REFERENCES

Bowen, N. L. and Schairer, J. F. Am. J. Sci. 5th Ser. 24 (1932): 200.

Broadbent, P. B. Journal of Phase Equilibria (1993): 93-113.

Campbell, F. E. and Roeder, P. The Stability of Olivine and Pyroxene in the Ni-Mg-Si-O System. Amer. Mineral. 53(1, 2) (1986):

Dalvi, A. D. and Sridhar, R. Thermodynamic of Fe-Ni-O and Fe-Ni Systems at 1065 to 1380 K. Canadian Metallurgical Quarterly 15(4) (1976): 349-356.

Davenport, W. G. and Partelpoeg, E. H. Flash Smelting A*nalysis, Control and Optimization*. London: Pergamon Press, 1984.

Elliot B. J., Campain, R. and Muller, R. G. Operation of the Integrated Flash Furnace at Kalgoorlie Nickel Smelter. Extraction Metallurgy '89. (1989): 467-499.

Floyd, J. M., Conochie, D. S., and Grave, N. C. Measurement of Oxygen Potential in Slags in a Nickel Smelter using Disposable-Tip EMF Cells. Proc. Australas. Inst. Min. Metall. 270 (June 1979): 15-23.

George-Kennedy, D. P. A Study of the Physical and Chemical Factors Affecting Uptake Shaft/Throat Accretion. K.N.S. Technical Report 220 (December 1984): 1-11.

Grimsey, E. J. and Biswas, A. K. Trans. Inst. Min. Metall. 86(C) (1977): 01-08.

Grimsey, E. J., and Santander, A. K. Trans. Inst. Min. Metall. 85(C) (1976): 200-207.

Kemori, N., Shibata, T. and Fukushima. Thermodynamic Consideration for Oxygen Pressure in a Copper Flash Smelting Furnace at Toyo Smelter. J. Metals (May 1985): 24-29.

Kemori, N., Shibata, Y. and Tomono, M. Measurements of Oxygen Pressure in a Copper Flash Smelting Furnace by a Emf Method. Metall Trans B 17B (March 1986): 111-117.

Kemori, N., Denholm, W. T. and Kurokawa, H. Reaction Mechanism in a Copper Flash Smelting Furnace. Metal Trans B (1989): 327-335.

Muan, A. and Osborn, E. F. Phase Equilibrium Diagram of Oxide Systems. Ceramic Foundation. American Ceramic Society and the Edward Orton, Jr: New York, 1960.

Mukhopadhyay, S and Jacob, K. T. Tie Lines and Activities in the System NiO-MgO-SiO_2 at 1373 K. Journal of Phase Equilibria (1995): 243-253.

Naldrett, A. J. and Clark, T. Econ. Geol. 67 (1972): 939.

Ono, K., Yokogawa, K., Yamagushi, A. and Moriyama, J. J. Japan Inst. Metals 35 (1979): 750.

Pelton, A. D., Schmalzried, H., and Sticher, J. J. Phy. Chem. Solid 40(12) (1979): 1103-1122.

Pleysier, R. A Study of Uptake Throat Accretion in the Kalgoorlie Nickel Smelter. Post Graduated Diploma, WAIT, December 1985.

Phillip, B., Hutta, J. J. and Warshaw, L. J. Am. Ceram. Soc., 46 (1963): 579.

Sahoo, P. and Reddy, R. G. Activity Coefficient of Nickel Oxide in $FeO-NiO-FeO_{1.5}-AlO_{1.5}-SiO_2$ Slag at 1573 K. Department of Chemical and Metallurgical Engineering, Mackay school of Mines, University of Navada-Reno (1985): 533-545.

Segnit, E. R. Nickel Slags From the Flash Smelter at Kalgoorlie. Western Australia. Proc. Australas. Inst. Min. Metall. 259 (September 1976): 37-44.

Shaw, R. W. and Willis, G. M. Thermodynamics of Nickel Solubility in Iron Silicate Slags. Can. Met. Quart. 20(2) (1981): 153-161.

Shima, M and Itoh, Y. Refractories of Flash Furnaces in Japan. J. Metals 32(11) (1980): 12-16.

Solar, M. Y., Neal, R. J., Antonioni, T. N. and Bell, M. C. Smelting Nickel Concentrate in Inco's Oxygen Flash Furnace. J. Metals 31(1) (1978): 26-32.

Smeltser, W. W. and Dalvi, A. D. J. Electrochem. Soc. 117 (1970): 1431.

