

This document was produced
by scanning the original publication.

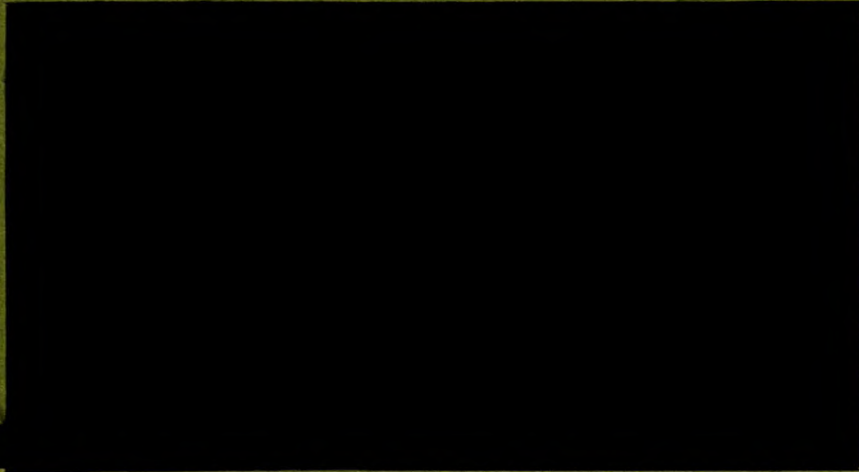
Ce document est le produit d'une
numérisation par balayage
de la publication originale.

DECLASSIFIED
DATE 1973
AUTHORIZED BY [Signature]

CANADA

DEPARTMENT OF ENERGY, MINES AND RESOURCES

OTTAWA



Mines Branch

IR 73-49

COPY NO 2

CANADA
DEPARTMENT OF ENERGY, MINES AND RESOURCES
OTTAWA

IR 73-49

July 12, 1973

PHASE EQUILIBRIA AND MATTE SOLIDIFICATION
IN THE TERNARY SYSTEM ZnS-FeS-PbS

R. C. Kerby

EXTRACTION METALLURGY DIVISION

Mines Branch Investigation Report IR 73-49

PHASE EQUILIBRIA AND MATTE SOLIDIFICATION STUDIES
IN THE TERNARY SYSTEM ZnS-FeS-PbS

by

R. C. Kerby*

ABSTRACT

Phase equilibria were determined for the simple eutectic systems FeS-ZnS, FeS-PbS and ZnS-PbS which bound the ZnS-FeS-PbS ternary phase diagram. Eutectic points were found at 6 mol % FeS - 94 mol % ZnS and 1135°C, 48 mol % PbS - 52 mol % FeS and 835°C, and 78 mol % PbS - 22 mol % ZnS and 988°C. The matte solidification studies in the systems FeS-ZnS and FeS-PbS indicated that grain size increased substantially (from 1 micron to 20 microns) as the rates of cooling of the mattes were decreased from 20°C/min to 0.5°C/min.

*Research Scientist, Extraction Metallurgy Division, Research Section, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada. K1A 0G1

CONTENTS

	<u>Page</u>
ABSTRACT	i
INTRODUCTION	1
EXPERIMENTAL	2
Materials	2
Apparatus and Procedure	3
RESULTS	4
Phase Equilibrium Studies	4
(a) The System FeS-ZnS	4
(b) The System FeS-PbS	8
(c) The System ZnS-PbS	8
Matte Solidification Studies	8
(a) The System FeS-ZnS	8
(b) The System FeS-PbS	11
SUMMARY	15
ACKNOWLEDGEMENTS	16
REFERENCES	16
FIGURES	
1. The FeS-ZnS Phase Diagram	7
2. The FeS-PbS Phase Diagram	9
3. The ZnS-PbS Phase Diagram	10
4. Microstructure of a 75 mol % FeS - 25 mol % ZnS matte after cooling at different rates from 1180°C	12
5. Microstructures of a 65 mol % FeS - 35 mol % PbS matte after cooling at different rates from 880° and 950°C	13 & 14
TABLES	
1. Experimental Liquidus and Eutectic Points	5

INTRODUCTION

Complex sulphide ores containing an intimate intergrowth of lead, zinc and copper sulphides in a matrix of pyrite occur in several regions of Canada, including the Bathurst area of New Brunswick. Milling experience has shown that appreciable amounts of zinc and lead are often lost in the pyrite tailings when these ores are floated^(1,2). Even very fine grinding (typically 80 % minus 400 mesh, Ref. 3) is not sufficient to allow a complete mineral separation during flotation.

The studies described here were undertaken to determine if the thermal treatment of these ores could be used to coarsen the grain size of the ore (i.e., increase the segregation of the constituents into larger grains that are separate and distinct chemical phases) to allow effective mineral recoveries by conventional flotation. This approach could be readily integrated into an existing milling circuit and would also be comparatively pollution-free.

