Phase relation of some sulfide systems-(5)
Especially Fe-Ni-S system

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Abstract:

Phase relation studies for ternary Fe-Ni-S system have been performed by author. Their results are described as mainly phase diagrams. Many diagrams were obtained by integrating after Sugaki *et al*, [1,2,3,4] and Kitakaze *at al.* [5,6], and adds additional new data and new knowledge were obtained by outhouses.

Phase relations at 1,100, 1,000, 900, 875, 750, 800, 750, 700, 650, 600, 550, 500 and 450°Cusing the dry method were showing. Further, cross sections for (Fe,Ni)-S and po-hx from 1,000 to 450°C by integrating after Kitakaze *et al.* [5,6]

***Key Words**:Fe-Ni-S, high-pentlandite SS, low-pentlandite SS, monosulfide-SS*

Introduction

Since the study by Kullerud[7,8], it has been accepted that pentlandite ($Fe_{4.5}Ni_{4.5}S_8$) breaks down to a mixture of pyrrhotite (monosulfide solid-solution) and phase $Ni_{3\pm x}S_2$ at 610°±3°C or above (Kullerud *et al.*[9], Craig & Scott1[10] , Barton & Skinner [11], Craig & Vaughan[12]). However, Sugaki & Kitakaze[13,14] found that pentlandite of composition $Fe_{4.5}Ni_{4.5}S_{7.9}$ does not break down but transforms into a high-form at 615°±3°C and that a continuous solid-solution between this high-form and phase $Ni_{3\pm x}S_2$ is stable in the Fe-Ni-S system at 800° and 650°C (Sugaki *et al.* [1,3]). Fedorova & Sinyakova[15] reported an extended heazlewoodite solid-solution $(Fe_xNi_{1-x})_{3\pm y}S_2$ at 820° and 600°C in the Fe-Ni-S system. Also, Karup-Møller & Makovicky[16] ascertained an elongated solid-solution with $(Ni,Fe)_{3\pm x}S_2$ in the system at 725°C. Kosyakov *et al.*[17] reported some schemes of polythermal cross sections in Fe-Ni-S Xs<50 mole %, but not ternary phase diagram of the ternary system were show. Sinyakova & Kosyakov[18] show the 600℃ section of the Fe-FeS-NiS-Ni phase diagram and recognized pentlandite, monosulfide solid-solution, heazlewoodite solid-solution and metal phases. But β_1 and β_2 in the Ni-S binary system described below were not found, so some problem was remained. Further, Hayashi (1985) recognized the existence of a $(Fe,Ni)_9S_8$-$Ni_{3\pm x}S_2$ solid-solution in his study of the quaternary Cu-Fe-Ni-S system at 850° and 650°C. All of these SS are the same phase. Peregoedova & Ohnenstetter[19] recently reported that a quaternary SS between hz SS $(Ni,Fe)_{3\pm x}S_2$ and intermediate SS $Cu_{1\pm x}Fe_{1\pm y}S_2$ was established in the system Fe-Ni-Cu-S at 760°C.