Wang, S. S., Santader, N. H., and Togue, J. M. Metall. Trans. B 5 (1974): 207-261, 1974.

APPENDIX

APPENDIX A

The Method of Controlling Oxygen Pressure Using CO/CO_2 Gas Mixtures.

The oxygen pressure in the experimented furnace was controlled by using the CO/CO_2 gas mixtures. A controlled oxygen pressure can be obtained by mixing various quantities of CO and CO_2 to maintain constant oxygen pressure. The method of calculating the CO/CO_2 ratio is based on;

- I. The Gibbs Free Energy of CO, CO_2 gas mixture;
- II. Dalton's Law;
- III. Le Chatelier's Principle.

I. The Gibb Free Energy of CO/CO_2 Gas Mixtures

The reaction of mixture of CO, O_2 and CO_2 at constant pressure and temperature can be written, as in equation (A1)

$$2CO_{(g)} + O_{2(g)} = 2CO_{2(g)} \tag{A1}$$

The standard Gibbs free-energy change for this reaction is represented as follows;

$$\Delta G^\circ = -RT\ ln\ [P^2_{CO2} / (P^2_{CO}.P_{O2})] \quad (A2)$$

$$= -135000 + 41.4T \quad \text{Calories} \quad (A3)$$

The oxygen pressure can be determined from equation [A4]

$$\mu(O_2) = RT\ ln\ [P_{O2}] \quad (A4)$$

($\mu(O_2)$ is a oxygen potential, Kcal)

Floyd *et al* (1979) and Kemori (1986) have studied the oxygen pressure in flash furnace and indicated that the oxygen pressure occurring in flash furnace are between -60 to -40 Kcal. Therefore, the oxygen potential equal -60, -50, -40 Kcal were selected and used for the study.

II. Dalton's Law

The sum of the partial pressure P_i of the components in the system is equal to the total pressure P_T.

$$P_T = P_i + P_{ii} + \ldots + P_{ith} \quad (A5)$$

III. Le Chatelier's principle

Consider a closed system in which a reversible reaction is taking place at constant pressure and temperature. Whenever a system at equilibrium is subjected to a change in one of the variables, temperature or pressure, the system will shift the composition of the equilibrium in the direction in which there is a decrease in the number of molecules.

For the reversible reaction $2CO_{(g)} + O_{2(g)} = 2CO_{2(g)}$, if initially the gases mixtures consists of x g.mole of CO, y g.mole of CO_2 and $y > x$. Let ξ represents the number of gram-moles of CO_2 that decompose at equilibrium. Therefore, equation (A1) can written as;

$$\begin{array}{lcccl} 2CO_{(g)} & + & O_{2(g)} & \leftarrow & 2CO_{2(g)} \\ (x + 2\xi) & & (+\xi) & & (y - 2\xi) \end{array} \qquad \text{(A6)}$$

From the Gibbs free energy, Dalton's Law, and Le chatelier's principle, the ratio of P_{CO}/P_{CO2} can determined as follows;

The equilibrium of CO, CO_2 and O_2 can written as;

$$2CO_{(g)} + O_{2(g)} = 2CO_{2(g)}$$

$$\Delta G^{\circ}_{[C1]} = -135{,}000 + 41.4T \qquad \text{Calories}$$

$$\Delta G^\circ_{[C1]} = -RT\, ln[P^2_{CO2} /(P^2_{CO}.P_{O2})]$$

Thus,

$$RT\, ln[P^2_{CO2} /(P^2_{CO}.P_{O2})] = 135,000 - 41.4T$$

$$RT\, ln[P^2_{CO2} /(P^2_{CO})] = 135,000 - 41.4T + \mu(O_2)$$

$$P_{CO2} / P_{CO} = \sqrt{} e^{(135,000 - 41.4T+ \mu(O2))/RT} \qquad (A7)$$

Thus, the composition of CO, CO_2 and O_2 can be determined by using equations (A5), (A7) and substituting $\mu(O_2)$= -40, -50, and -60 Kcal, T = 298 K in equation (A7).

Since the increment of temperature affects the composition of initial equilibrium, the composition of the new equilibrium at a higher temperature can be calculated by using equations (A3) and (A6) to determine ξ. The initial and equilibrium composition, ξ and oxygen potential at given temperature (1350,1400, and 1450 °C) are shown in Table A1. The composition of CO and CO_2 at given temperatures were selected to control oxygen pressure in the furnace.

Table A1 The composition of CO and CO_2 gas mixtures at ambient and given temperature and oxygen pressure.