Data on the system Zn-Fe-Pb-Cu-S has been reviewed previously⁽⁴⁾. The system Fe_xS -ZnS was reported to have an eutectic either at 6 mol per cent ZnS and 1170°C⁽⁵⁾ or 6 mol per cent ZnS and 1180°C⁽⁷⁾. In both cases, pyrrhotite (Fe_xS) with a melting point of 1188°C was used as one of the constituents. The maximum solubility of Fe_xS in β -ZnS was reported as 36.5 mol per cent at the inversion temperature of 894°C and decreased with decreasing temperature to 2 mol per cent at room temperature. More recent work has shown that these figures may be in error⁽⁶⁾. The maximum solubility of ZnS in Fe_xS was less than 3 mol per cent.

The system Fe_xS -PbS was reported to show an eutectic at either 48 mol per cent PbS and 863°C ^(7,8), 48 mol per cent PbS and 860°C ⁽⁹⁾, or 55 mol per cent PbS and 782°C ⁽¹⁰⁾. Solid solubility appears to be low in this system, although no accurate measurements are reported. The system ZnS-PbS was reported to have an eutectic at either 82 mol per cent PbS and 1040°C ⁽⁷⁾ or at 84 mol per cent PbS and 1045°C ⁽¹¹⁾. The solubility of ZnS in PbS was shown to be 0.6 mol per cent at 800°C and 1.5 mol per cent at 1000°C ⁽¹²⁾. The solubility of PbS in ZnS is probably low, although no accurate measurements are available. The system Fe_xS -ZnS-PbS was found to have an eutectic at 820°C and 8.5 mol per cent ZnS, 30 mol per cent FeS and 61.5 mol per cent PbS⁽⁷⁾.

Nixon et al.⁽¹³⁾ studied the recrystallization of mixtures of precipitated lead and zinc sulphides heated at 800°C in stainless steel bombs for three days. Crystals of sphalerite and galena up to 0.5 mm long were formed, and some of the galena contained an eutectic textural intergrowth of sphalerite.

EXPERIMENTAL

Materials

Lead sulphide (99.99+) and zinc sulphide (99.9995+), obtained from Electronic Space Products, Los Angeles, were dried at 120°C in a vacuum oven before use. Stoichiometric FeS (troilite) was prepared by heating hydrogen-reduced iron wire (99.9+) in the presence of sulphur vapour (99.999+)⁽¹⁴⁾. The FeS was found to undergo a small amount of oxidation while left standing, even under desiccating conditions. High-purity gold,

silver, and aluminum were used as temperature calibration materials for the DTA studies.

Apparatus and Procedure

The liquidus, eutectic and solid-state transformation temperatures of the sulphide systems were determined by means of differential thermal analysis (DTA). The samples, after grinding to minus 100 mesh, were vacuum-sealed into silica glass DTA ampoules and placed in a Stone DTA controlled-atmosphere system⁽¹⁷⁾. The thermocouples were contained in small wells in the bottom of the DTA ampoules. The samples were heated at a rate of 1°/min through the temperature zone at which transitions were observed. The apparatus was calibrated by determining the peak melting temperatures of gold (1063.0°C), silver (960.80°C) and aluminum (660°C). Sample temperatures were determined by taking the peak temperatures for the heating cycle and applying a correction factor of 5° to 7°C as determined by the calibration experiments. The temperature data were recorded on a multi-function meter and digital recorder and on an X-Y recorder. Selected samples were analyzed by X-ray powder diffraction after they had been heated and cooled.

The crystallization studies were carried out on samples vacuum-sealed into silica glass ampoules (7 mm I.D.) which were then sealed under vacuum within larger ampoules (11 mm I.D.). This system was necessary because the smaller ampoule would sometimes crack on cooling. The ampoules were heated and cooled at programmed rates in a small vertical tube furnace (Fisher DTA Model 260). Temperatures were measured by a

chromel-alumel thermocouple located next to the ampoule and were recorded on a Varian recorder. After cooling, the samples were mounted and polished and photomicrographs were made of representative areas of the samples. Selected samples were analyzed by X-ray powder diffraction and electronprobe.

RESULTS

Phase Equilibrium Studies

(a) The System FeS-ZnS

The results of the phase equilibrium analyses for this system are listed in Table 1 and shown in Figure 1. Liquidus temperatures were determined up to 1200°C, which corresponded to ZnS concentrations less than 12 mol per cent. The stoichiometric FeS (troilite) used in the study melted incongruently, with a solidus temperature of 1150°C and a liquidus temperature of 1161°C, in agreement with previous studies⁽¹⁵⁾. The system was eutectic in nature, with the eutectic point occurring at 6 mol per cent ZnS and 1135°C. This eutectic temperature was lower than that found previously^(5,7) when pyrrhotite (Fe_xS) with a melting point of 1188°C was used. Due to the differences in composition and liquidus temperatures of the iron sulphides used, the lower eutectic temperatures found in this study would be expected. The liquidus and eutectic temperatures would also be expected to vary with the sulphur vapour pressure over the mattes. In this study, these vapour pressures were not measured, but since the samples were sealed in silica glass ampoules, the vapour pressures should be equivalent to the equilibrium vapour pressure.