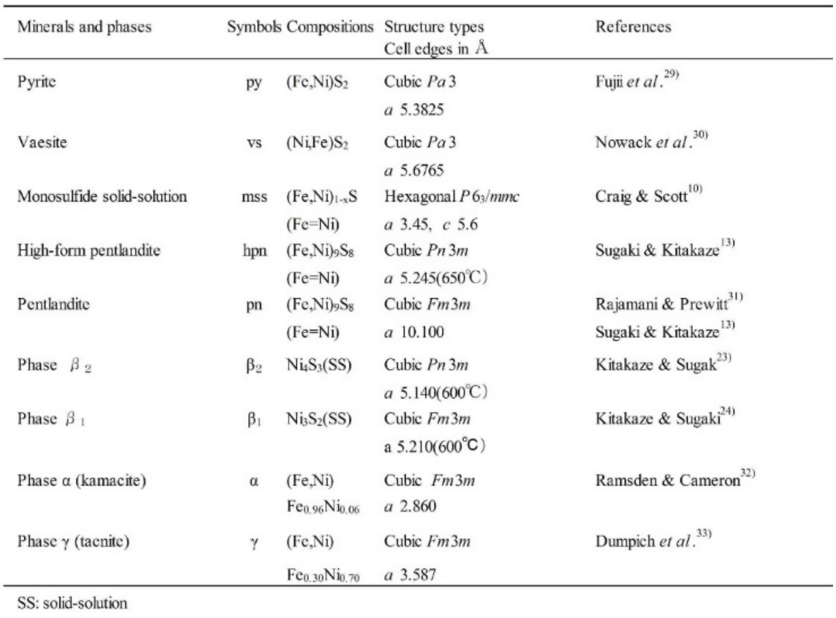
On the other hand, Lin *et al.*[20], Sharma & Chang[21], Singleton *et al.*[22] and Kitakaze & Sugaki [23,24] found that phase $Ni_{3\pm x}S_2$ (β) (Kullerud & Yund[9] , Liné & Huber[20], Rau[25] in the binary Ni-S is not a mono-phase but consists of two limited SS of phases β1 (Ni_3S_2 corresponding to a h-hz and β2 (Ni_4S_3, a high-temperature phase) with a narrow field of immiscibility between them over the temperature range from 524° to 806°C. Accordingly, the h-pn –$Ni_{3\pm x}S_2$ SS mentioned above is incorrect. It is possible for h-pn to form a continuous solid-solution with either β1 or β2, but not both.

The appearance of h-pn, β1 and β2 as stable phases required the reexamination and revision of the phase relations of the systems Fe-Ni-S and Cu-Fe-Ni-S above 500°C obtained by the previous authors (Kullerud8), Kullerud *et al*·9), Craig & Kullerud26), Hsieh *et al.* 27), Barker28), Hayashi29), Fedorova & Sinyakova15), Karup-Møller & Makovicky16), Peregoedova & Ohnenstetter 19). In order to clarify the phase relations among high-form pentlandite,

low-form pentlandite, β1 and β2 and their thermal stabilities, we have investigated seven isotherms of the Fe-Ni-S system at 50°to 20℃ intervals from 650° to 450°C especially where both high- and/or low-pentlandites and β1 coexist. There have been found a lot of phase changes such as pseudoperitectoids, pseudoeutectoids, ternary peritectoid and eutectoids and tie-line changes besides a polymorphic phase-transition, and so the phase relations of the system became more complicate than those described by the preceding researchers as above. The experimental results ascertained by us are already reported by Sugaki & Kitakaze14), Kitakaze *et al.*5) at temperatures from 650 to 450°C and Kitakaze *et al.*6) at temperatures from 875 to 650°C. Therefore, this report combined our previous data and added some new data on phase relation is described below.

Chemical compositions and crystallographic data for minerals and solid phases appeared in this study are compiled in Table 1.

Table 1. Minerals appeared in this study belonging within the Fe-Ni-S system



Minerals and phases	Symbols	Compositions	Structure types Cell edges in Å	References
Pyrite	py	$(Fe,Ni)S_2$	Cubic *Pa*3 *a* 5.3825	Fujii *et al.*29)
Vaesite	vs	$(Ni,Fe)S_2$	Cubic *Pa*3 *a* 5.6765	Nowack *et al.*30)
Monosulfide solid-solution	mss	$(Fe,Ni)_{1-x}S$ (Fe=Ni)	Hexagonal $P6_3/mmc$ *a* 3.45, *c* 5.6	Craig & Scott10)
High-form pentlandite	hpn	$(Fe,Ni)_9S_8$ (Fe=Ni)	Cubic *Pn*3*m* *a* 5.245(650℃)	Sugaki & Kitakaze13)
Pentlandite	pn	$(Fe,Ni)_9S_8$ (Fe=Ni)	Cubic *Fm*3*m* *a* 10.100	Rajamani & Prewitt31) Sugaki & Kitakaze13)
Phase β2	β2	Ni_4S_3(SS)	Cubic *Pn*3*m* *a* 5.140(600℃)	Kitakaze & Sugak23)
Phase β1	β1	Ni_3S_2(SS)	Cubic *Fm*3*m* a 5.210(600℃)	Kitakaze & Sugaki24)
Phase α (kamacite)	α	(Fe,Ni) $Fe_{0.96}Ni_{0.06}$	Cubic *Fm*3*m* *a* 2.860	Ramsden & Cameron32)
Phase γ (tacnite)	γ	(Fe,Ni) $Fe_{0.30}Ni_{0.70}$	Cubic *Fm*3*m* *a* 3.587	Dumpich *et al.*33)