T° C	$\%CO_{2ini}$	$\%CO_{ini}$	ξ	$\%CO_{2T}$	$\%CO_T$	$\mu(O_2)$ Kcal
1350	0.1	99.9	$1.64x10^{-7}$	0.1	99.9	-41.91
1350	0.5	99.5	$6.48x10^{-9}$	0.5	99.5	-50.57
1350	2	98	$3.94x10^{-10}$	2	98	-58.08
1350	15	85	$5.3x10^{12}$	15	85	-69.64
1400	0.2	99.8	$2.46x10^{-7}$	0.2	99.8	-42.33
1400	0.6	99.6	$9.67x10^{-9}$	0.6	99.6	-51.34
1400	5	95	$3.56x10^{-10}$	5	95	-60.52
1400	7	93	$1.58x10^{-11}$	7	93	-69.18
1450	1	99	$5.16x10^{-8}$	1	99	-48.34
1450	7	93	$9.28x10^{-10}$	7	93	-59.92
1450	8	92	$6.96x10^{-10}$	8	92	-60.75
1450	30	70	$2.86x10^{-11}$	30	70	-69.94

APPENDIX B

Microstructure of Accretions.

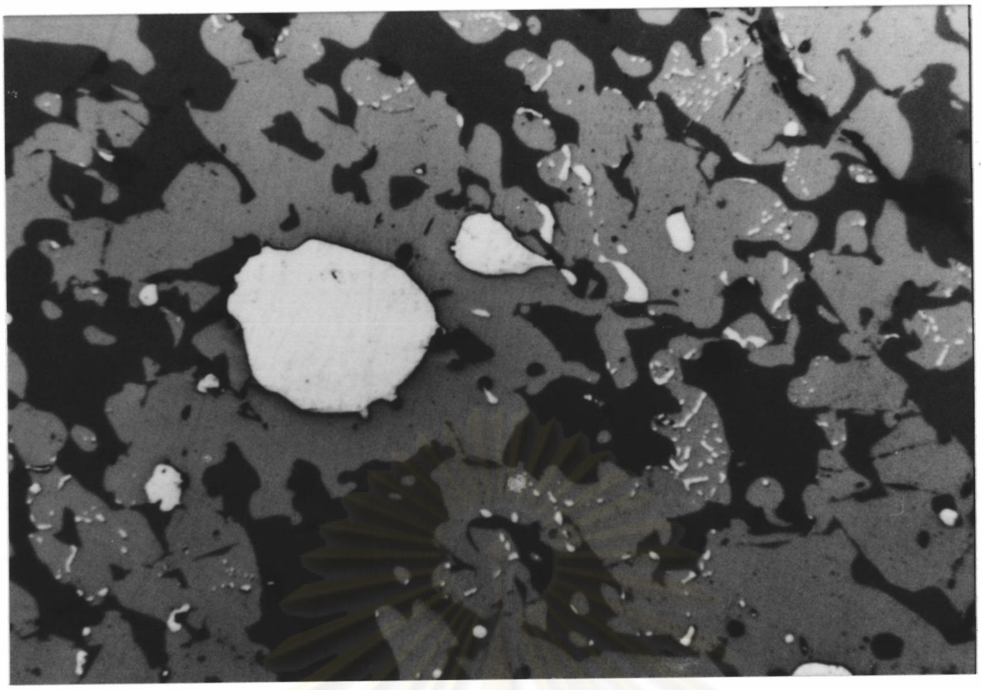

Figure B1 Microstructure of G-3 sample shows the large spherical particle of nickel sulphide, nickel metal formed rim around Fe_3O_4 spinel, x200.