TABLE 1
Experimental Liquidus and Eutectic Points

System	Composition (mole %)			Temperature		
	FeS	PbS	ZnS	Liquidus	Eutectic	Transition
FeS-PbS	0	100		1114		
	5	95			834	
	10	90			835	
	15	85			837	
	20	80				
	25	75		1051	840	
	30	70		1043		
	35	65		1018	837	
	40	60		967	836	
	45	55		910	836	
	50	50		864	835	
	55	45		859	830	
	60	40		895	837	
	65	35		930	834	
	70	30		952	834	
	75	25		987	837	
	80	20		1022	834	
	85	15		1060	837	
	90	10		1092	837	
	95	5			837	
100	0		1161			

...cont'd

TABLE (cont'd)

System	Composition (mole %)			Temperature (°C)		
	FeS	PbS	ZnS	Liquidus	Eutectic	Transition
FeS-ZnS	50		50			814
	55		45			814
	60		40		1135	814
	65		35		1137	814
	70		30		1135	814
	75		25		1137	814
	80		20		1137	814
	85		15		1135	814
	90		10	1190	1135	814
	95		5		1135	814
	100		0	1161		
PbS-ZnS		50	50	1183	988	811
		55	45	1154	988	814
		60	40		988	811
		65	35		988	811
		70	30	1048	990	811
		75	25	1010	988	811
		80	20	1014	989	811
		85	15	1040	988	811
		90	10		989	811
		95	5		988	811
	100		0	1114		

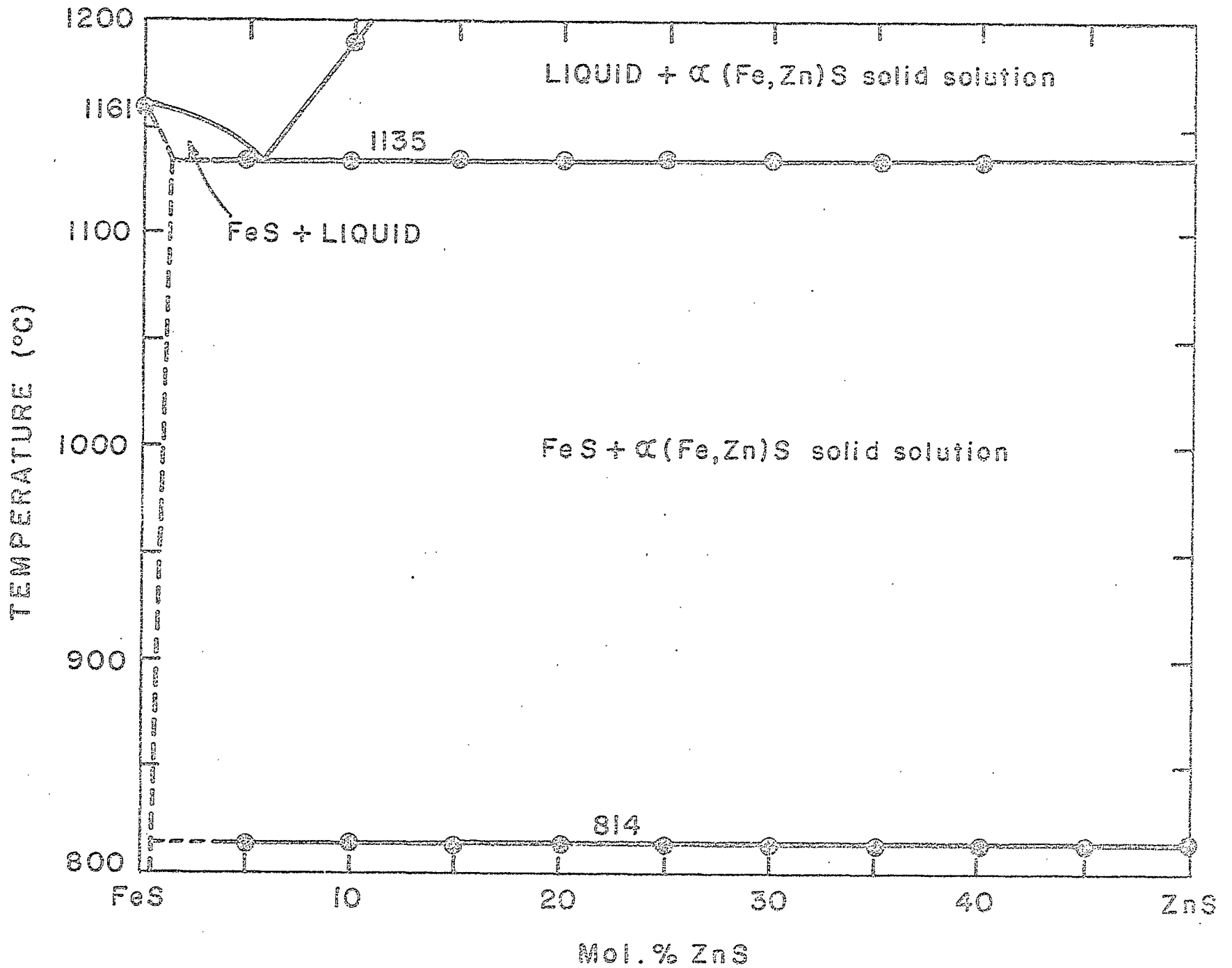


Figure 1: The FeS-ZnS Phase Diagram

The solid-state transformation from FeS plus α (Fe,Zn)S solid solution to FeS plus β (Fe,Zn)S solid solution was found to occur at 814°C, which was lower than previously reported (894°C) when pyrrhotite (Fe_xS) was used⁽⁵⁾.

