Phase relation of some sulfide systems-(3)

Arashi KITAKAZE (Museum of Sugaki Ore Collection)

Abstract:

Phase relation studies for binary system of Bi-Se, and ternary system such as Bi-Te-S, Cu-Bi-S, Fe-Mn-S and Fe-Bi-S have been performed by author and some students. Their results are described as mainly phase diagrams and re-determined for some synthetic phases in their systems.

***Key Words**: Bi-Te-S, Cu-Bi-S, Fe-Mn-S, Fe-Bi-S*

1. Introduction

I have been done the phase equilibrium studies of many sulfide systems since 1966 in Yamaguchi University and Tohoku University association with the staff and students in both universities as bachelor thesis, master's thesis and doctoral thesis. For some sulfide systems, I have been already published in some journals of scientific Societies [1),2)] or publication of University[3),4)]. However, because many experimental results are still unpublished or described by Japanese, I have wanted to continue to publish in conjunction with published results[2)].

The results ternary systems such as Bi-Te-S, Cu-Bi-S, Fe-Mn-S and Fe-Bi-S are described in this time.

2. Experimental Procedures

Synthetic experiments were mainly carried out by the silica-glass tube method which is about same described by Kitakaze *et. al.*[1),2)] and Kitakaze[3),4)]. Some systems were studied using the thermal gradient transporting method under hydrothermal conditions.

All the run products were examined by reflected light microscope and XRD by diffractometer for determination of phases and phase assemblages. Sometimes, XRD for some synthetic phases were performed using the Guinier method and cell parameters are refined by their data as same as Kitakaze[5)]. Some hydrothermally synthetic minerals were observed by SEM, and their chemical compositions for synthetic materials were analyzed by EPMA.

Differential thermal analysis (DTA) in the evacuated silica-glass tube was performed to obtain the temperatures of reactions causing the melting, decomposition, phase transition, or tie-line changes[1),2)].

3 Ternary systems

3-1. Bi-Te-S system

There are known hedleyite Bi_7Te_3, pilsenite Bi_4Te_3, tsumoite BiTe and tellurobismuthite Bi_2Te_3 as natural phases belonging to the Bi-Te join. There is only a phase, bismuthinite

Bi_2S_3 in the binary Bi-S, but no phase in the binary Te-S.

As the natural phases of the ternary compounds belonging to the system Bi-Te-S, a lot of minerals such as joseite-B: Bi_4Te_2S, joseite-A: Bi_4TeS_2, ptotojoseite Bi_4TeS_2, baksanite $Bi_6Te_2S_3$, sztrokayite Bi_3TeS_2, ingodite Bi(S,Te), sulfotsumoite Bi_3Te_2S and tetradymite Bi_2Te_2S are known. Their composition and crystal data are summarized in Table 3-1-1.

Table 3-1-1. Crystallographic data for the phases in the Bi-Te-S system

Minerals	Abbreviation	Chemical compositions	a	c
Hedleyite	hld	Bi_7Te_3	4.4700	119.0000
Pilsenite	pls	Bi_4Te_3	4.4460	41.9400
Tsumoite	Tsm	BiTe	4.4220	24.0500
Tellurobismuthite	tlb	Bi_2Te_3	4.3810	30.4707
Joseite B	js B	Bi_4Te_2S	4.3400	40.8300
Protojoseite		Bi_4TeS_2	4.3350	57.9200
Joseite A	js A	Bi_4TeS_2	4.2500	39.7700
Baksanite		$Bi_6Te_2S_3$	4.2490	62.8200
Sulphotsumoite		Bi_3Te_2S	4.3160	23.4300
Ingodite		Bi(S,Te)	4.2480	23.2200
Sztrokayite		Bi_3TeS_2		
Tetradymite	tdy	Bi_2Te_2S	4.2388	29.5755

The phase relation of the Bi_2Te_3-Bi_2S_3 join in the Bi-Te-S system was investigated by Yusa(1979)[6], Yusa *et al.* (1979)[7),8)]. As the phases of the Bi_2Te_3-Bi_2S_3 join, tetradymite (Bi_2Te_2S) besides tellurobismuthite (Bi_2Te_3) and bismuthinite (Bi_2S_3) exist in the join. The phase relations among them above 350°C are shown in Fig. 3-1-1. According to the figure, there is tetradymite only between tellurobismuthite and bismuthinite of the end members, but no csiklovaite above 350°C. Tetradymite forms a limited solid solution (33.8 to 43.0 mol % Bi_2S_3 at 500°C) as enlarging in proportion to temperature increase, and congruently melts at 640°C in 40.8 mol % Bi_2S_3. As seen in the diagram, two eutectic points are found at 580°C (8.0 mol % Bi_2S_3) and 628°C (50.3 mol % Bi_2S_3) between tellurobismuthite and tetradymite, and tetradymite and bismuthinite, respectively.

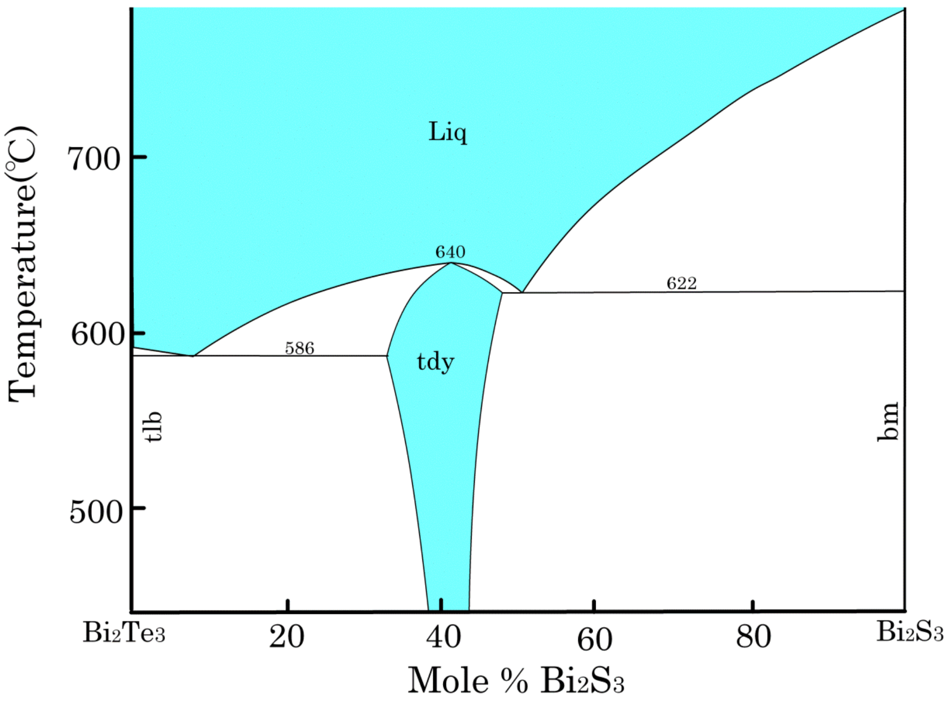

Fig. 3-1-1. Phase diagram for Bi_2Te_3-Bi_2S_3 join in the Bi-Te-S system above 450°C (modified after Yusa; 1979[7]). Abbreviations are shown in Table 3-1-1.

The phase relations of the ternary system Bi-Te-S at 500° and 400°C were made study by Yusa . (1979)[6] and Yusa *et al*. (1979)[7],[8]. The phase diagram of the isothermal section in the system Bi-Te-S at 500°C is shown in Fig. 3-1-2. There are found five crystalline phases of wehrlite, tellurobismuthite, bismuthinite, tetradymite, and joseite-A at 500°C. Two liquid phases of bismuth and tellurium-sulfur also exist in a considerable field. Seven univariant assemblages such as bismuthinite + joseite-A + bismuth-rich liquid, bismuthinite + joseite-A + tetradymite, bismuthinite + tetradymite + tellurium-rich liquid, joseite-A + tetradymite + bismuth-rich liquid, tetradymite + wehrlite + bismuth-rich liquid, tetradymite + tellurobismuthite + tellurium-rich liquid and tetradymite + wehrlite + tellurobismuthite are recognized in the isothermal diagram.

Joseite-A, tetradymite and wehrlite form a limited range solid solution. Compositions of joseite-A solid solution are $Bi_{4.2}Te_{0.7}S_{2.1}$ to $Bi_{4.1}Te_{0.8}S_{2.1}$ and assembles with bismuthinite, tetradymite and bismuth-rich liquid. But it can not associate with wehrlite, tellurobismuthite and tellurium-rich liquid. Joseite B, protojoseite, gruenlingite, and sulphotsumoite of natural phases with the ternary composition do not appear in the isothermal diagram at 500°C.

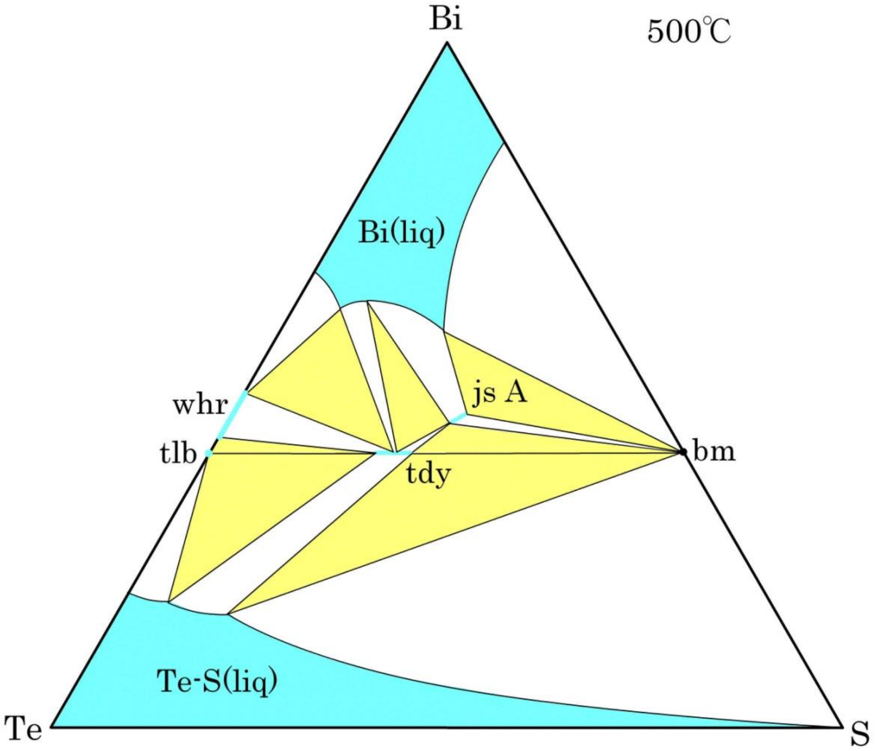

Figure 3-1-2. Isothermal section of Bi-Te-S ternary system at 500°C (modified after Yusa; 1979)[7].

Abbreviations seen in Table 3-1-1.

The isothermal diagram at 400°C is shown in Fig. 3-1-3 (Yusa 1979)[7]. Joseite-B appears at this temperature as a limited solid solution from $Bi_{3.95}Te_{0.90}S_{2.15}$ to $Bi_{4.15}Te_{1.75}S_{2.10}$ at 400°C. Joseite-A, tetradymite and wehrlite also form the solid solution of the limited range similar to those at 500°C. Joseite-A has compositions from $Bi_{4.0}Te_{0.8}S_{2.2}$ to $Bi_{3.7}Te_{1.2}S_{2.1}$ which are more wide range and less sulfur composition than those at 500°C. Compositions of tetradymite and wehrlite solid solutions are Bi_2Te_2S to $Bi_{2.0}Te_{1.8}S_{1.2}$ and $Bi_{57}Te_{43}$ to $Bi_{43}Te_{57}$, respectively. The tie line between tetradymite and bismuth-rich liquid at 500°C (Fig. 3-1-2) disappears because joseite-B appears at 400°C, and the tie lines from joseite-B to joseite-A, tetradymite, wehrlite and bismuth-rich liquid are newly formed. Continuous and considerably wide range of tellurium-sulfur liquid observed at 500°C abruptly reduces its field to very narrow area of sulfur (-tellurium) liquid, and tellurium appears as a crystalline phase with a very small solid solution field.

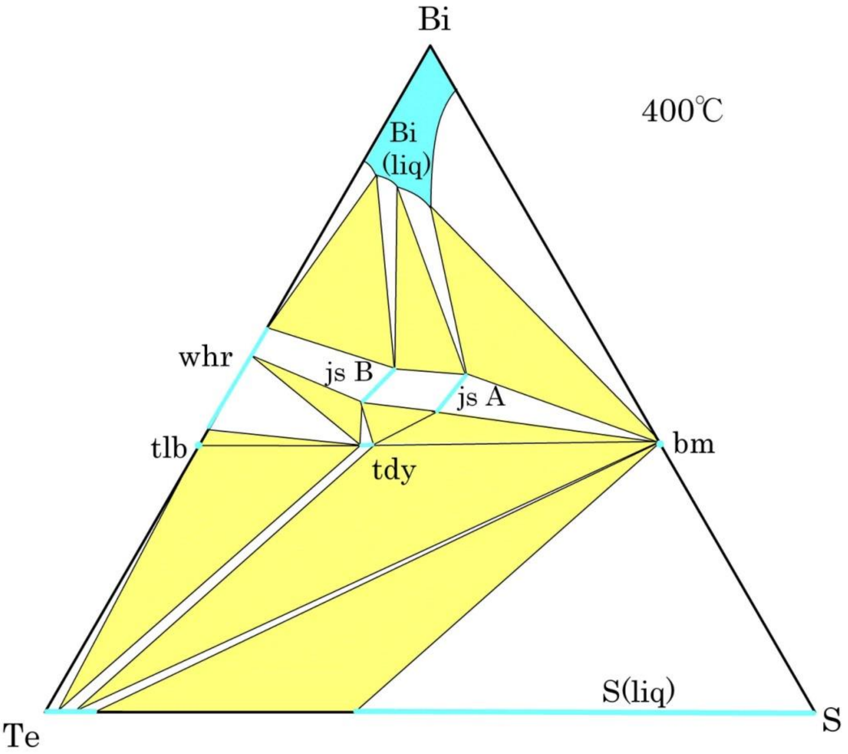

Figure 3-1-3. Isothermal section of Bi-Te-S ternary system at 400°C (modified after Yusa; 1979)[7)]

Abbreviations are seen in Table 3-1-1.