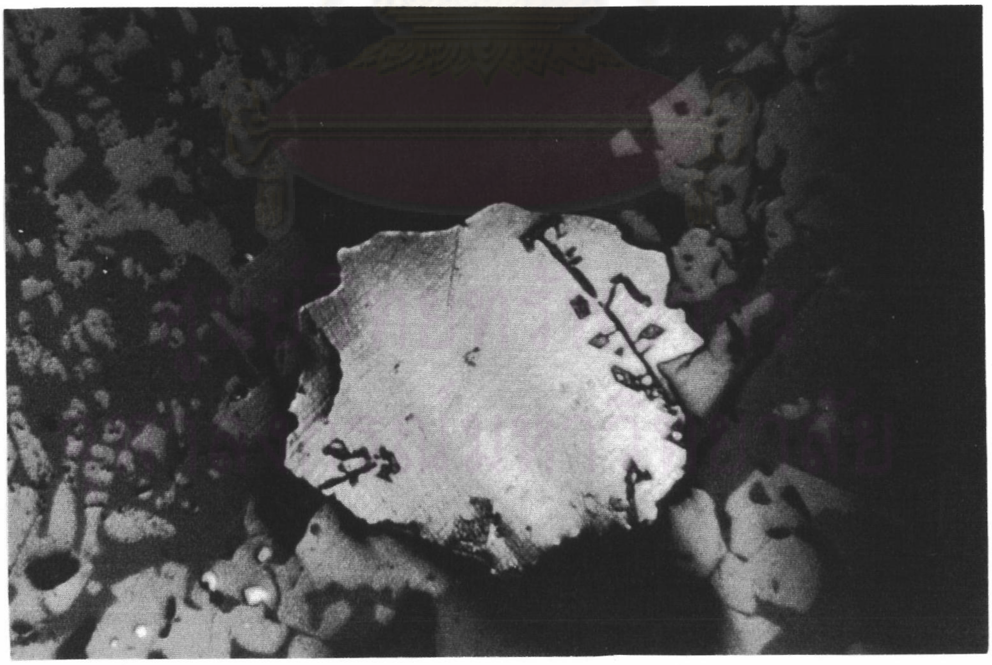

Figure B2 Nickel metal formed in the nickel sulphide of G-3 sample, x200.

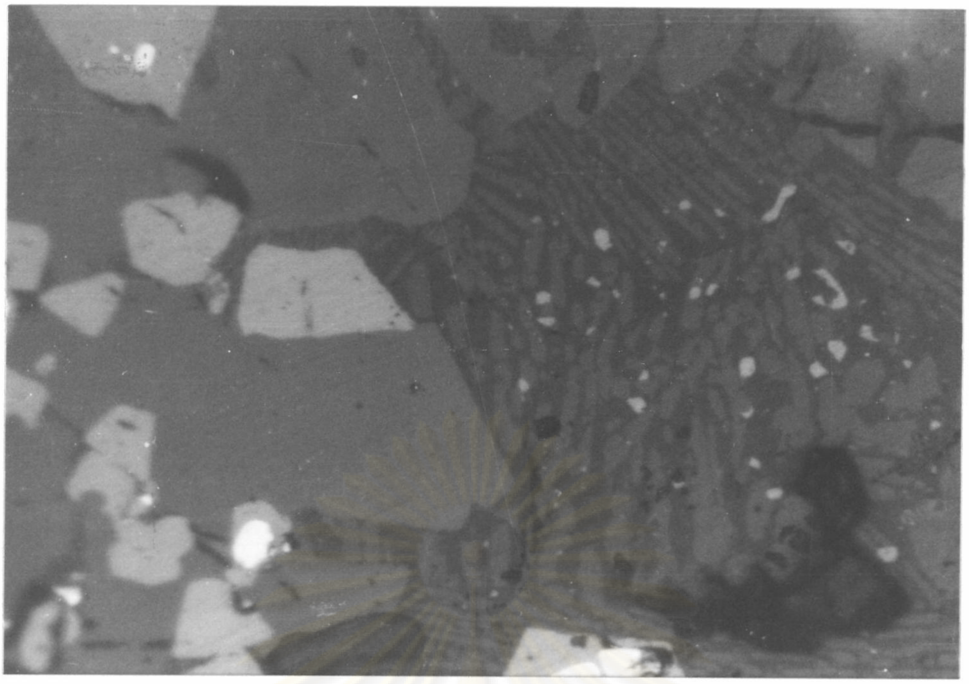

Figure B3 Microstructure of G-3 sample shows the lamellar Structure, large grain of nickel sulphide, small particle of nickel metal, x200.