(b) The System FeS-PbS

The results of the phase equilibrium analyses are listed in Table 1 and shown in Figure 2. The system was eutectic in nature, with the eutectic point occurring at 48 mol per cent PbS and 835°C. As with the previous system, the eutectic temperature was lower than the values reported^(7,8,9) using pyrrhotite (Fe_xS) rather than troilite (FeS). The PbS used in this study melted congruently at 1114°C, which agrees with the reported melting temperature of galena (1114°C)^(7,8).

(c) The System ZnS-PbS

The results of the phase equilibrium analyses are listed in Table 1 and shown in Figure 3. The system was eutectic in nature, with the eutectic point occurring at 78 mol per cent PbS and 988°C. The eutectic temperature was lower than those reported previously^(7,11). The solid-state transformation from PbS plus α -ZnS to PbS plus β -ZnS was found to occur at 811°C.

Matte Solidification Studies

(a) The System FeS-ZnS

Two heat treatments were used to examine the recrystallization behaviour of various compositions in the system FeS-ZnS. In the first program, samples were heated at 20°C/min to 1180°C, then cooled immediately at 20°C/min to room temperature. In the second program, the samples were heated at 20°C/min to 1180°C,

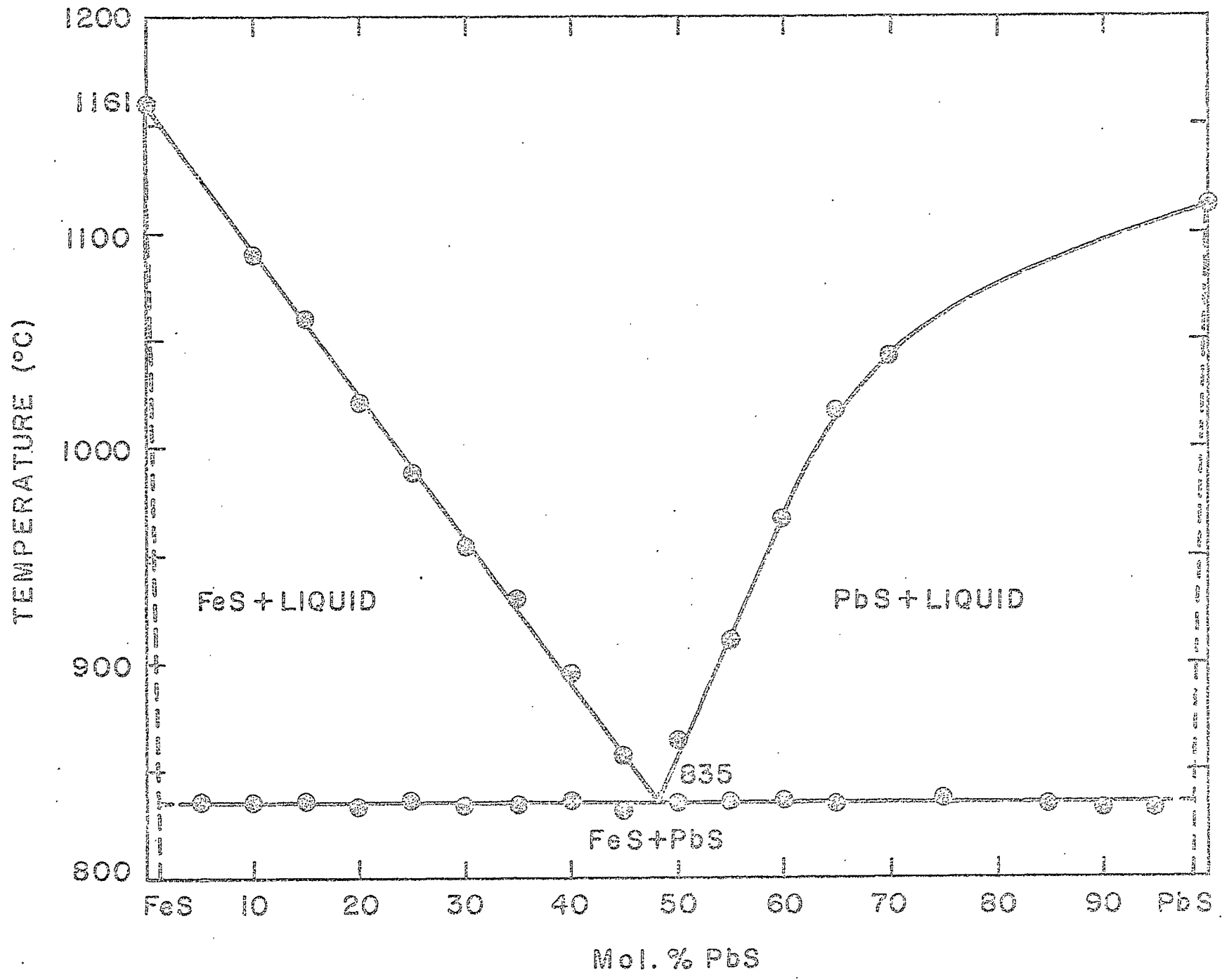


Figure 2: The FeS-PbS Phase Diagram

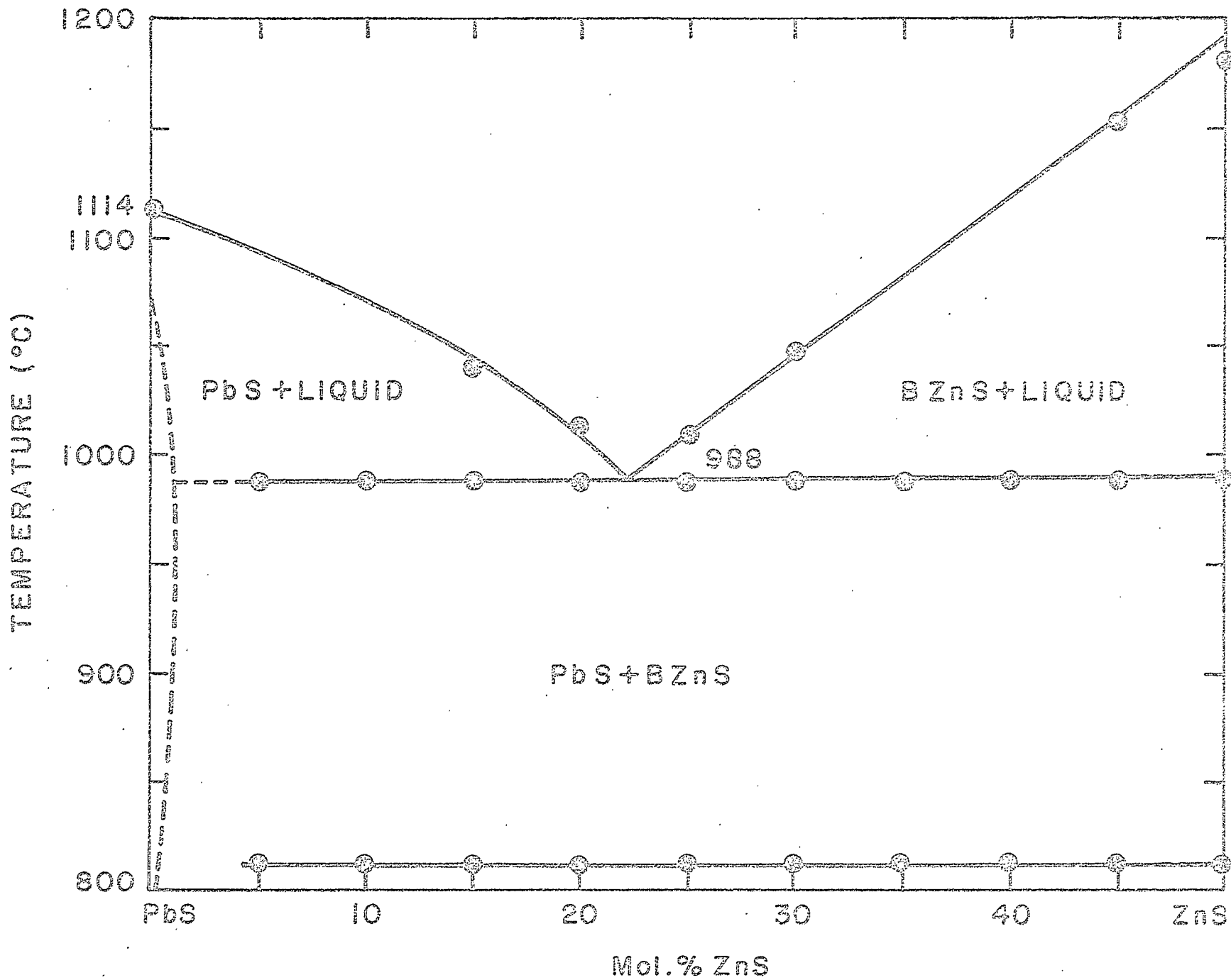


Figure 3: The PbS-ZnS Phase Diagram

held at this temperature for one hour, then cooled at 0.5°/min to room temperature.