SS: solid-solution

Experimental Procedure

Evacuated silica glass tube method

Synthetic experiments were mainly carried out by the evacuated silica-glass tube method which is about same described by Kitakaze *et al.*5,6) using pure iron and nickel metals (over 99.99% in purity) and sulfur (99.99%).

Identification of phases

All the run products obtained using the evacuated glass tube method were fine to coarse grained sulfide and their mixture, and examined by ore microscope, XRD by diffractometer and high-temperature XRD by high temperature diffractometer under N_2 gas 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.

Phase relation of Fe-Ni-S system

Phase relation at 1,100°C

The phase relations at1,100°C obtained using by the evacuated silica-glass tube method are shown in Fig. 1. Monosulfide SS (mss) appears as the first sulfide phase ($Fe_{0.92}S_{1.00}$) in the system at 1,188℃ (Rau[25], Kubaschewski[35]), has a limited SS to extend its field successively toward Ni-S direction and assemble with central sulfide liquid. There are two liquid fields for the central sulfide liquid -sulfur and -metal.

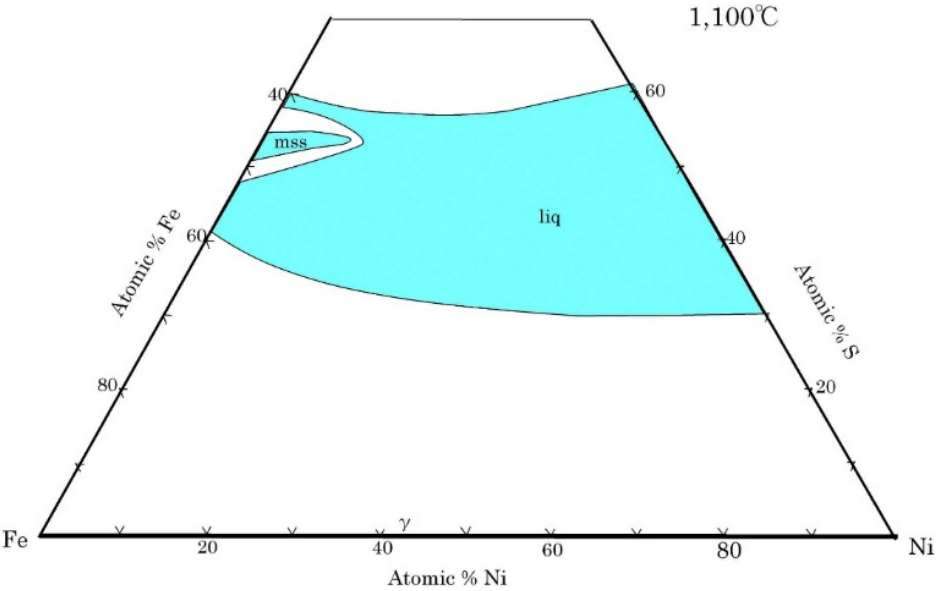


Fig. 1. Isothermal section in central portion of Fe-Ni-S system at 1,100°C.

Phase relation at 1,000℃

The phase relations at 1,000°C obtained using the evacuated silica-glass tube method are shown in Fig. 2. There are the central sulfide liquids, two sulfide phases of monosulfide SS(mss) and vaesite (vs)in central portion of Fe-Ni-S system. Vaesite (vs), which crystallized as a stable phase NiS_2 by a reaction between two immiscible liquids, Ni-rich liquid and sulfur liquid at 1,022±3℃ (Arnold & Malik[36], Lin *et al.*[20], Sharma & Chang[21]; Singleton *et al.*[22]). The mss filed was suddenly wider than that at 1,100°C spreading to Ni-S join. A univariant assemblages of mss-vs-sulfur liquid (S(l)) was appeared. Sulfide liquid field becomes narrower than that of 1,100°C.

