram in Figure 2.11, at low oxygen partial pressure and high temperature nickel metal is oxidized to nickel oxide or forms a spinel solid solution. Furthermore, it can be seen that the nickel content of the spinel phase has a small change when the oxygen pressure is decreased. If the nickel content in the system Fe-Ni-O (Figure 2.11) is lower than about 20 percent, the nickel oxide will not appear in the system. Optical microscope examination shows that there is a lot of nickel metal and nickel sulphide in the flash furnace accretion while it rarely was found in the laboratory accretion samples. Nevertheless, the nickel content in spinel of the laboratory accretions is similar to the nickel content in the furnace accretion samples. This is because of the limit of solubility of nickel in spinel, the excess nickel will be oxidized to nickel oxide.

Considering the increment of nickel content in the system Fe-Ni-O-SiO$_2$ at 1200 °C (Figure 6.11) given by Shaw and Willis (1975), when nickel content is increased at constant oxygen pressure (log P(O$_2$) = -9 to -8), a (Ni,Fe)$_2$SiO$_4$ solid solution will be formed in equilibrium with Fe$_3$O$_4$ spinel and SiO$_2$, which results in the Fe /(Fe+Ni) atomic ratio in spinel being decreased. The mechanism of formation of the solid solution of (Ni,Fe)$_2$SiO$_4$ and olivine in furnace accretions can be expressed by the schematic diagram in Figure 6.12.

The Fe_3O_4 spinel in the dust particles will react with the nickel oxide from the oxidation reaction of nickel metal and form a solid solution of $(Ni,Fe)_2O_4$. The $(Ni,Fe)_2O_4$ would react with SiO_2 in olivine (dark phase of dust particle) resulting the higher iron content in the olivine phase. It should be noted that the spinel solid solution between Fe_3O_4 and $(Ni,Fe)_2O_4$ is ideal (Dalvi and Sridhar, 1976). It was hoped to use thermodynamic data from the literature to explain the formation of $(Ni,Fe)_2SiO_4$ and silica in olivine at different oxygen pressures and temperatures, and the transformation of Fe_3O_4 spinel to $(Ni,Fe)_2SiO_4$. Unfortunately, there is not enough time to complete this. However, these experiments showed that $(Ni,Fe)_2SiO_4$ did not occur at 1350 to 1400° C and oxygen potential -60 to -40 Kcal.

The %element (in spinel)/ %element (in olivine) ratio given in Table 6.3 shows that these ratios in laboratory and furnace accretions are lower than the ratios in dust. This is indicates that the increase of magnesium content in olivine is because the magnesium was removed from spinel to olivine. Calcium and aluminium were probably removed from spinel and formed the crystals of $CaO-Al_2O_3-SiO_2$ which could be transformed to the lamellar structure later.

Table 6.2 Comparison of Spinel and Olivine Phases of Flash Furnace

Accretions, Laboratory Accretions and Furnace Dusts.

Element	1353-40		1403-40		Accretion		Dust	
	Spinel	Ortho.	Spinel	Ortho.	Spinel	Olivine	Spinel	Olivine
Fe	47.71	5.59	55.73	3.97	70.12	29.88	59.05	36.77
Si	0.88	16.68	0.26	24.68	0.41	14	3.68	15.94
Ni	17.44	24.39	20.61	17.56	11.98	18	3.08	0.56
Mg	3.11	19.11	1.82	15.97	0.4	5.45	3.83	7.87
Ca	-	-	-	-	0.02	0.23	0.2	0.72
Al	1.29	-	0.86	1.08	0.3	0.1	1.26	0.96

(Ortho = Orthosilicate) (w/w %)

Table 6.3   Comparison Ratio of % in Spinel/% in Olivine of

Magnesium and Calcium of Furnace Accretions

and Furnace Dusts.