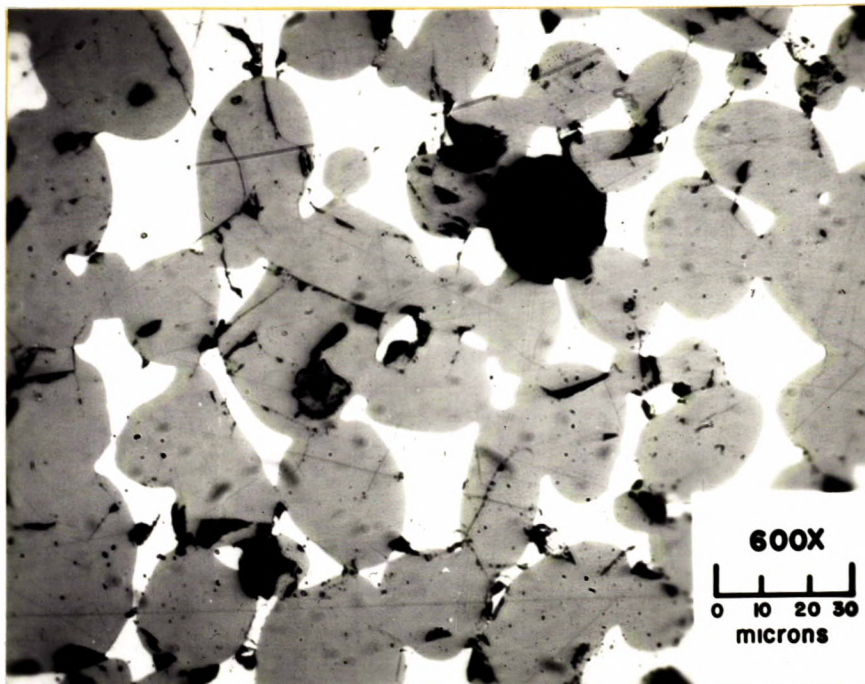
Two representative polished section of the samples subjected to each of these heating - cooling cycles are shown in Figure 4. The grains (\approx 15 microns diameter) in the first photomicrograph of the sample that had been cooled quickly are smaller than those in the second photomicrograph, (\approx 40 microns diameter, 350 mesh) of the sample that had been cooled slowly. The light phases in the photomicrographs are FeS and the darker phases are β .(Fe,Zn)S solid solution.

(b) The System FeS-PbS

Three heat treatments were used to examine the crystallization behaviour of various compositions in the FeS-PbS system. In the first program, samples were heated at 20°C/min to 880°C, then cooled immediately at 20°C/min to room temperature. In the second program, samples were heated at 20°C/min to 880°C, held for 1 hour at this temperature, then cooled at 0.5°/min to 600°C before being allowed to cool at 5°/min to room temperature. In the third program, samples were heated at 20°C/min to 950°C, held for 1 hour at this temperature, then cooled at 0.5°/min to room temperature.

Three representative polished section of the samples treated according to each of the programmes are shown in Figure 5. The grains (\approx 2 microns in width) in the first photomicrograph of the sample that had been cooled quickly are smaller than those in the other two photomicrographs (10 to 100 microns in width) of the samples that had been cooled less quickly. The light phases in the photomicrographs are PbS and the darker phases are FeS.

(a)



(b)

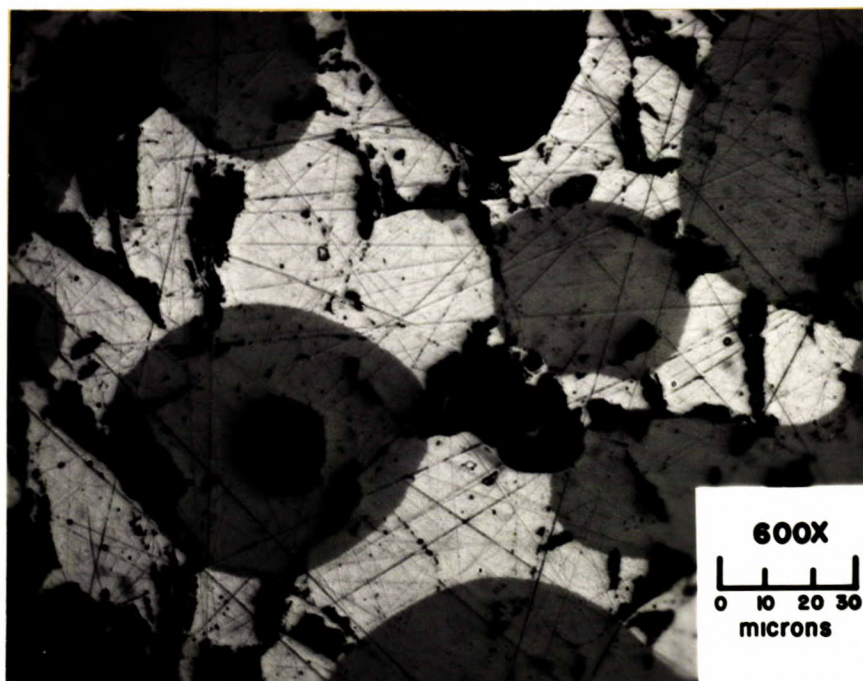


Figure 4: Photomicrographs of two samples (75 mol % FeS, 25 mol % ZnS) cooled from 1180°C at (a) 20°C/min and (b) 0.5°C/min.

(a)