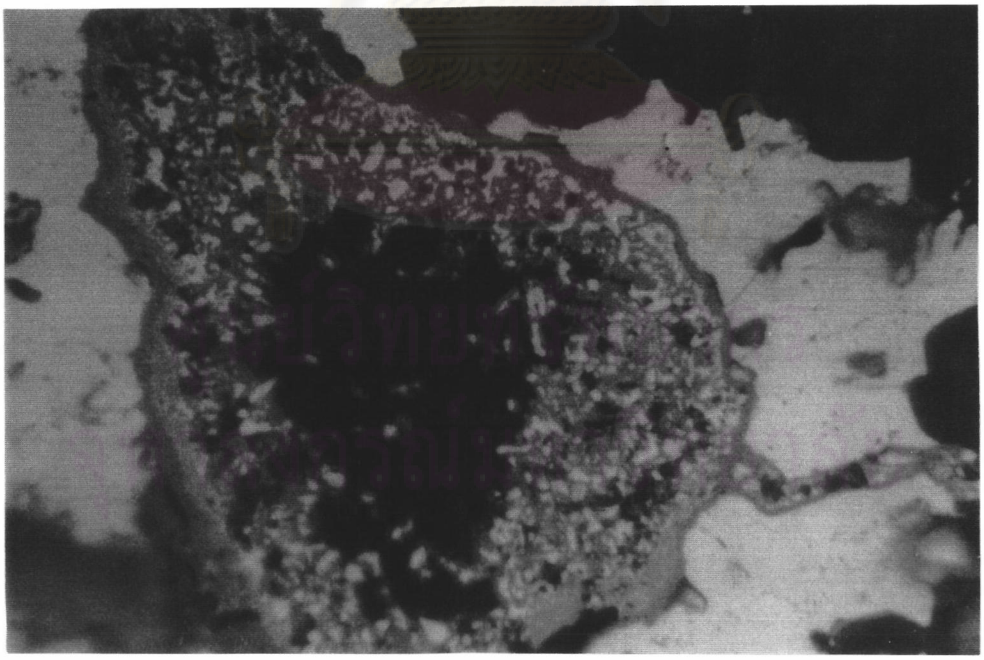

Figure B4 Unknown structure was found in G-4 sample, 500.

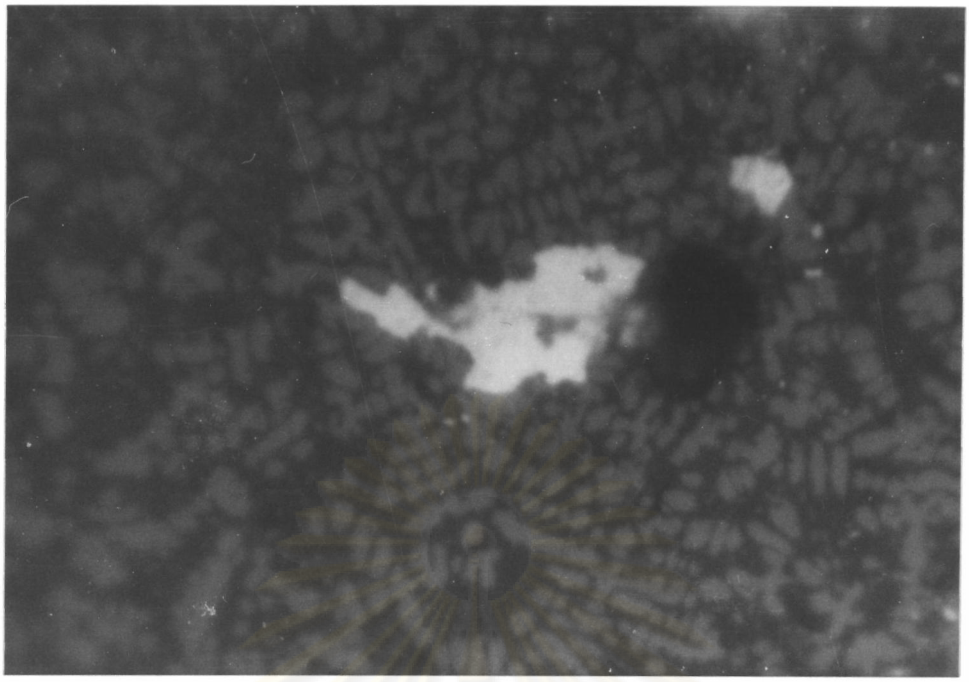

Figure B5 Dendritic structure of Fe_3O_4 spinel of G-4 sample, x500.

Figure B6 Ternary eutectic structure of FeO-Fe_2SiO_4-Fe_2O_3 and dendritic structure in H-32 sample, x500.