In the isothermal diagram at 400°C, there are ten univariant assemblages as follows: bismuthinite + joseite A + bismuth-rich liquid, joseite A + joseite B + bismuth-rich liquid, joseite B + wehrlite + bismuth-rich liquid, bismuthinite + tetradymite + joseite A, tetradymite + joseite A + joseite B, tetradymite + joseite B + wehrlite, bismuthinite + tellurium + sulfur liquid, bismuthinite + tetradymite + tellurium, tetradymite + tellurobismuthite + tellurium and tetradymite + tellurobismuthite + wehrlite. Other ternary minerals such as csiklovaite, gruenligite, sulphotsumoite, protojoseite and joseite-C do not appear during the phase equilibrium works at 400°C.

The pseudo-binary phase diagram along the Bi_4Te_3-Bi_4S_3 join in the system Bi-Te-S was shown in Fig. 3-1-4 (Yusa 1979). There are recognized many divariant and univariant assemblages in the join, and joseite B and joseite A are stable up to about 495°C and about 545°C, respectively, according to their compositions, and incongruently melts to tetradymite + joseite A + bismuth-rich liquid, and tetradymite + bismuthinite + bismuth-rich liquid, respectively at those temperatures as above.

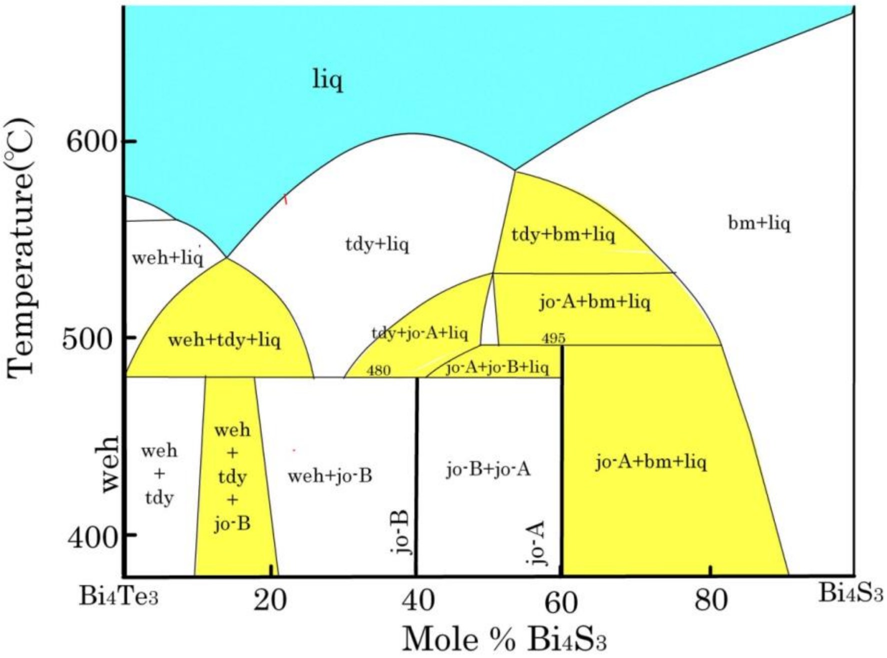

Figure 3-1-4. Pseudo-binary phase diagram for Bi_4Te_3-Bi_4S_3 join in the Bi-Te-S system above 390°C (modified after Yusa; 1979). Abbreviations are seen in Table 3-1-1.

Phase relations of Bi-rich region for Bi-Te-S system at about 300°C are shown in Fig. 3-1-5. Joseite A, joseite B and tetradymite are appeared as ternary compounds. Joseite B has narrow solid solution range from $Bi_{3.98}Te_{1.97}S_{1.05}$ to $Bi_{4.12}Te_{1.71}S_{1.17}$, which are somewhat sulfur rich than ideal composition of Bi_4Te_2S and their range for joseite A is from $Bi_{3.99}Te_{0.83}S_{2.17}$ to $Bi_{4.00}Te_{2.00}S_{1.00}$ including the stoichiometric composition of $Bi_4Te_2S_3$ which is very narrower than joseite B. Both solid solution range at 300℃ are very similar to those of natural specimens.

There are univariant assemblages of hedleyite + joseite B + Bi, joseite B + joseite A + Bi and joseite B + wehrlite + tetradymite which are observed in natural occurrence (Sugaki et al, (1980)[9] and Kitakaze unpublished data).

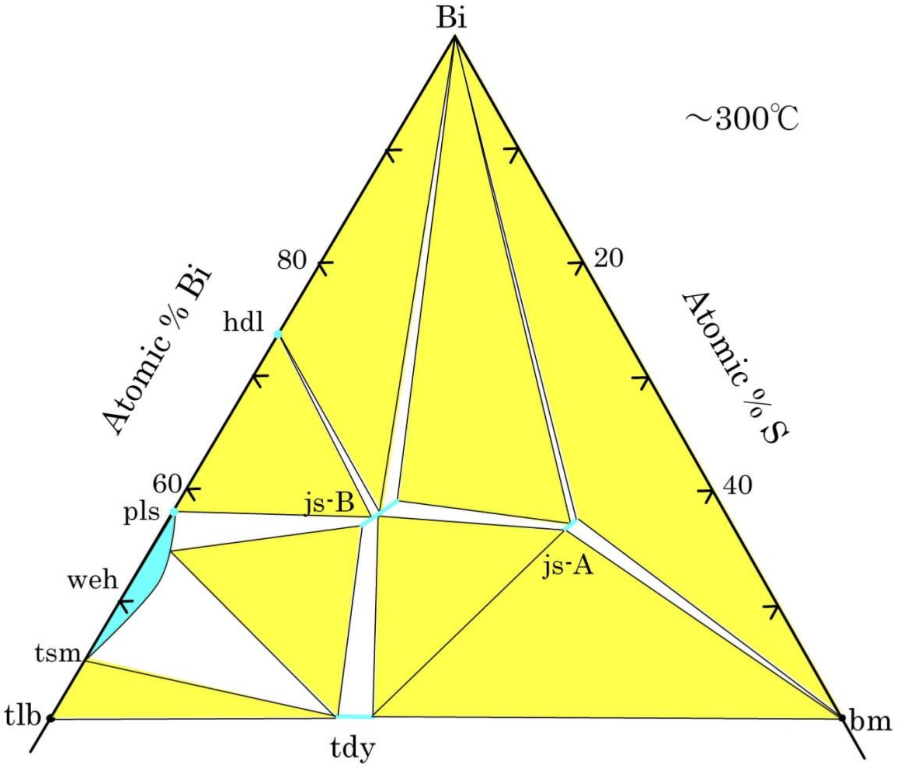

Figure 3-1-5. Tentative phase diagram of Bi-rich region in the Bi-Te-S system at about 300°C. Abbreviations are seen in Table 3-1-1.

3-2 Cu-Bi-S system

In the Cu-Bi-S system, common copper bismuth sulfosalt minerals such as wittichenite (Cu_3BiS_3), emplectite ($CuBiS_2$) and cuprobismutite ($Cu_{10}Bi_{12}S_{23}$) were known widely. Also as synthetic phases such as Cu_9BiS_6 (phase X), $Cu_3Bi_5S_9$ (phase D) and $CuBi_3S_9$ (phase D) belonging in Cu_2S-Bi_2S_3 join and $Cu_4Bi_4S_9$ (phase Y) as sulfur rich phase were appeared in the Cu-Bi-S ternary system. There crystallographic data are shown in the Table 3-2-1, and their thermal stabilities are also given in Table 3-2-2.

Table 3-2-1. Minerals and synthetic phases in the Cu-Bi-S ternary system

Mineral names	Abbreviations	Chemical composition	Cell parameters			
			a	*b*	*c*	*β*
Phase X	X	Cu_9BiS_6	5.563(1)	-	-	-
wittichenite	wit	Cu_3BiS_3	7.694(1)	10.393(3)	6.710(1)	-
High-form witthenite	h-wit	Cu_3BiS_3	-	-	-	-
Emplectite	emp	$CuBiS_2$	6.144(1)	14.525(1)	3.925(1)	-
cuprobismutite	cpb	$Cu_{10}Bi_{12}S_{23}$	17.513(3)	3.909(1)	15.255(3)	101.09(2)
Phase D	D	$Cu_3Bi_5S_9$	13.08(1)	4.00(1)	14.70(1)	99.4(1)
Phase E	E	$CuBi_3S_5$	13.221(2)	4.023(1)	14.077(4)	115.46(3)
Phase Y	Y	$Cu_4Bi_4S_9$	11.146(3)	32.05(1)	3.953(3)	-

Table 3-3-2. Stability range of the minerals and synthetic phases in Cu-Bi-S system.

Mineral names	Chemical composition	Thermal stability		Reactions
		Low limit	High limit	
Phase X	Cu_9BiS_6	390	650	Incongruent melting
Wittichenite	Cu_3BiS_3	-	350	Inversiton to high form
high-form witthenite	Cu_3BiS_3	350	527	Conguruent melting
Emplectite	$CuBiS_2$	-	318	Decompose to witthenite + cuprobismutite
cuprobismutite	$Cu_{10}Bi_{12}S_{23}$	316	474	Decomposed to witthenite + phase D
Phase D	$Cu_3Bi_5S_9$	442	620	Incongruent melting
Phase E	$CuBi_3S_5$	280	649	Incongruent melting
Phase Y	$Cu_4Bi_4S_9$	-	>500	

The phase equilibrium of the Cu_2S-Bi_2S_3 join in the Cu-Bi-S system was studied by Sugaki and Shima (1972) 10) using the evacuated glass-tube method, and Sugaki *et al*. (1980 11), 1984 12)) using a hydrothermal re-crystallization technique. The phase diagram of the Cu_2S-Bi_2S_3 join summarized experimental data by Sugaki & Shima (1972) 10) and Sugaki *et al*. (1980) 11) is shown in Fig. 3-2-1.

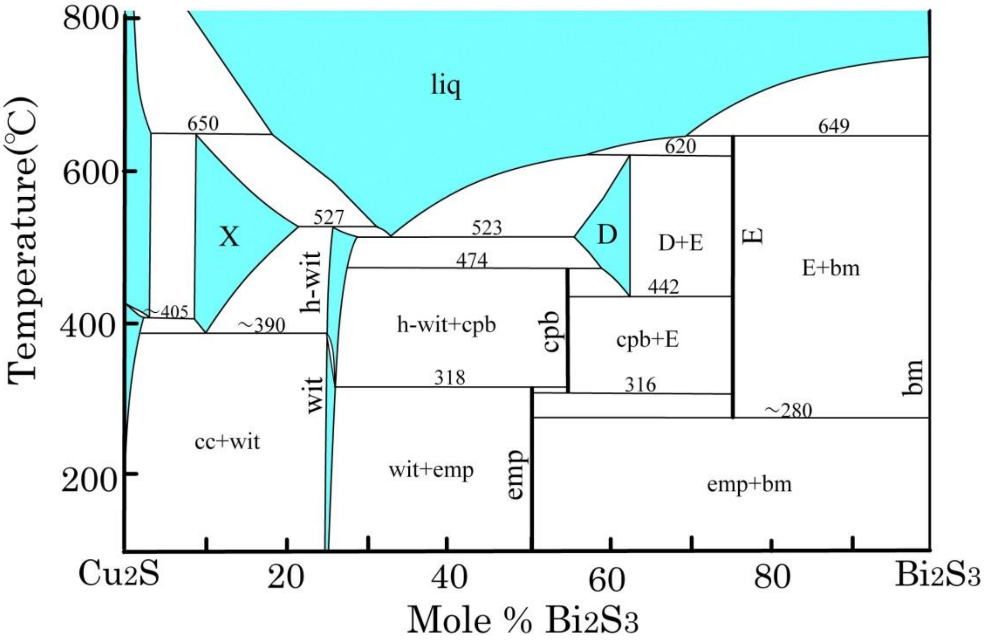

Figure 3-2-1. Phase relations for Cu_2S-Bi_2S_3 join in the Cu-Bi-S system (modified after Sugaki *et al.*, 1980 11)). Abbreviations are seen in Table 3-3-1.