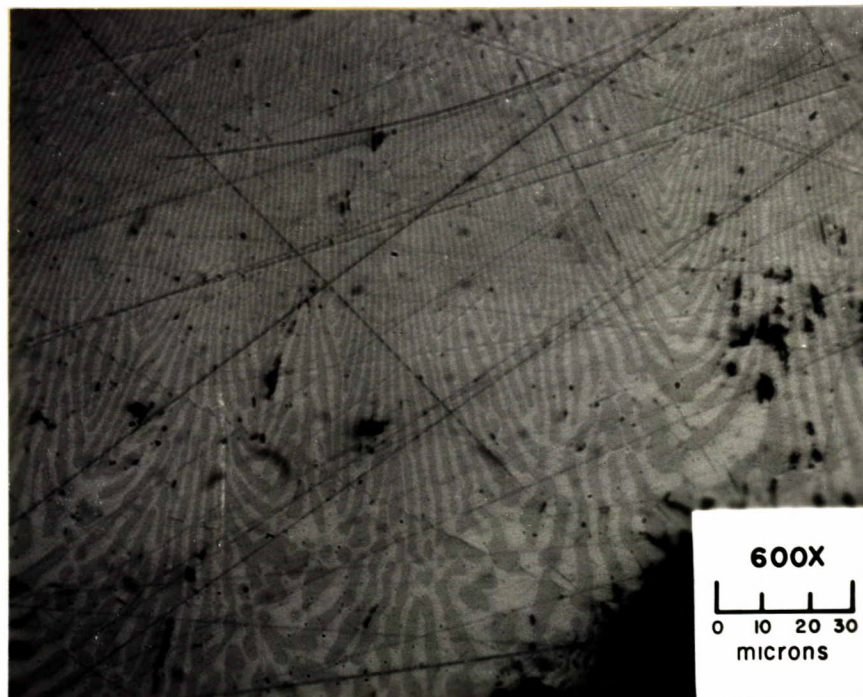
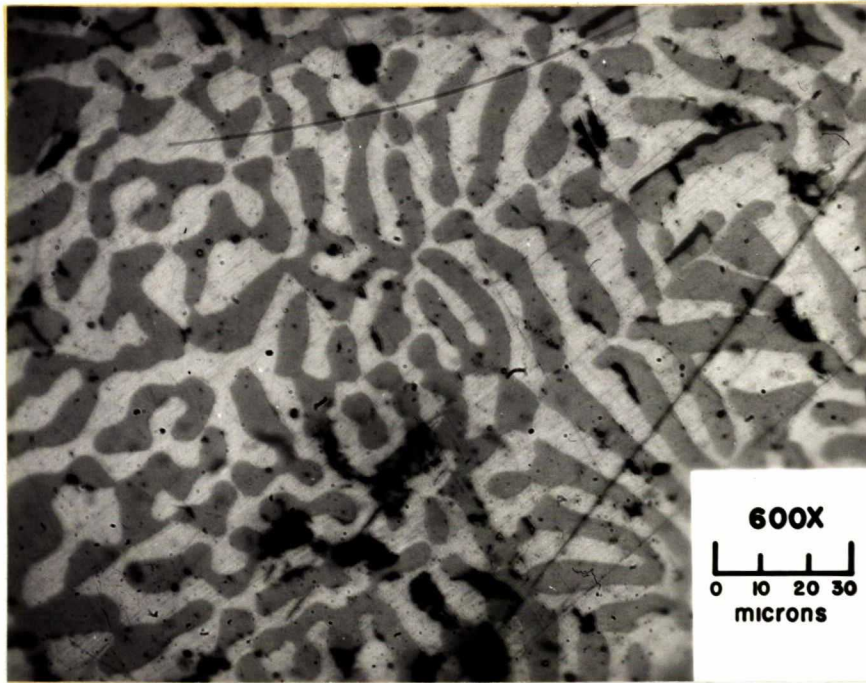


Figure 5: Photomicrographs of three samples (65 mol % FeS, 35 mol % PbS) cooled (a) from 880°C at 20°C/min, (b) from 880°C at 0.5°C/min and (c) from 950°C at 0.5°C/min.

(b)



(c)

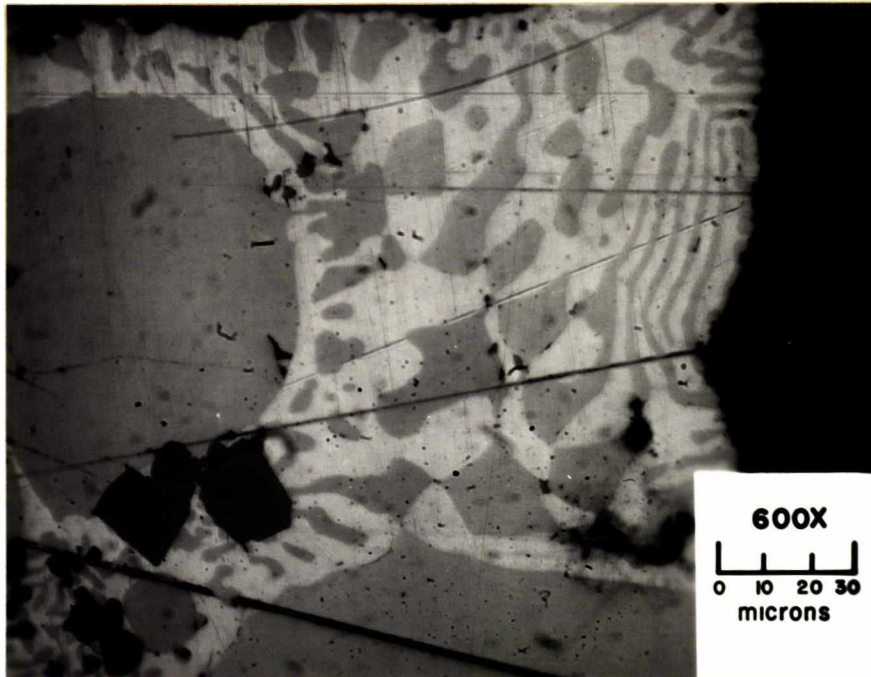


Figure 5: (Continued)

SUMMARY

The results of this study show that it is possible to coarsen the grain size of FeS-ZnS and FeS-PbS mattes by decreasing the rates of cooling. The grains consist of separate phases of FeS with a small amount of dissolved ZnS or PbS or PbS with a small amount of dissolved FeS, and of ZnS containing appreciable amounts of FeS in solid solution⁽⁴⁾. The grain sizes appear to be still too small (generally minus 325 mesh) to allow effective mineral separation of the crushed mattes by flotation. Slower cooling rates than those used in this study (0.5°C/min) will be necessary to increase the grain size sufficiently to allow good mineral separation.