% in spinel/% in olivine	Accretion	1353	1403	Dust
Magnesium	0.074	0.16	0.13	0.43
Calcium	0.087	-	-	0.28
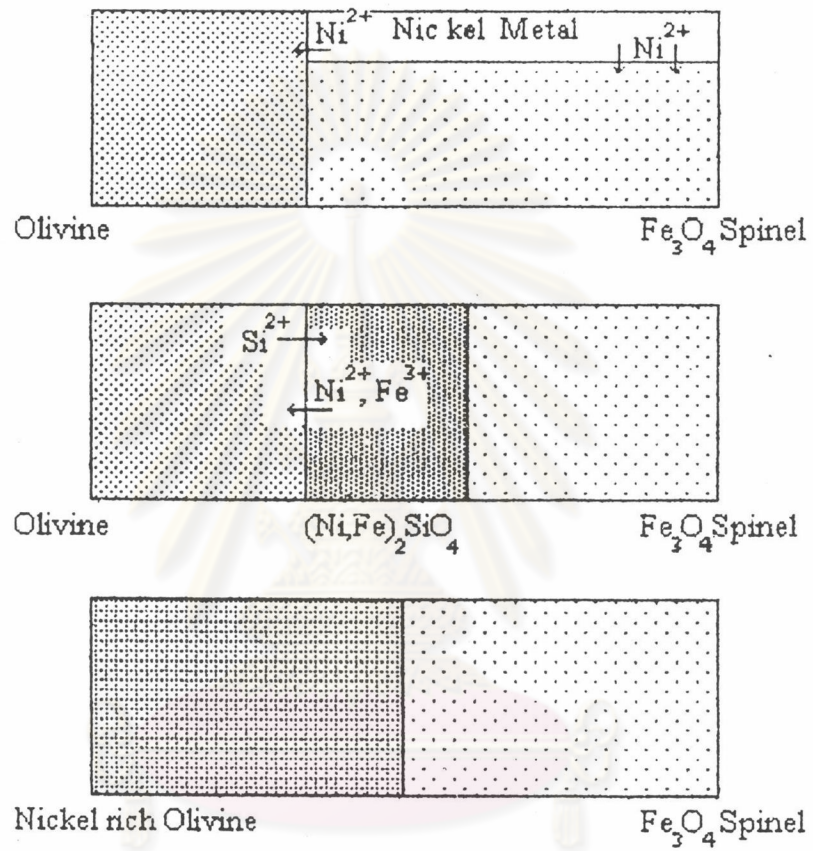
Figure 6.12 The schematic diagram of formation of accretion phases

6.5   SUMMARY

All phases in dust particles, laboratory and furnace accretions were identified,   and can be summarised as;

dust particles Fe_3O_4 spinel,   nickel oxide,   nickel metal,   olivine and nickel-copper alloy.

furnace accretions $(Ni,Fe)_2SiO_4$,   olivine,   free silica (SiO_2), nickel sulphide,   nickel oxide,   nickel metal,   nickel-copper alloy, lamellar structure of mullite and pseudowollastonite $(CaO-SiO_2)$;

laboratory accretions Fe_3O_4 spinel,   orthosilicate $(Ni,Mg)_2SiO_4$, crystals of aluminium rich pseudowollastonite,   and mullite.   Wustite and nickel metal were found in 1353-60 and 1353-55.

The high nickel content in the light phase and dark phase of laboratory and furnace is because nickel metal oxidized to nickel oxide (NiO) and entered into these phases.   The increment of nickel content in Fe_3O_4 spinel effects the Fe_3O_4 spinel which transforms into Fe_3O_4 spinel and $(Ni,Fe)_2O_4$ solid solution.   This solid solution is probably reacted with SiO_2 in olivine resulting in higher iron content in olivine. The reaction between $(Ni,Fe)_2SiO_4$ solid solution and olivine was not

proved by thermodynamic data. The mechanism of formation of the predominant accretion phases were shown in Figure 6.12. The lamellar structure would form from the crystals of aluminium rich pseudowollastonite which were found in the laboratory accretion.