As the crystalline phases, chalcocite (Cu_2S), phase X, wittichenite, emplectite, cuprobismutite, phase D, phase E and bismuthinite (Bi_2S_3) are found in the join. The phases X, phase D and phase E have not been found in natural ores because they are unstable at room temperature. The phase X is stable between 650 and 390°C. Synthetic wittichenite is identical with the natural one in every respect. Though it has the composition of stoichiometric Cu_3BiS_3 at room temperature, it transform to high-temperature phase at from 318 to 390°C, and forms a solid solution in a very limited range, shifting toward Cu_2S-poor composition at high temperature as seen in the figure. The wittichenite solid solution extends from 26.5 to 28.5 mol % Bi_2S_3 at 500°C.

The solid solution of nearly 27.5 mol % Bi_2S_3 incongruently melts to phase X and liquid at 527°±5°C. Cuprobismutite breaks down to wittichenite and phase D at 474°C. The phase D is stable in the temperature range between 442± 5°Cand 620±5°C, at which it incongruent1y melts to phase E and liquid. It dissolves a considerable amount of the Cu_2S molecule in solid solution, and its maximum limit is 56.5 mol % at 523°C. The eutectic point between the wittichenite solid solution and phase D solid solution is 523±5°C at about 35 mole % Bi_2S_3.

The phase E is stable below 640±5°C and incongruently melts at this temperature to bismuthinite Bi_2S_3 and liquid. Emplectite has a stoichiometric composition of $CuBiS_2$ but cuprobismutite has a little bismuth-rich composition of $Cu_{10}Bi_{12}S_{23}$. Emplectite is only stable below 318±3°C, while cuprobismutite is never synthesized below 316±3 °C. There is a narrow field of coexistence of both minerals at temperature from 316° to 318℃ in a composition range from 50 to 54.5 mol % Bi_2S_3. From the results of our experiments, emplectite and cuprobismutite are not in dimorph, but are two independent phases with different compositions.

The phase E is stable above approximately 280°C and does not appear below this temperature, but the assemblage of emplectite and bismuthinite forms as found in natural ores. Thus, the phase E could not be expected to be found in nature, while wittichenite could not associate with bismuthinite in an equilibrium state.

The phase relations of the Cu-Bi-S ternary system are studied by Sugaki *et al.* (1980)[11)] which is 500, 460, 400, 300, 250 and 200°C were determined by using the evacuated glass-tube method (Nomiyama 1976)[12)] and using a hydrothermal synthetic method (Sugaki *et al.* 1980[11)]). The phase $Cu_4Bi_4S_9$ (Nomiyama 1968)[12)] which is more sulfur-rich compound than the sulfosalts along the Cu_2S-Bi_2S_3 join appears to be stable in the ternary system.

The isothermal section of the phase diagram in the system at 500°C is shown in Fig. 3-2-2. In this figure, high digenite solid solution, covellite, phase X solid solution ($Cu_{9-x}Bi_{1+x}S_{6+x}$), high-wittichenite, phase D, phase E, phase Y and Cu metal are found as stably crystalline phases with three liquids of intermediate sulfide, bismuth and sulfur. In the S-rich field of the diagram, the crystalline phases assemble with the intermediate sulfide liquid or/and S (1), while in the S-poor side of the diagram they associate with bismuth liquid which dissolves some amount of Cu and S. The phase Y assembles with the phase D solid solution, the intermediate sulfide liquid and S(l). High-wittichenite associates with phase X, phase D, intermediate sulfide liquid and bismuth liquids. But it cannot be assemble with digenite solid solution, covellite and bismuthinite. There are found 16 univariant assemblages in the diagram (Fig. 3-2-2).

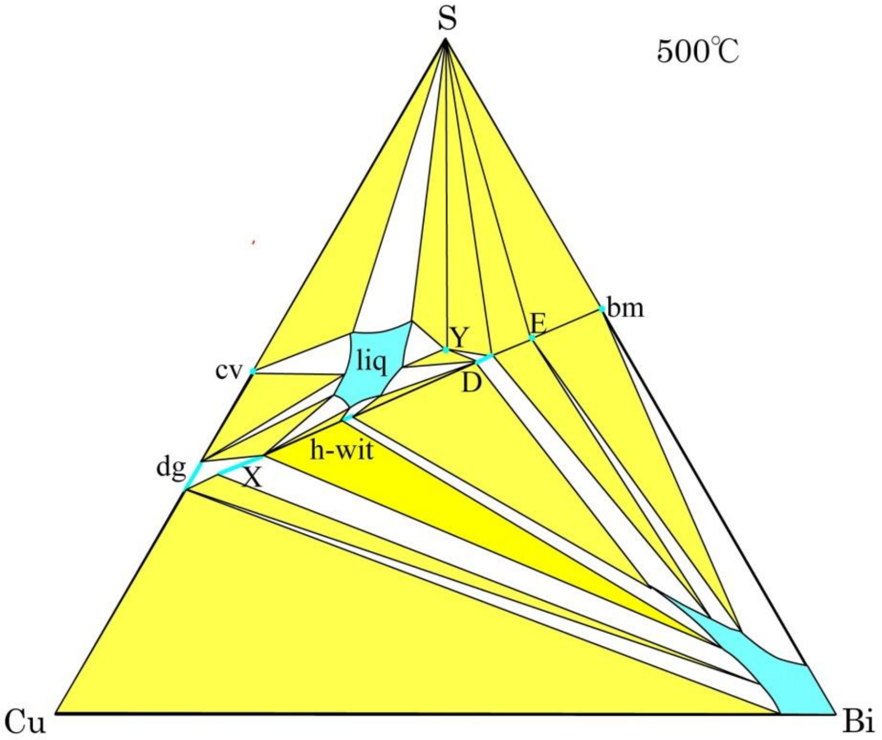

Figure 3-2-2. Isothermal section of Cu-Bi-S system at 500°C (compiled after Nomiyama 1968)[12).].

Abbreviations are seen in Table 3-2-1.

At 474°C cuprobismutite appears. The phase relation in the isothermal section at 460°C is shown in Fig. 3-2-3. The intermediate sulfide liquid found at 500°C disappears at about 470°C, and as its result the tie lines of covellite-high-form wittichenite, high-wittichenite-phase Y and covellite-phase Y occur newly. High-wittichenite, phase D, phase X form a limited range solid solution besides high digenite(-chalcocite) solid solution at 460°C. Cuprobismutite associates with wittichenite, phase D, phase Y and bismuth liquid, but cannot assemble with high digenite solid solution, covellite and sulfur (1). The 16 univariant assemblages are found in the diagram.

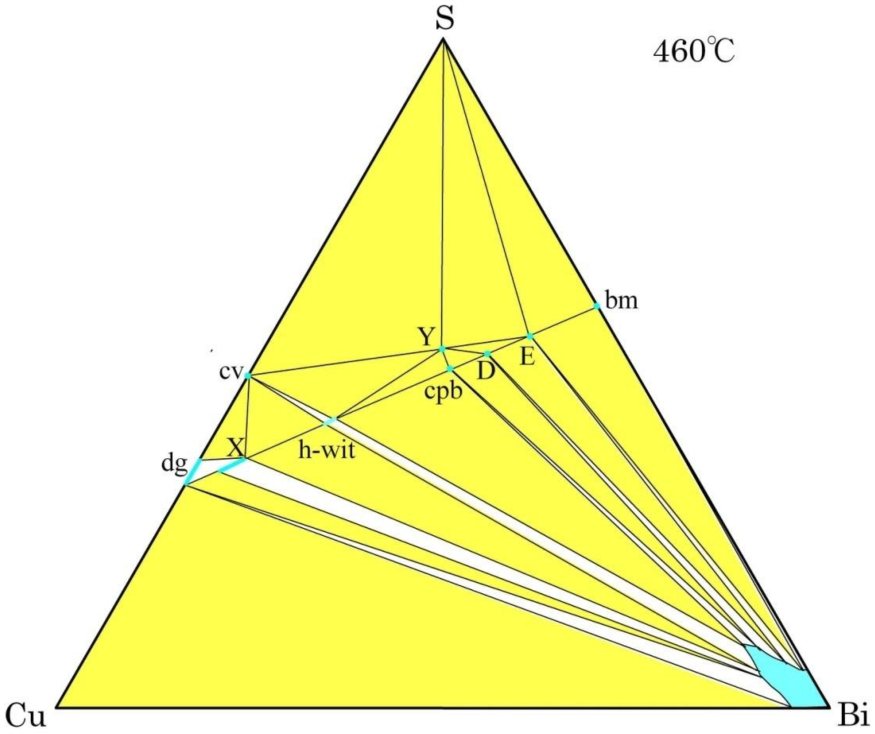

Figure 3-2-3. Isothermal section of Cu-Bi-S system at 460°C (compiled after Sugaki *et al*., 1980)[11).]

The isothermal diagram of the system at 400°C is shown in Fig. 3-2-4. The phase D disappears at 442°C and tie line of phase E –S(l) changes to phase Y - bismuthinite assemblage at about 410°C. Thus, cuprobismutite assembles with phase E, high-wittichenite, phase Y and bismuth liquid, but not with high digenite solid solution, covellite, bismuthinite and S(l). The phase X, high-wittichenite and high digenite have a very limited range of the solid solution at 400°C. There are also 15 univariant assemblages as shown in the figure.

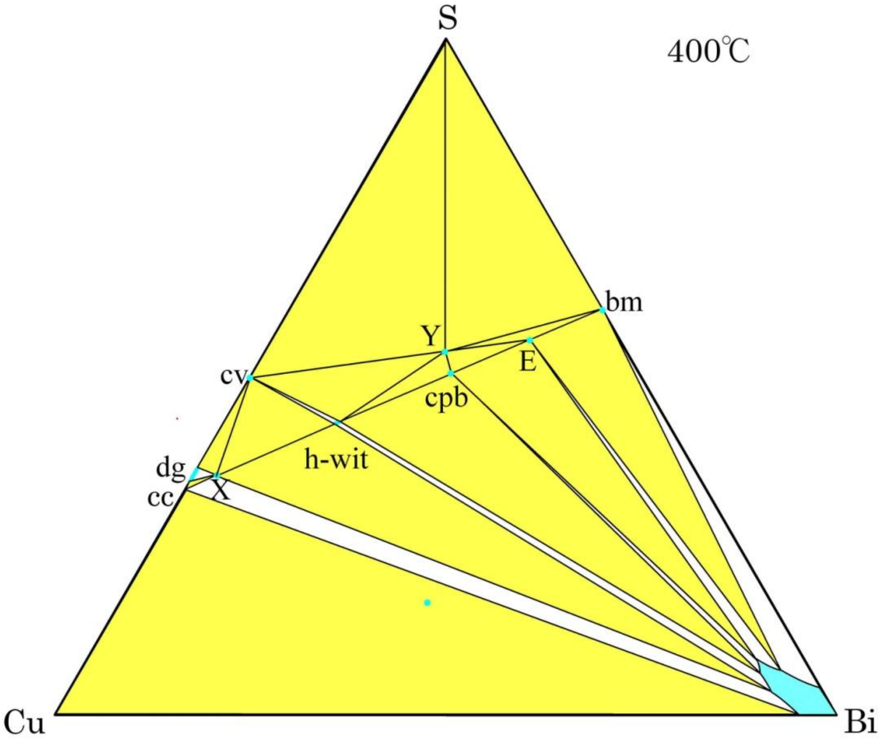

Figure 3-2-4. Isothermal section of Cu-Bi-S system at 400°C. (compiled after Nomiyama 1968)[12)].

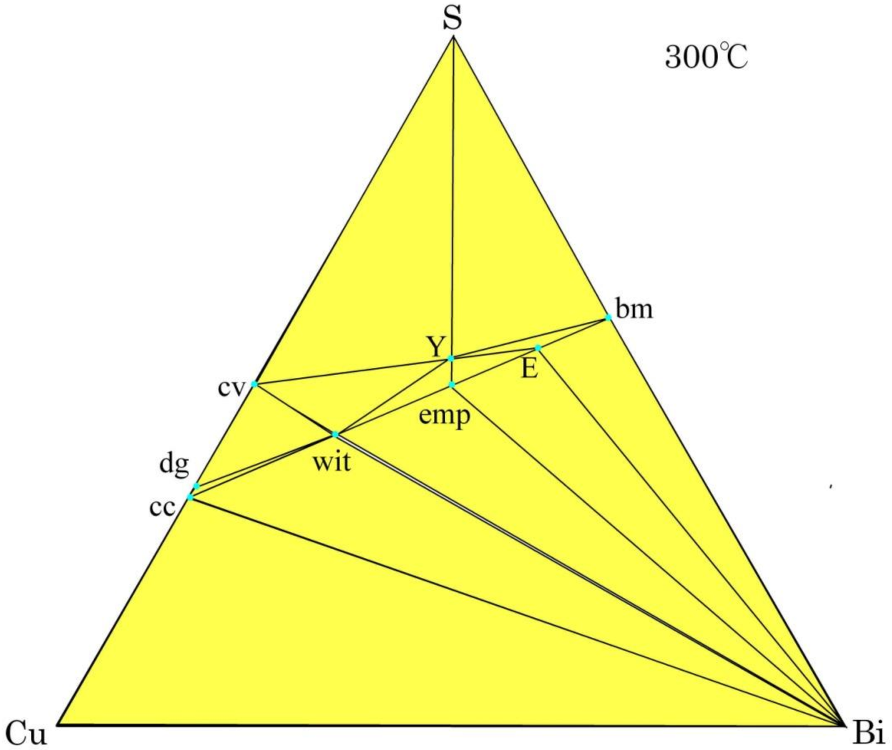

Figure 3-2-5. Isothermal phase diagram of Cu-Bi-S system at 300°C.