The samples had been heated above the eutectic temperatures, as determined by the phase equilibrium analysis, so that a molten phase was present before cooling occurred. No attempt was made to determine if relatively rapid grain growth would occur if the samples were not first heated above the eutectic temperatures.

In all cases, the samples were heated in sealed, evacuated silica glass ampoules to prevent decomposition and volatilization of a portion of the sulphides and the oxidation of the remainder. When these studies are extended to determine the crystallization behaviour of Zn-Fe-Pb-S concentrates during thermal treatment in large furnaces, provision must be made both for preventing excessive thermal decomposition, volatilization and oxidation of the concentrates and for cleaning the off-gases from the furnace.

ACKNOWLEDGEMENTS

The author thanks Dr. K. Haque, a Winter Works employee, for doing a number of the experiments. The X-ray analyses were done by Mr. P. Belanger and the electronprobe analyses were done by Mr. D. Owens. Mr. P. O'Donovan mounted and polished the matte samples and P. Carriere photographed them. Helpful discussions with Dr. J. Dutrizac are acknowledged.

REFERENCES

1. Neumann, G. W., and Schmarr, J. R., "Concentrator Operation at Brunswick Mining and Smelting Corporations No. 12 Mine", Can. Inst. Min. Met. Bull. 74(9), 51-61 (1971).
2. Erskine, R. T., "No. 6 concentrator Operations at Brunswick Mining and Smelting Corporation Ltd.", Can. Inst. Min. Met. Bull., 74(9), 62-68 (1971).
3. Neumann, G. W., "Upgrading Brunswick's Concentrates", Eng. Mining J. 171(5), 78-79 (1970).
4. Dutrizac, J. E., "Literature Review on the Alkaline Leaching of Zinc Ores and on the Phase System Zn-Fe-Pb-Cu-S", Can. Mines Branch, Extraction Metallurgy Division Internal Report EMI 72-19 (1972).
5. Kullerud, G., "The Ferrous Sulphide - Zinc Sulphide System. A Geological Thermometer", Norsk. Geol. Tidsskr. 32, 61-147 (1953).
6. Toulmin, P., and Barton, P. B., "A Thermodynamic Study of Pyrite and Pyrrhotite", Geochim. Cosmochim. Acta 28, 641-671 (1964).

7. Avetisyan, Kh. K., and Gnatyshenko, G. I., "Thermal and Metallographic Study of the PbS-ZnS-FeS System", Izv. Akad. Nauk Kaz. SSR, Ser. Gorn. Dela, Met. Stroit it Stroim. 6, 11-25 (1956).
8. Friedrich, K., "The Melting Points of the Systems Galena-Pyrrhotite and Galena-Silver Sulphide", Metallurgie 4, 479-485 (1907).
9. Kopylov, N. I., "The FeS-Na₂S-PbS System", Rus. J. Inorg. Chem. 12(10) 1494-1498 (1967).
10. Wedmann-Aachen, H., "Galena", Metallurgie 3, 660-664 (1906).
11. Friedrich, K., "Zinc Sulphide as a Constituent of Mattes", Metallurgie 5, 114-128 (1908).
12. Bundel, A. A., Vishnyakov, A. V., "Solubility of Zinc Sulphide in Lead Sulphide in a Solid State", Tr. Mosk. Khim.-Tekhnol. Inst. 62, 87-89 (1969).
13. Nixon, J. C., Hayton, J. D., Lawrie, D. C. and Tyman, A. E., "Recrystallization of Lead and Zinc Sulphides", Nature 192, 516-518 (1961).
14. Dutrizac, J. E. and MacDonald, R.J.C., "The Synthesis of some Copper Sulphides and Copper Sulphosalts in 500-700 gram Quantities", Materials Research Bulletin 8(8), (1973, in press); Can. Mines Branch, Extraction Metallurgy Division Internal Report EMA 73-5 (1973).
15. Hansen, M., "Constitution of Binary Alloys", McGraw-Hill N.Y., 2nd ed. (1958), pp 704-708.

16. Bloem, J., and Kröger, F.A., "The p-T-x Phase Diagram of the Lead-Sulphur System", Z. Physik. Chem., Neue Folge 7, 1-14 (1956).
17. Ingraham, T. R., and Marier, P., "Heats of some Polymorphic Metal Sulphate Transitions Estimated by Semi-Quantitative Differential Thermal Analysis", Can. Met. Quart. 4(3), 169-175 (1965).