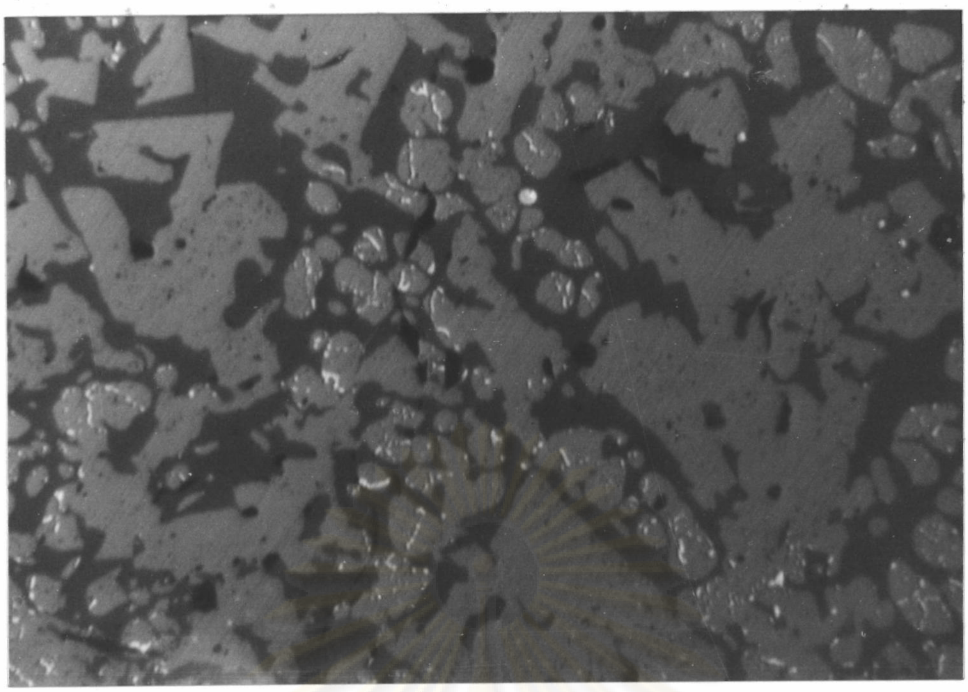

Figure B7 Nickel metal form rims around Fe_3O_4 spinel, H-34 sample, x100.

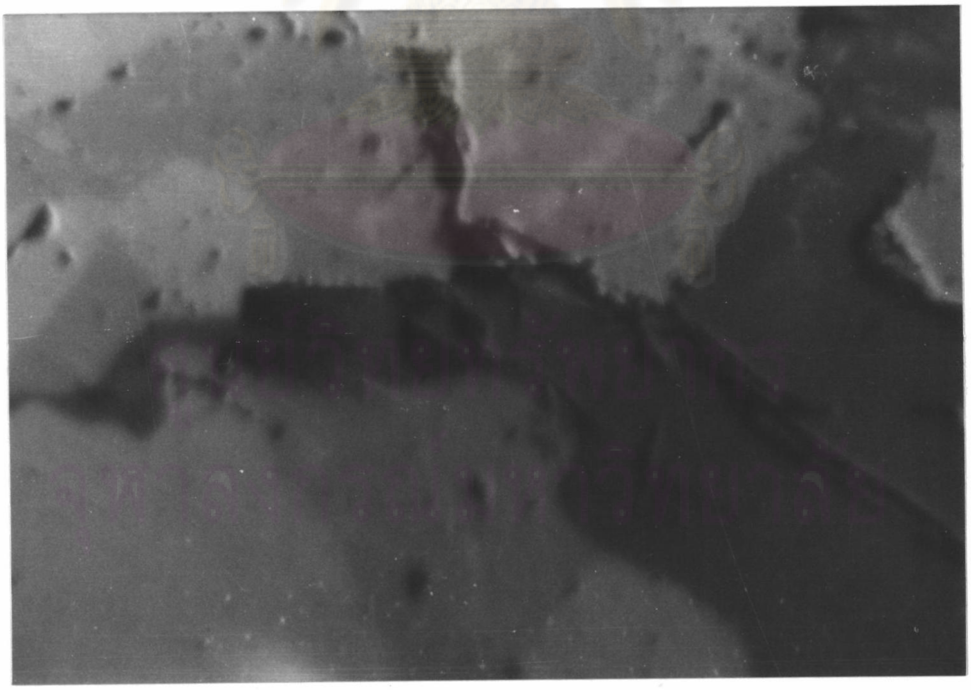

Figure B8 Wustite (light phase) was found in the Fe_3O_4 spinel, H-34 sample, x 500.

BIOGRAPHY

Mr. Maetee Sujiwatthana was born on September 15, 1969 in Bangkok, Thailand. He received his B. Eng. in Metallurgical Engineer from Chulalongkorn University in 1991. He has 4 year experiences in metal melting. He has been working for master degree in Metallurgical Engineer at Chulalongkorn University since 1992.