At 390°C the phase X disappears. While emplectite appears at 318°C, is as a stab1e phase until room temperature. However, cuprobismutite disappears at 316°C. High-form wittichenite is inverted to low form at 350°C. The phase relation of the isothermal section at 300°C are shown in Fig. 3-2-5. The assemblages of high digenite solid solution wittichenite, wittichenite-emplectite, emplectite-phase Y and emplectite-phase E occur. Wittichenite has a solid solution of very limited range. There are found 12 univariant assemblages as shown in the figure.

The phase E and cuprobismutite disappear below about 280 and 316°C, and emplectite appears below 318°C. Tie line between phase Y and sulfur liquid disappears about 325°C. There are three phases only such as wittichenite, emplectite and phase Y as stable phases of the ternary compounds as shown in Fig. 3-2-6 at 250°C. They become almost a stoichiometric composition at this temperature. Emplectite coexists with bismuthinite, wittichenite and bismuth, but wittichenite can not assemble with bismuthinite at 250°C as shown in the figures.

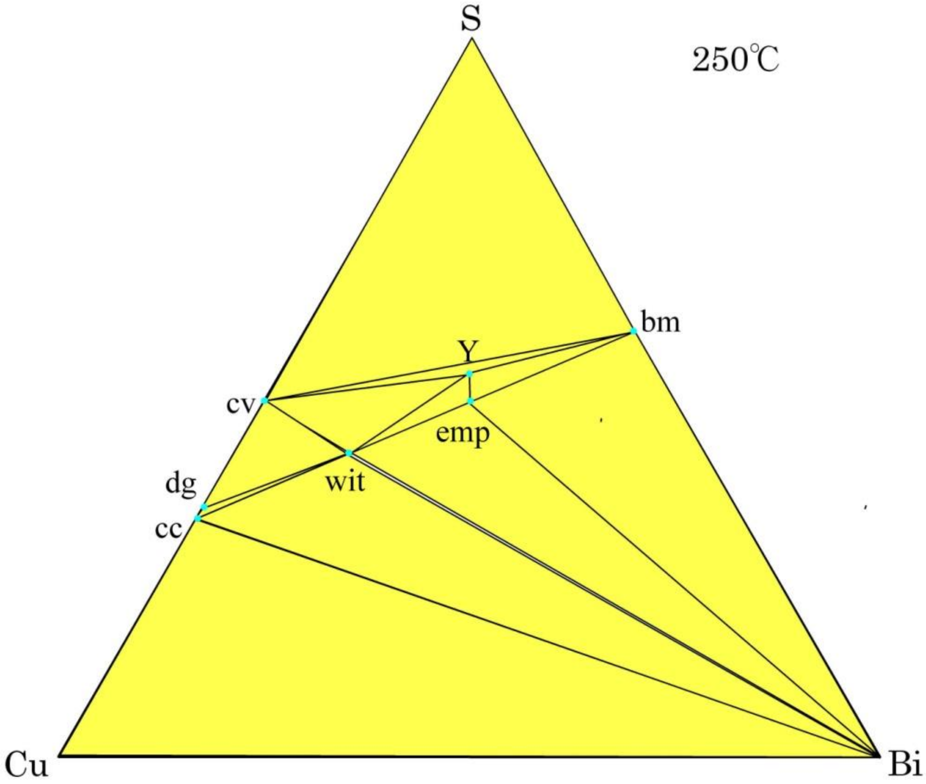

Figure 3-2-6. Isothermal phase diagram of Cu-Bi-S system at 250°C.

Tentative phase relations at 25°C are given in Fig. 3-2-7. All crystalline phases at this temperature have a stoichiometric composition, and their phase relations are almost the same as those at 260 °C except appearance of the copper sulfide minerals such as djurleite, anilite, and blaublender covellite instead of digenite which disappears below about 70°C. Thus, wittichenite also assembles with copper sulfides such as chalcocite, djurleite, anilite, blaublender covellite, and covellite, in addition to emplectite and phase Y, not with bismuthinite in the equilibrium state.

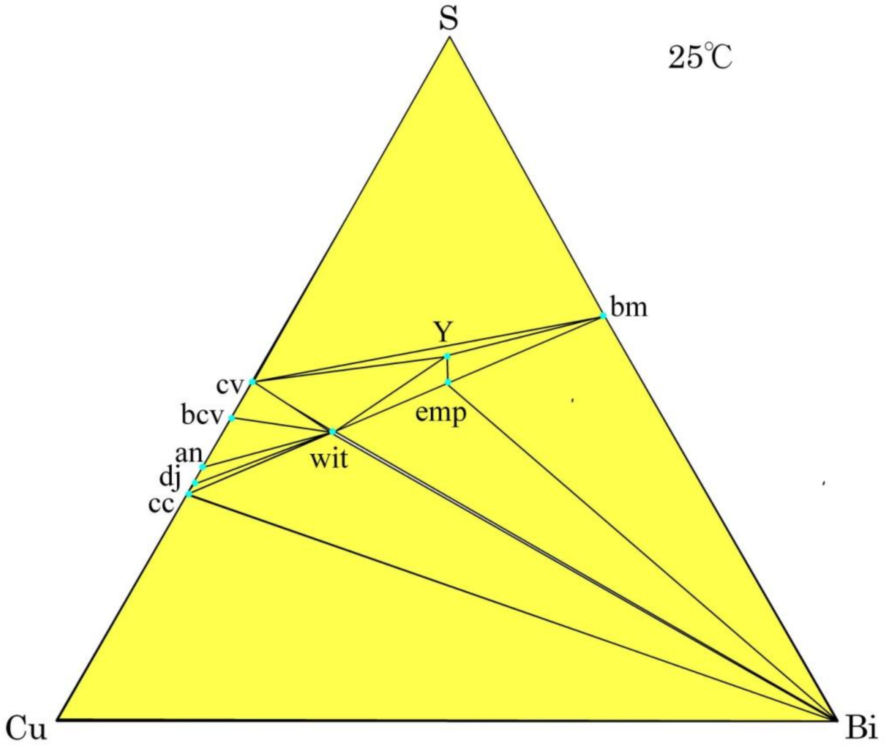

Figure 3-2-7. Isothermal phase diagram of Cu-Bi-S system at 250°C.

The sulfur fugacites (fs_2) of the univariant assemblages at temperature (T in °K) from 300°C to 500°C were measured by Kitakaze (unpublished data) using the electrum tarnish and pyrrhotite indicator methods, and the sulfur fugacity (log fs_2) and temperature (1/T) diagram for following univariant assemblages was obtained as shown in Fig. 3-2-8. Phase Y + bismuthinite + phase E, phase Y + wittichenite + cuprobismutite (or emplectite), bismuthinite + phase E + bismuth (1), phase D + cuprobismutite + bismuth (1), cuprobismutite + wittichenite + bismuth (1), wittichenite + phase X + bismuth (1) and phase X + chalcocite + bismuth (1). Also, in the figure the log fs_2-1,000/T relation curves of coexistence of sulfur vapor (V)-sulfur liquid (1), pyrite-pyrrhotite and troilite-iron are shown as a standard. As seen in the figure, the assemblages with phase Y exists in the pyrite field (high sulfur fugacity region), meanwhile the assemblages accompanied by bismuth (1) are in the pyrrhotite field (low sulfur fugacity region). Then, if phase Y occurs naturally, it may be found in ores crystallized under high sulfur fugacity conditions such as stable of originally crystallized covellite and/or pyrite.

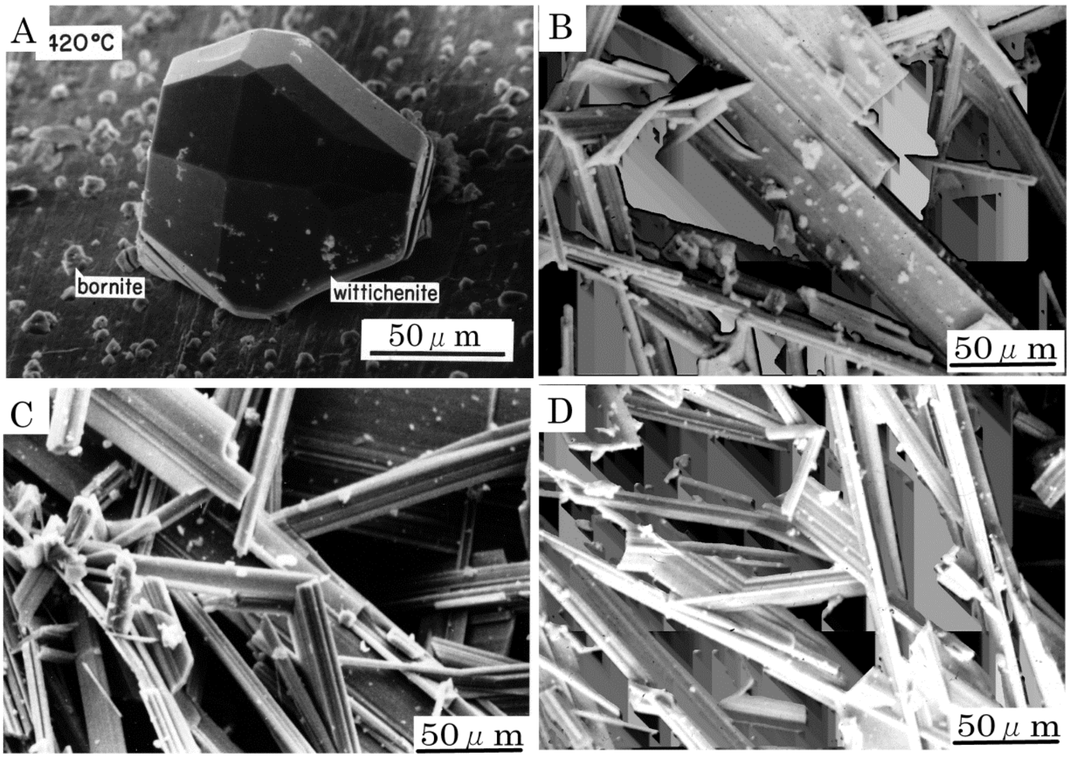

Figure 3-2-9. Hydrothermally synthetic minerals of SEM photographs.

A: wittichenite of polyhedral form, B: platy crystal of emplectite, C,D: acicular crystal of cuprobismutite

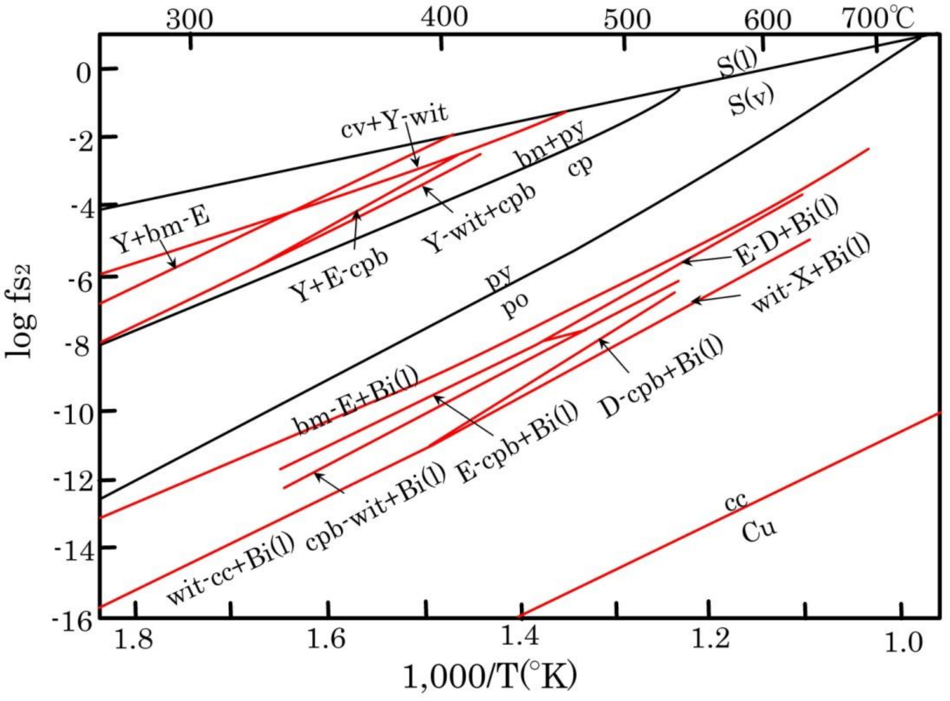

Figure 3-2-9. Relationship between sulfur fugacity (log fs2) and temperature (1,000/T as °K) for univariant assemblages in the Cu-Bi-S system.

3.4 Fe-Mn-S system

Phase relations in the Fe-Mn-S system are mainly performed by Kashiwada *et al*. (1971), Ishida *et al*. (1977) and Ishida (1983) using evacuated silica-tube method and Sugaki *et al*. (1971) and Sugaki and Kitakaze (1972) using hydrothermal synthetic method. In this time, their all data are compiled and deprived below.

The phase relations of the isothermal section in the Fe-Mn-S system at 800°C are shown in Fig. 3-3-1. There are only two sulfide solid solutions pyrrhotite and alabandite, besides β-Fe and γ-Fe and β-Mn alloys as seen in the figure. Alabandite forms a solid solution of considerable range extended linearly over a half way to the FeS end, while pyrrhotite also contains some amounts of Mn as a solid solution. Alabandite solid solution which assembles with troilite and α-iFe in equilibrium has most Fe-rich composition of 63.0 mol% FeS. Also the composition of the alabandite solid solution associated with pyrrhotite are from 63.0 to 22.3 mol% FeS, but it with S (l), 22.3 to 0.0 mol% FeS.

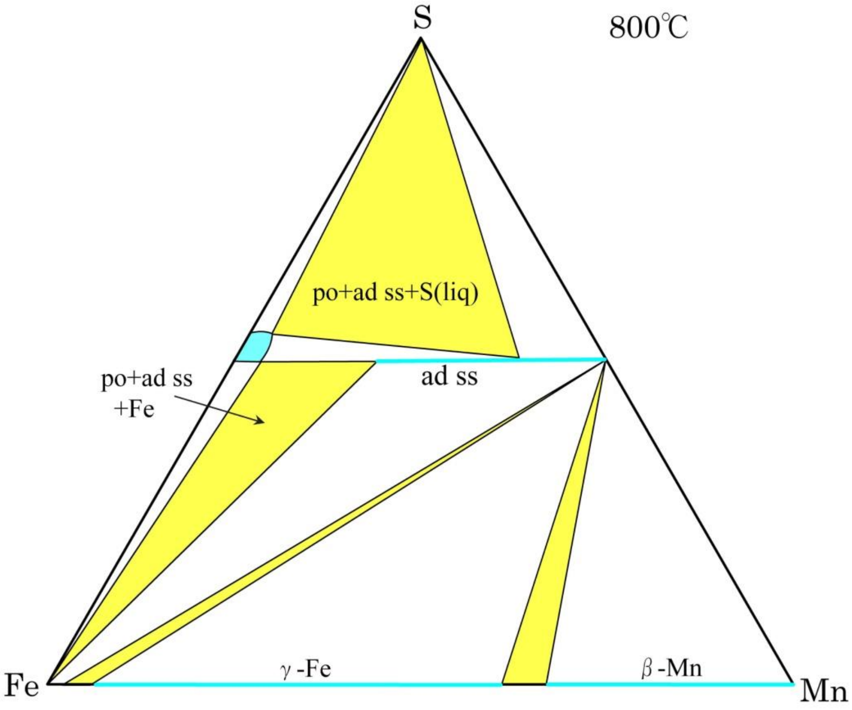

Figure 3-3-1. Isothermal section of phase diagram for Fe-Mn-S system at 800°C (modified after Ishida; 1983)[15).]

Pyrite appears at 743°C, and can assemble with pyrrhotite, alabandite solid solution and S (1). As shown in Fig. 3-3-2, alabandite solid solution slightly recedes to the Fe-poor composition at 700°C, and accompanies by pyrrhotite, pyrite, S(l), and γ-Fe alloys, α- and β-Mn alloys. The composition of the alabandite solid solution with troilite and γ-Fe is 57.3 mol % FeS which corresponds to maximum solubility, but it associated with pyrrhotite has a range from 57.3 to 19.7 mol% FeS. The composition range of the alabandite solid solution coexisting pyrrhotite and pyrite are 19.7 mol % FeS, meanwhile the alabandite solid solution with pyrite contains from 19.7 to 11.4 mole% FeS. It with pyrite and S(l) contains up to

11.4 mol% FeS.

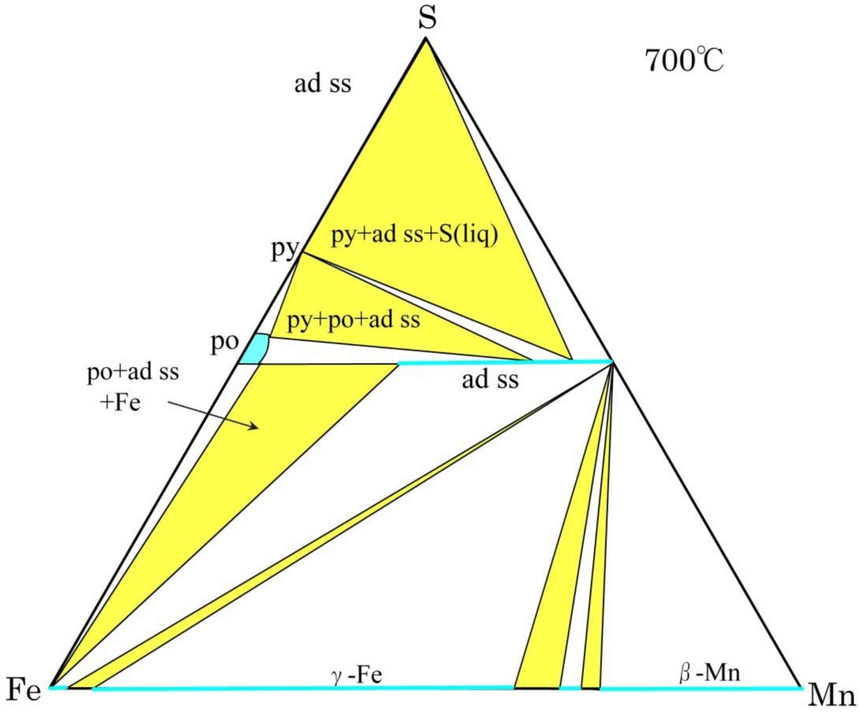

Figure 3-3-2. Isothermal phase diagram of Fe-Mn-S system at 700°C (modified after Ishida; 1983)[15].

Also, the isothermal phase relations at 600°C are shown in Fig. 3-3-3. The alabandite solid solution reduces still more its range, but its phase assemblages are the same as those at 700°C. The composition of the most Fe-rich alabandite solid solution in equilibrium with troilite and γ-Fe at 600°C is 51.5 mol% FeS, and its compositions coexisting with pyrrhotite and pyrite or pyrite and S (l) are 19.6 or 2.2 mol% FeS, respectively.

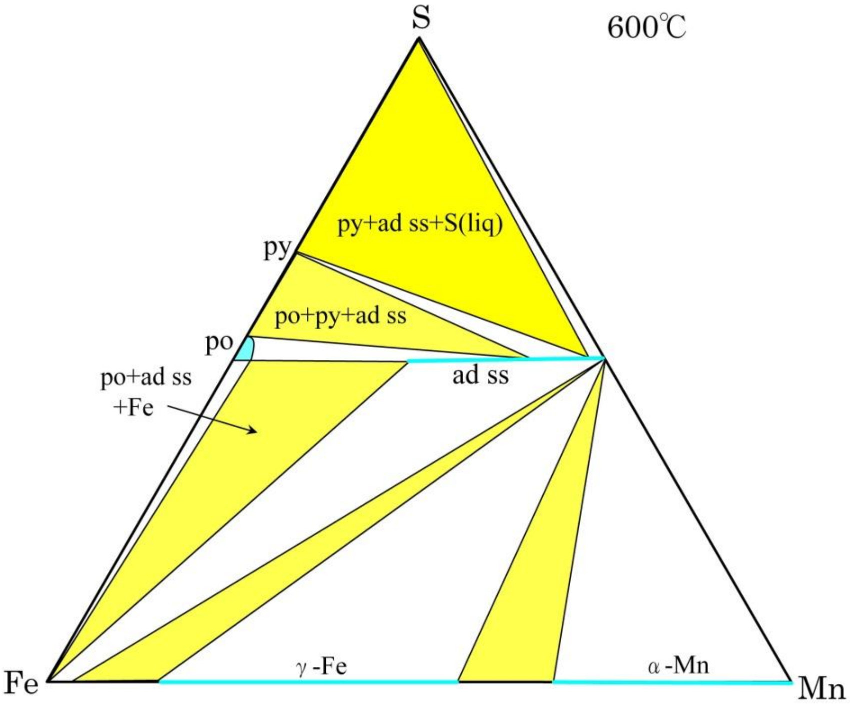

Figure 3-3-3. Isothermal phase relations for Fe-Mn-S system at 600°C (compiled after Ishida; 1983)[15].

Also, the compositions of the alabandite solid solutions coexisted with troilite + Fe, pyrrhotite + pyrite, and pyrite + S(l) at 500°C are 47.2, 18.8 and 0.7 mol% FeS, respectively. It is interested in that the compositions of the alabandite solid solution varies with the kinds of minerals assembled as entirely similar to sphalerite solid solution in the Fe-Zn-S system.

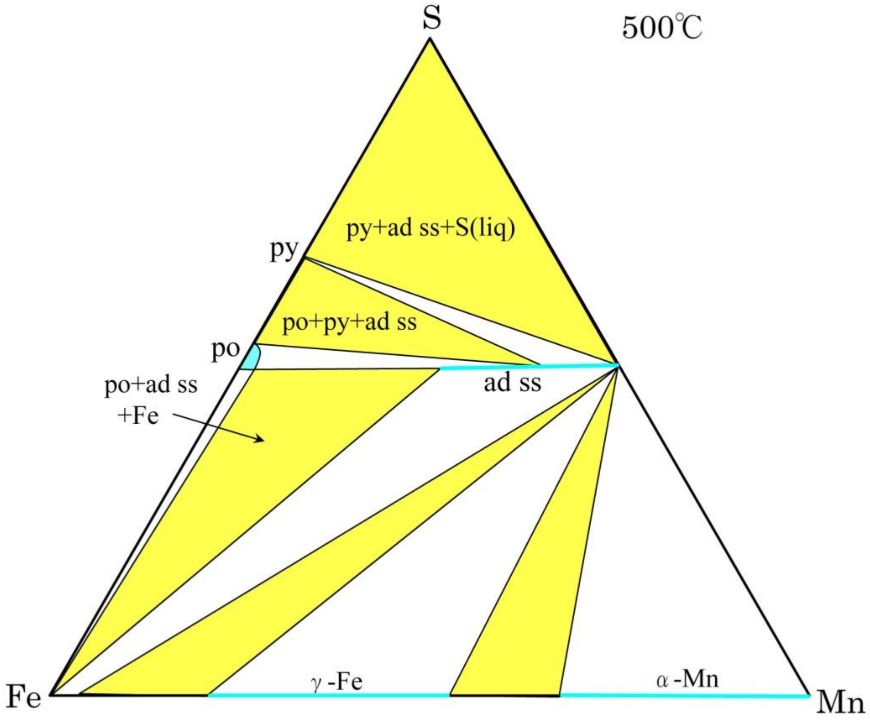

Figure 3-3-4. Isothermal phase diagram of Fe-Mn-S system at 500°C (compiled after Ishida; 1983)$^{15)}$.

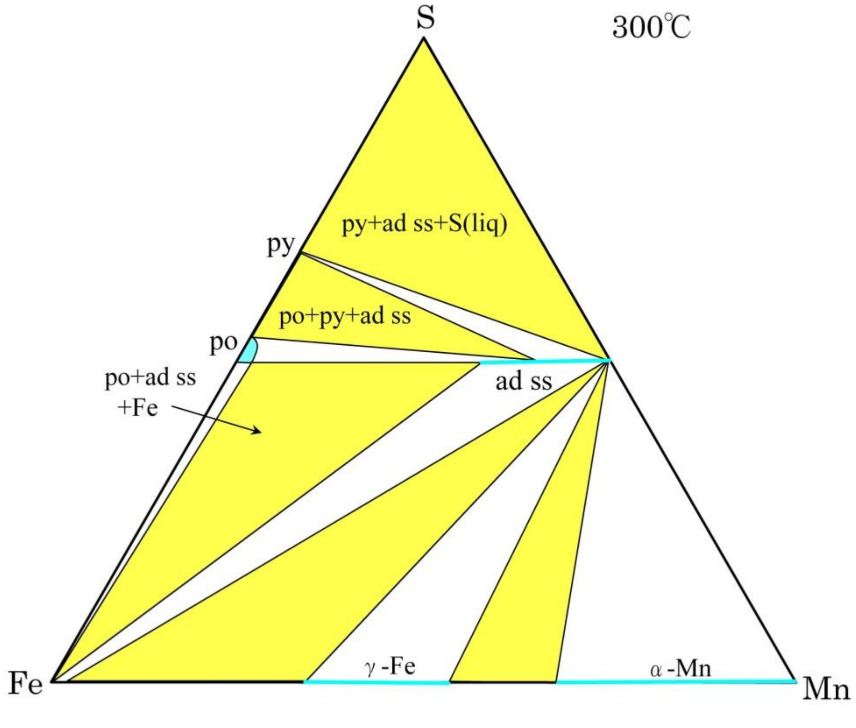

Figure 3-3-5. Isothermal phase relations for Fe-Mn-S system at 300°C obtained using thermal synthetic method (compiled after Sugaki and Kitakaze; 1972)$^{17)}$..

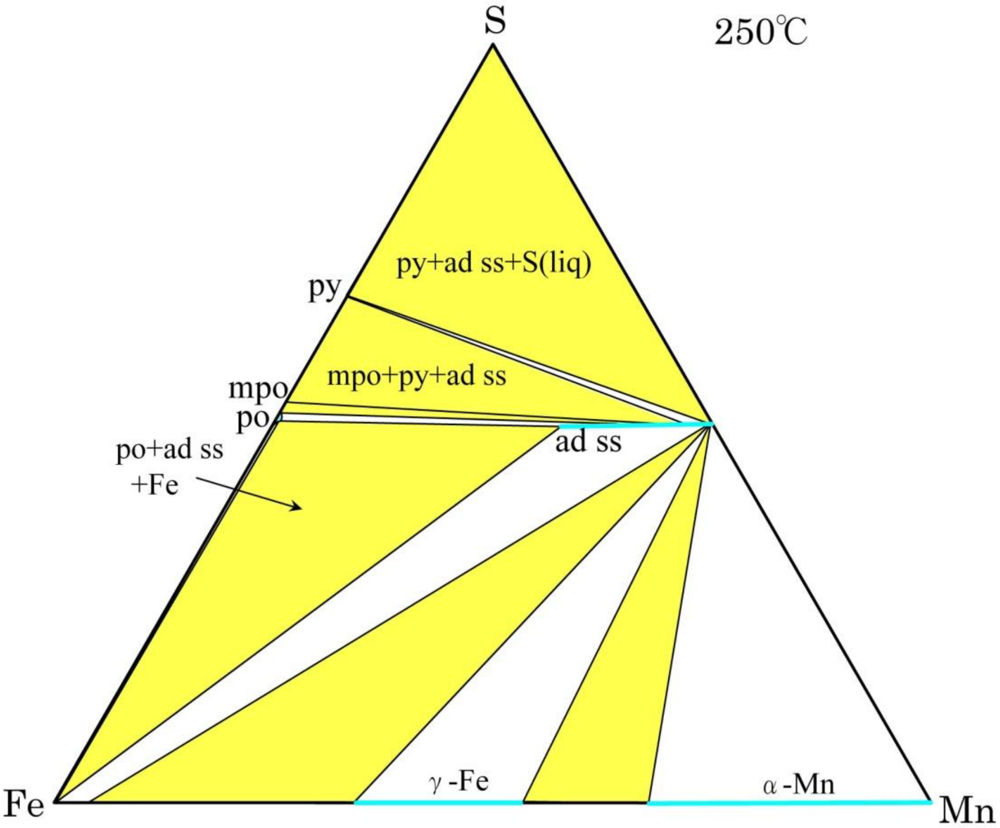

Figure 3-3-6. Tentative isothermal phase relations at 250°C for Fe-Mn-S system obtained using hydrothermal synthetic method (compiled after Sugaki and Kitakaze; 1972)[17].

The solvuses of the alabandite solid solution associated with troilite and γ-Fe, pyrrhotite and S(l), pyrrhotite and pyrite, and pyrite and S(l) as the univariant assemblages are shown together with that of pyrrhotite solid solution as a function of temperature in Fig. 3-3-7.

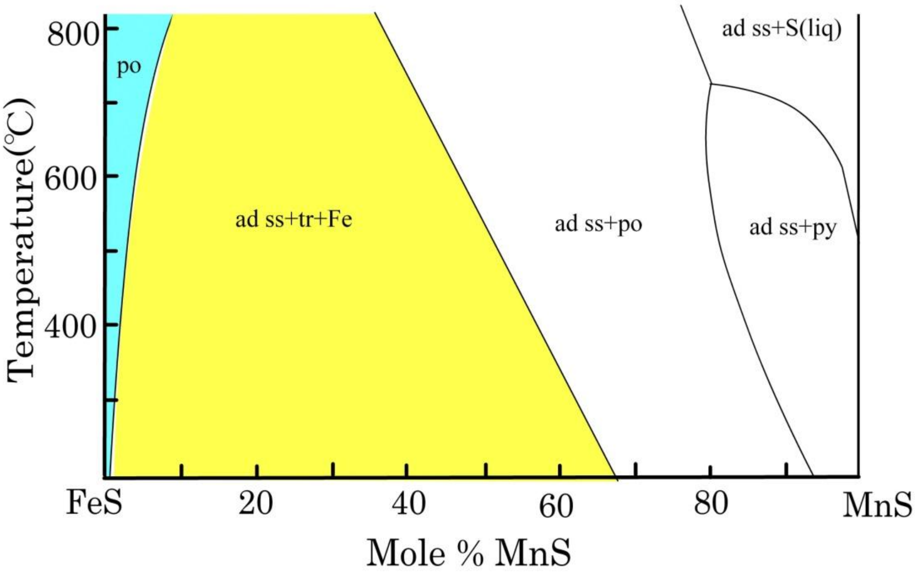

Figure 3-3-7. Phase relation of FeS - MnS join with excess sulfur in Fe-Mn-S system shown the solvases of alabandite - S(l), alabandite + pyrite, alabandite + pyrrhotite and pyrrhotite (modified after Sugaki and Kitakaze; 1972[17)], and Ishida; 1983[15)])..

As seen in the figure, the compositions of the alabandite solid solution in the univariant assemblages as above reduces iron contents with decreasing temperature except a part (of high temperature) of its solvus with pyrrhotite and pyrite. These solvuses were mostly determined using the evacuated silica glass-tube method. But it is difficult to get phase equilibrium below 400°C.

Thus, Sugaki & Kitakaze (1972) obtained the solvus of the alabandite solid solution coexisted with pyrrhotite and pyrite from 400° to 250°C as given in Fig. 3-5-7 by using the hydrothermally temperature gradient transporting method. The solvus obtained is in good accordance with the line extended the solvus above 450°C determined by the evacuated silica tube method.

A cell constant of the alabandite solid solution decreases straightly with increasing of FeS content as shown in Fig. 3-5-8, and its FeS (mol%) content is obtained from following formula;

$$a(\text{Å}) = 5.2221 - 1.4899 \times 10^{-3}(\text{FeS}) - 3.5076 \times 10^{-6}(\text{FeS})^2$$

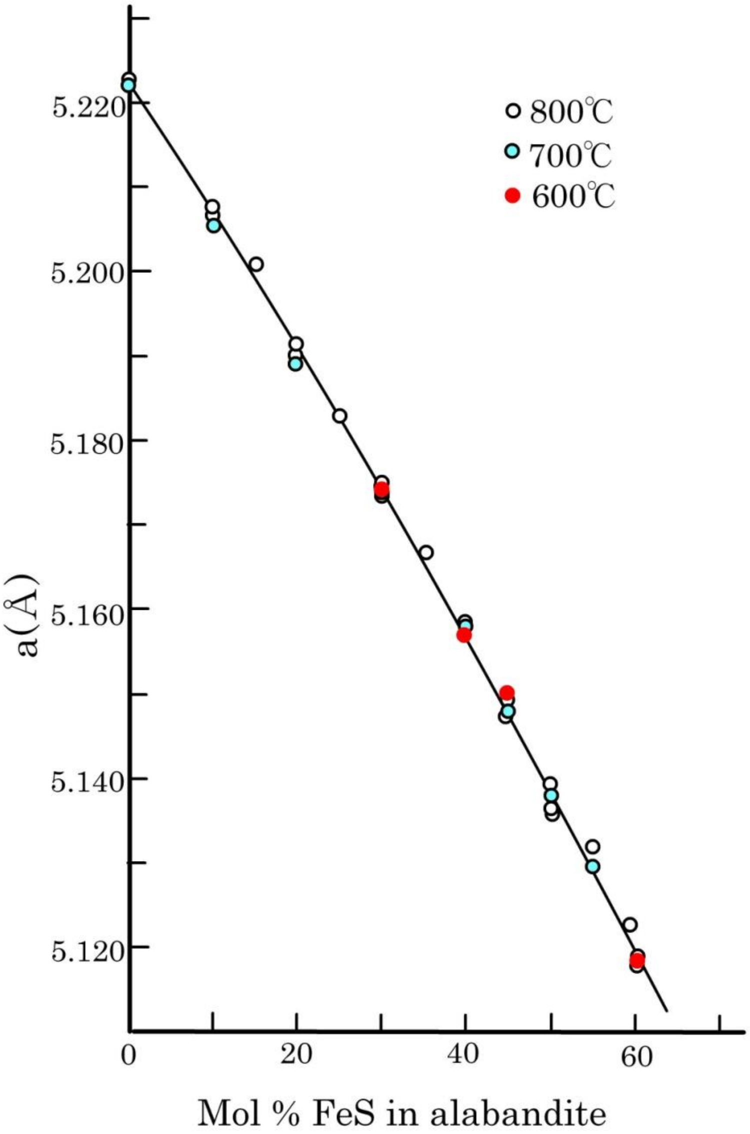

Figure 3-3-7. X-ray determinative curve for the compositions of alabandite solid solution as a function of cell parameters (Å) (modified after Ishida; 1983)[15].

On the other hand, pyrrhotite contains some amounts of manganese above 500 °C. The solid solution fields of pyrrhotite at 800°, 700°, 600° and 500°C are given in Fig. 3-3-8.

The maximum manganese contents of the pyrrhotite solid solution at 800°, 700°, 600° and 500°C are 7.46, 6.20. 4.50 and 2.78 mol% MnS, respectively.

]

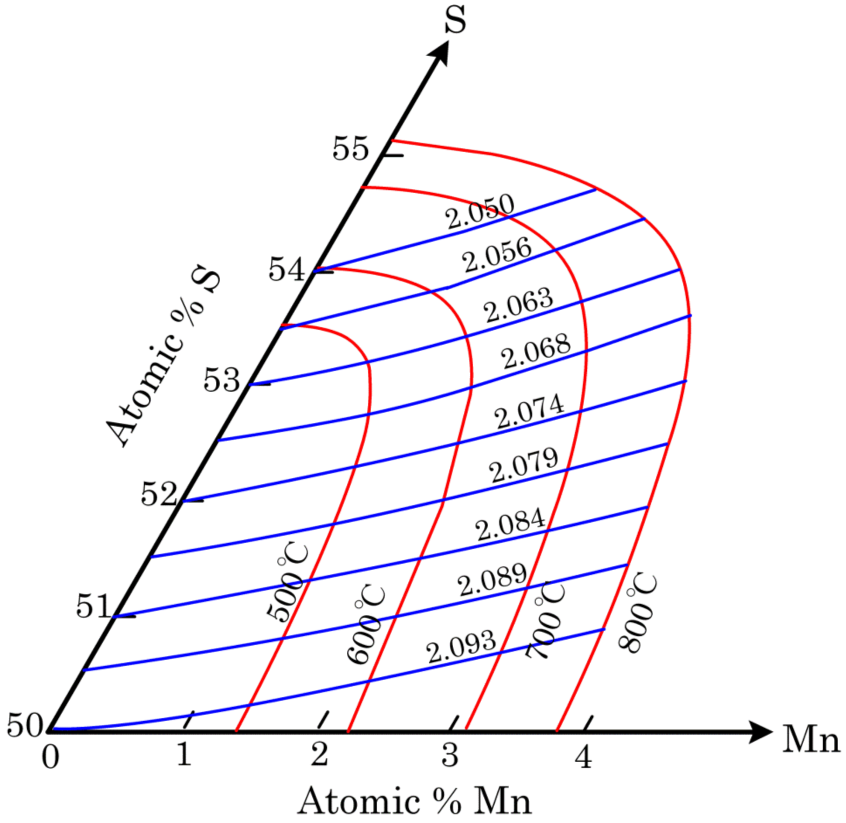

Figure 3-3-8. Pyrrhotite solid solution aria including Mn and their d_{102} values at 800, 700. 600 and 500°C (modified after Ishida: 1983)[15].

Sulfur fugacity (fS_2) values of the alabandite solid solution with pyrrhotite at temperatures from 800° to 500°C were determined from the compositions of pyrrhotite coexisted in equilibrium as shown in Fig. 3-3-9. In the figure, the relation between temperature, sulfur fugacity and composition of alabandite solid solution with pyrrhotite is represented as its iso-compositional curves from 25 to 60 mol% FeS with 5 mol% interval. Similarly the as values in the alabandite solid solution with pyrrhotite are given as iso-activity curves from 0 to -12 in log fS_2 in Fig. 3-3-10.

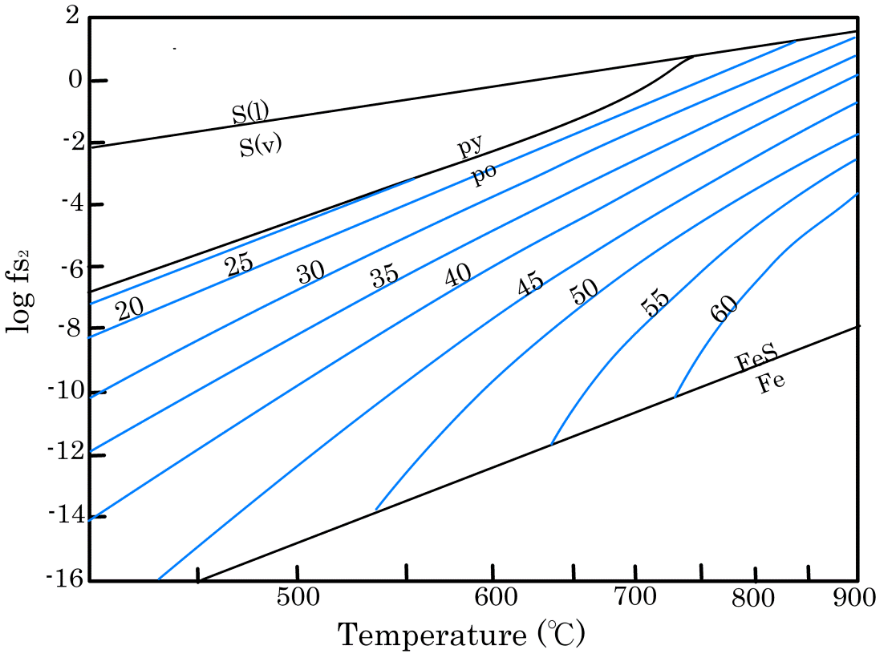

Figure 3-3-9. Composition of alabandite solid solution in mol % FeS as a function for fugacity of S_2 and temperature. The curves in co-existence of sulfur (liquid) and sulfur (vapor), pyrite (py) and pyrrhotite (po), and iron (Fe) and troilite (FeS) are indicated together as standard in the figure (modified after Ishida; 1983)[15)]..

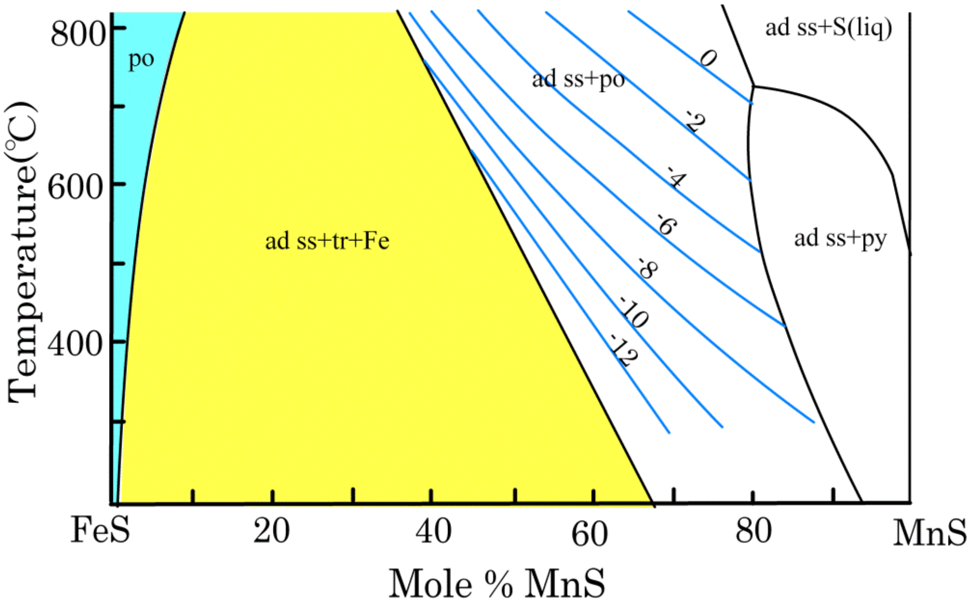

Figure 3-3-10. Iso-sulfur fugacity values of alabandite + pyrrhotite field in FeS - MnS join (modified after Ishida; 1983)[15)].

Alabandite and pyrrhotite crystals were obtained using hydrothermal synthesis as shown in Fug. 3-3-10. Alabandite has polyhedral form, sometime twin. Pyrrhotite has platy hexagonal form.

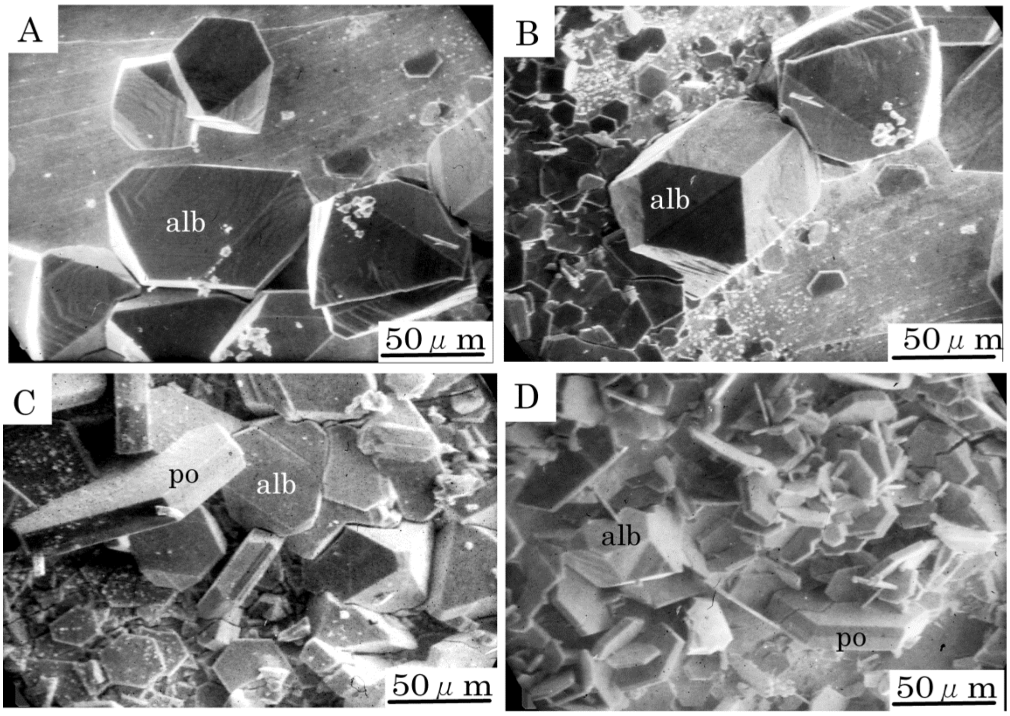

Figure 3-3-11. SEM photographs for hydrothermal synthetic alabandite (alb) and pyrrhotite (po).
A: alabandite crystal with polyhedral form, B:twinned alabandite,
C, D: pyrrhotite with platy hexagonal form associating alabandite

3-4 Ni-Bi-S system

The phase relations in the Ni-Bi-S ternary system at temperature range from 580° to 350°C have been studied by Fujiyama (1981)[18)] and Sasaki (1982)[19)]. In the Ni-Bi-S system, the three ternary phases are appeared in their studies; parkerite ($Ni_3Bi_2S_2$), phase A (Ni_6BiS_3) and phase B (Ni_3BiS). Their crystallographic and thermal stability data for the three ternary phases are given in Table 3-4-1 and Table 3-4-2, respectively.

Table 3-6-1. Chemical compositions of ternary compounds in the Ni-Bi-S system

Mineral and phase	Abbreviations	Chemical composition	Crystal system	Space group	Cell Parameters		
					a	*b*	*c*
Parkerite	prk	$Ni_3Bi_2S_2$	Orth	*Pmam*	5.548(1)	5.726(1)	4.039(1)
Phase A	Phase A	Ni_6BiS_3	Orth		7.819(1)	11.387(2)	6.349(1)
Phase B	Phase B	Ni_3BiS	Cub		5.8346(1)	-	-

Table 3-6-2. Thermal stability for the ternary phases in the Ni-Bi-S system.

Mineral and phase	Chemical composition	Thermal stability	
		Low limit	High limit
Parkerite	$Ni_3Bi_2S_2$	-	>580
Phase A	Ni_6BiS_3	-	>580
Phase B	Ni_3BiS	475	>580

Isothermal section of phase relations for Ni-Bi-S ternary system at 580°C is shown in Fig. 3-4-1. Parkerite, phase A and phase B are found in the central portion of this system. Parkerite has stable tie-lines with $Ni_{1-x}S$, β_1, β_2, phase A, phase B, NiBi alloy and bismuth liquid phases except vaesite, bismuthinite and sulfur liquid.

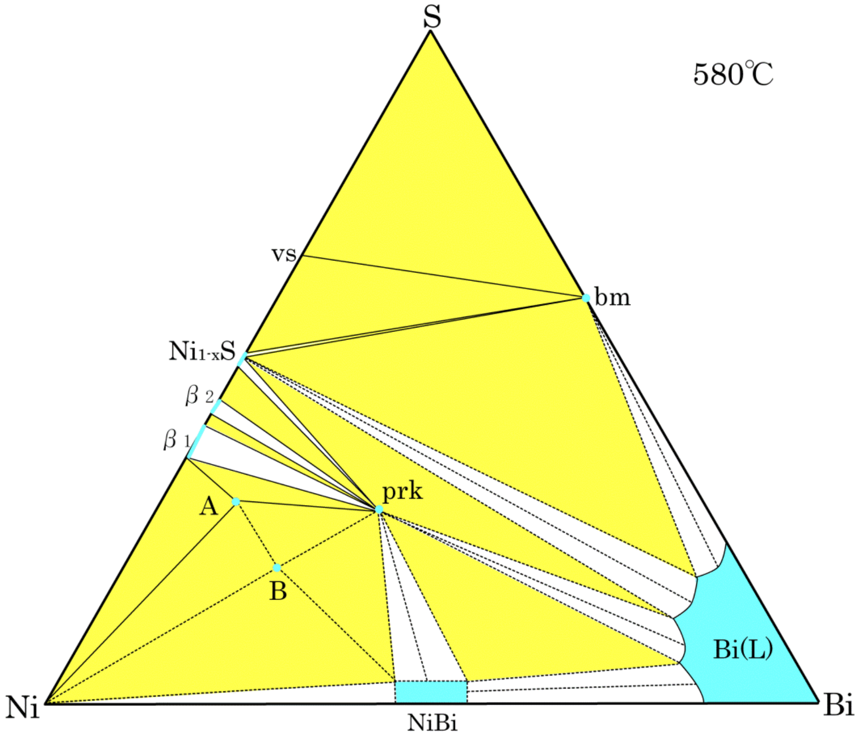

Figure 3-4-1. Isothermal phase diagram of the Ni-Bi-S system at 580°C (modified after Sasaki; 1982). Abbreviations are seen in Table 3-4-1.

The phase relations at 550 and 500°C are about same to that at 580°C except phases in Ni-S binary system. Parkerite assembles with the phases in Ni-S binary.

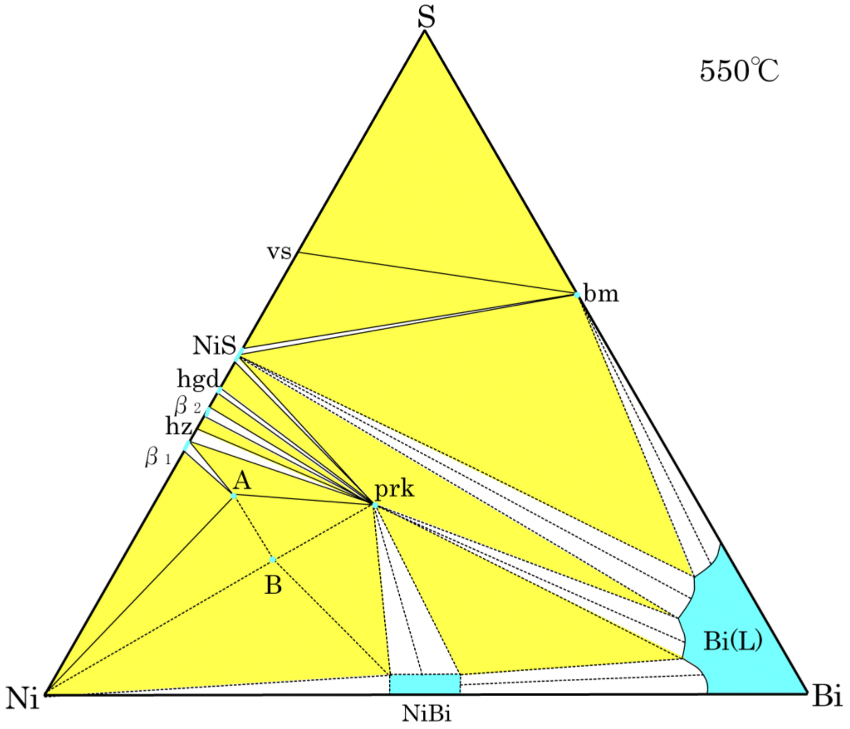

Figure 3-4-2. Isothermal section of phase diagram for the Ni-Bi-S system at 550°C (modified after Sasaki; 1982).

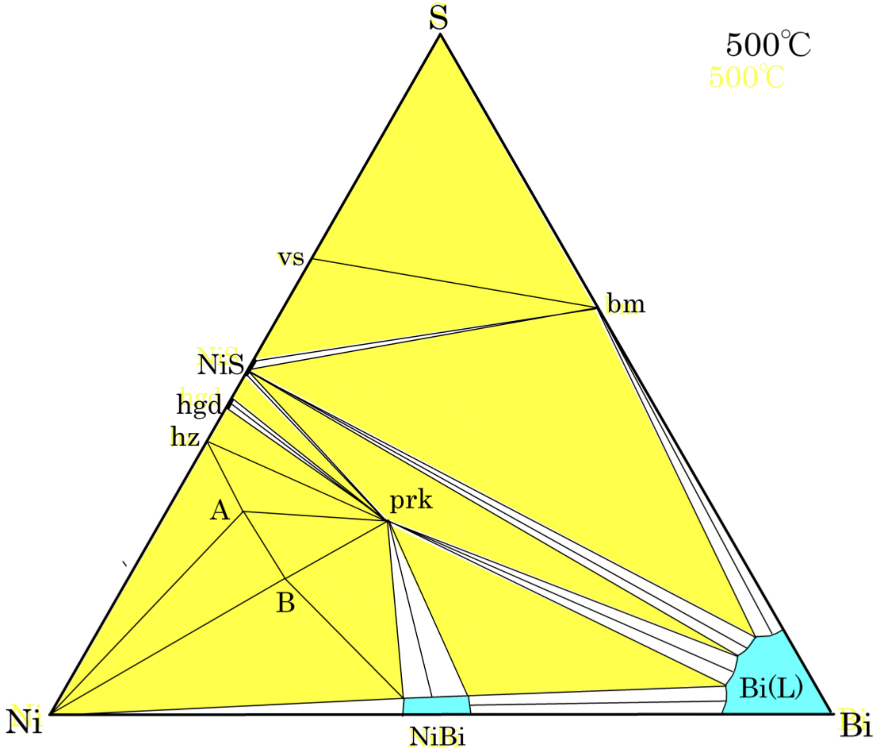

Figure 3-4-3. Isothermal phase diagram of the Ni-Bi-S system at 500°C (modified after Sasaki; 1982).

Phase B decompose to parkerite + Ni metal below 475℃, then it is not appear at 450℃. The tie line between Ni$_{1-x}$S and Bi-liquid changes to that between parkerite and bismuthinite at 455°C, so the two invariant assemblages parkerite + bismuthinite + Bi-liquid and parkerite + Ni$_{1-x}$S + bismuthinite become stable at 450°C. The compositional field of the Bi-liquid at this temperature is much narrower than that of at 500°C.

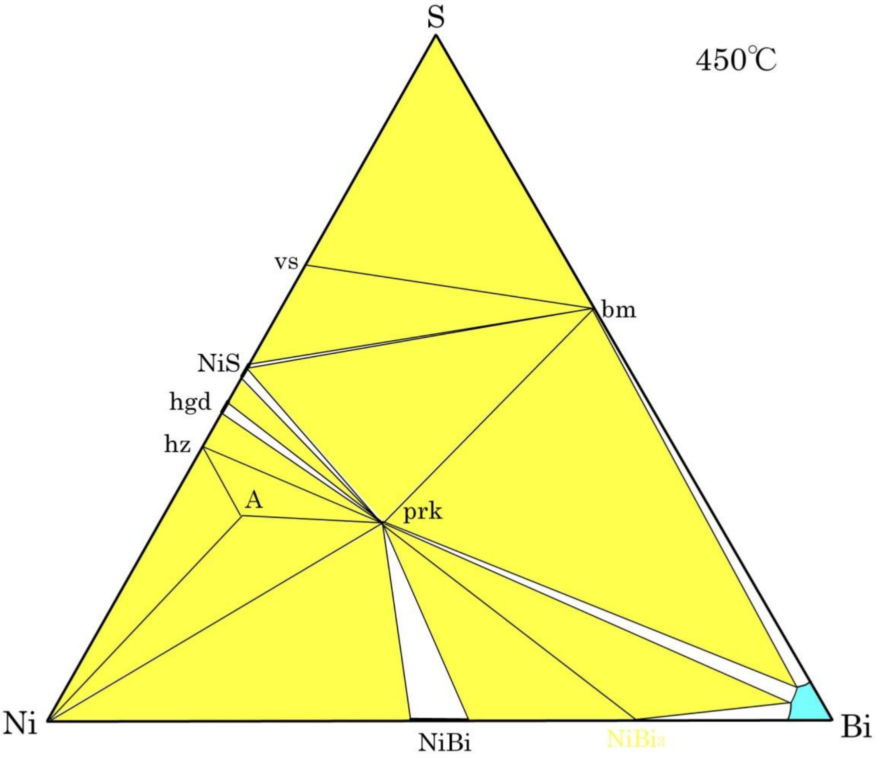

Figure 3-4-4. Isothermal phase diagram of the Ni-Bi-S system at 450°C (modified after Sasaki; 1982)..

As shown in Fig. 3-4-5, the compositional field of Bi-liquid extends to the outer system so the liquid dissolves small amounts of Ni and S. There are univariant assemblages as parkerite + phase A + β1, heazlewoodite, parkerite + heazlewoodite + godlevskite, parkerite + godlevskite + millerite, parkerite + millerite + bismuthinite, parkerite + bismuthinite + Bi-liquid, parkerite + phase A+ Ni, parkerite + NiBi + NiBi$_3$ and Bi-liquid, parkerite + Ni + NiBi at 400° and 350°C.

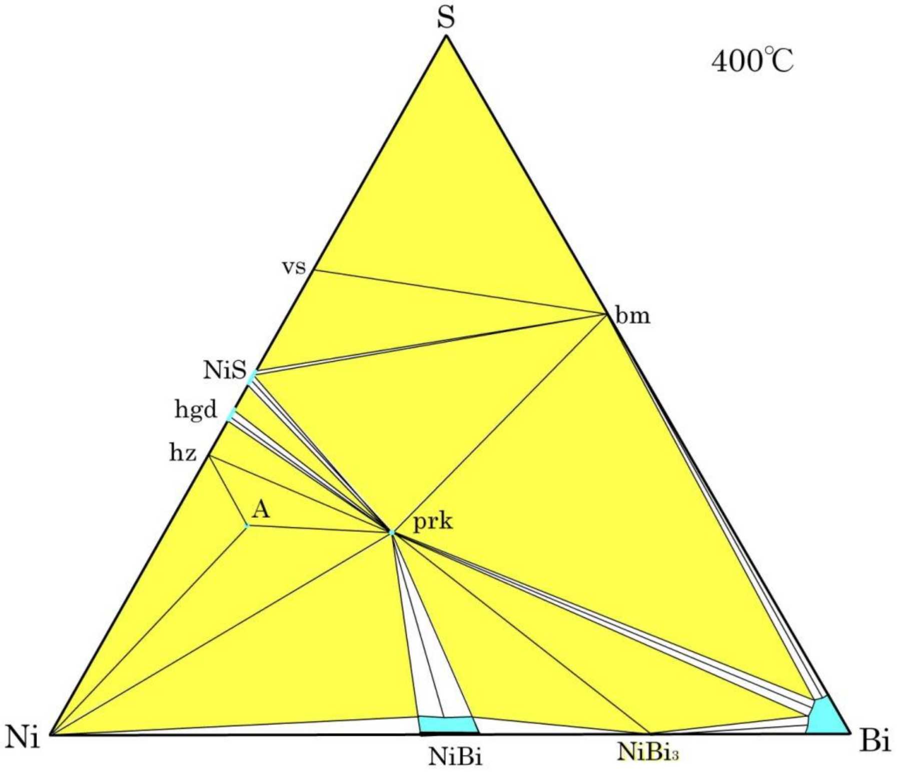

Figure 3-4-5. Isothermal phase diagram of the Ni-Bi-S system at 400°C (modified after Sasaki; 1982).

At 400°C, phase assemblages with polydymite are unstable because polydymite decomposes to millerite and vaesite at 356°C.

Besides the three phases at 350°C, heazlewoodite (Ni_3S_2), godlevskite (Ni_7S_6), millerite ($Ni_{1-x}S$), vaesite (NiS_2), bismuthinite (Bi_2S_3), sulfur liquid, Bi-liquid, two Ni-Bi alloys with compositions NiBi and $NiBi_3$, and metallic nickel (Ni) exist in the system. Consequently they have given very similar isothermal phase diagrams, which are displayed in Figs. 3-4-4 to 3-4-5.

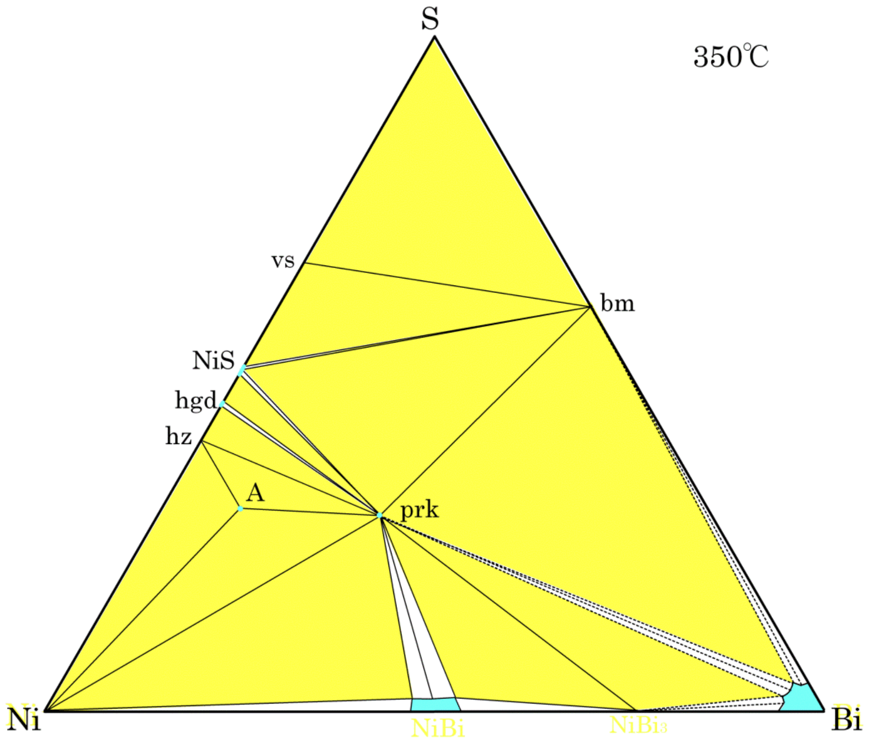

Figure 3-4-7. Isothermal phase diagram of the Ni-Bi-S system at 350°C (modified after Sasaki; 1982)..

Reference

[1] Kitakaze, A., Itoh, H. and Komatsu, R. “A revision of phase relations in the system Fe-Ni-S from 650° to 450°C”, Can. Mineral., **49**, 1687-1710, 2011.

[2] Kitakaze, A., Machida, T. and Komatsu, R. Phase relations in the Fe-Ni-S system from 875 to 650°C. Canad. Mineral.. **54,** 1175-1186, 2016.

[3] Kitakaze, A., “Phase relation of some sulfide system-(1)”, Memoirs of the Faculty of Engineering, Yamaguchi University, **66**, 67-74, 2016.

[4] Kitakaze, A., “Phase relation of some sulfide system-(2)”, Memoirs of the Faculty of Engineering, Yamaguchi University, **67**,19-33, 2016.

[5] Kitakaze, A. “Cell parameters refinement using Guinier Method”, Mineral. Mag., **25,** 69-76.

[6] Yusa, K. “Phase equilibrium study of the Bi-Te-S system”. Master thesis’s of Department of Mineralogists, Petrologists and Economic Geologists, Faculty of Science, Tohoku University 1979.

[7] Yusa, K., Sugaki, A. and Kitakaze, A. “Studies on the phase relations in the ternary Bi-Te-S system (2) (Abstract in Japanese)”. *Journal of Japanese Association of Mineralogists, Petrologists and Economic Geologists,* **74**, 162, 1979.

[8] Yusa, K., Sugaki, A. and Kitakaze, A. “Studies on the Bi-Te-S minerals (abstract in Japanese)”. J*ournal of the Japanese Association of Mineralogists, Petrologists and Economic Geologists,* **75,** 131, 1980.

[9] Sugaki, A., Kitakaze, A. and Yusa, K. “Studies on the natural occurred Bi-Te-S minerals-Specially joseite-A and joseite-B (abstract in Japanese)”. Annual Meeting Abstracts, Mineralogical Society of Japan, 126, 1980.

[10] Sugaki, A. and Shima, H.”Phase relations of the Cu_2S-Bi_2S_3”.

Tech. Rept. Yamaguchi Uni., 1, 71-85, 1972.

[11] Sugaki, A. Shima, H. and Kitakaze, A."The phase equilibrium of the system Cu-Bi-S below 400°C, specially the relation between Emplectite and cuprobismutite". Pro. 9'th IMA 1978, Sulph. Pt, Miner. Ore Micro., 100-109 1980..

[12] Nomiyama, S."Study on the phase relations of Cu-Bi-S system". Master thesis's in Fac. Eng. Yamaguchi Univ. 1968.

[13] Kashiwada, Y., Sugaki, A. and Shima, H., "Study on the phase relations in the Mn-Fe-S system", (abst.. in Japan.), *Jour. Mining Geol.*, **21**, 40-41, 1971.

[14] Ishida, H., Sugaki, A. Shima, H. and Kitakaze, A., "Study on the phase relations in the Mn-Fe-S system (3)" (abst. In Japanese), Join Meeting of Soc. Mining Geol., Soc. Mineral. Petrol. Econ. Geol. Soc. Mineral., 102, 1977.

[15] Ishida, H., "Studies on the alabandite solid solution and their phase relations in the Mn-Fe-S system". Master theses at Faculty of Engineering, Yamaguchi University, 1983.

[16] Sugaki, A., Kitakaze, A. and Kashiwada, Y., "Study on the phase relations in the Mn-Fe-S system (2)"-Especially hydrothermal synthesis of alabandite (abst.. in Japan.), Collected Abstracts, Mineral. Soc. Japan., 33, 1971.

[17] Sugaki, A. and Kitakaze, A."Chemical composition f synthetic alabandite solid solution and its phase relations in the Fe-Mn-S". Proc. IMA-IAGOD 70' IMA Vol., 1, 45-70, 1972.

[18] Fujiyama, S., "Mineral synthesis in the Ni-Bi-S system and their phase relation". Master theses at Faculty of Engineering, Yamaguchi University, 1981.

[19] Sasaki, N., "Mineral synthesis in the Ni-Bi-S system and their phase relation". Master theses at Faculty of Engineering, Yamaguchi University, 1982.

(Received Nov.10,2017)