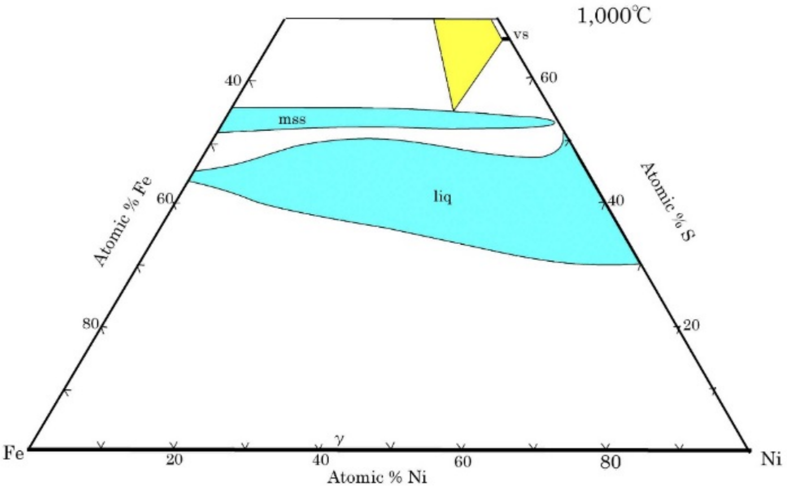


Fig. 2. Isothermal section in central portion of Fe-Ni-S system at 1,000°C.

Phase relation at 900℃

The phase relations in the ternary system at 900°C are shown Fig.3. There are two sulfides such as vs and mss, and sulfide liquid. Mss extends its field successively toward Ni-S join with decreasing temperatures and forms a complete SS between $Fe_{1-x}S$ (1C) and $Ni_{1-x}S$. There are two univariant assemblages of mss-vs-S(l) and mss-sulfide liquid-γ which were appeared in this temperature.

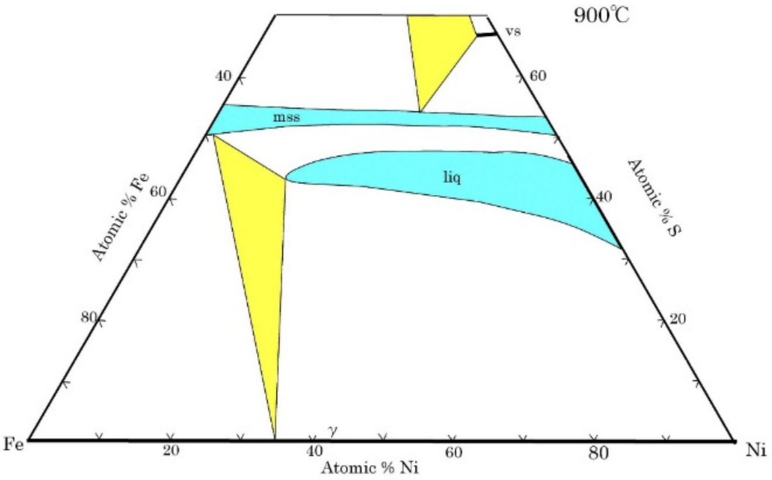


Fig. 3. Isothermal section in central portion of Fe-Ni-S system at 900°C

Phase relation at 875℃

Phase relations of Fe-Ni-S system at 875℃ obtained from the equilibrium run data and the EPMA data for the synthetic products are shown in Fig. 4 (modified diagram after Kitakaze *et al.*[6]). Only six phases appeared at this temperature, four solid phases such as vs, mss, α and γ, and two liquid phases as sulfide liquid and sulfur liquid. Vs has a limited SS ranging from NiS_2 to $Fe_{0.18}Ni_{0.82}S_2$ along the FeS_2-NiS_2 join at 875℃. Sulfide liquid phase occupies a wide field extending from the Ni-S join toward the inside of the ternary composition.

In the figure, three univariant assembles are found as vs+ mss + S(l), mss + sulfide liquid+ γand mss +α+γ.

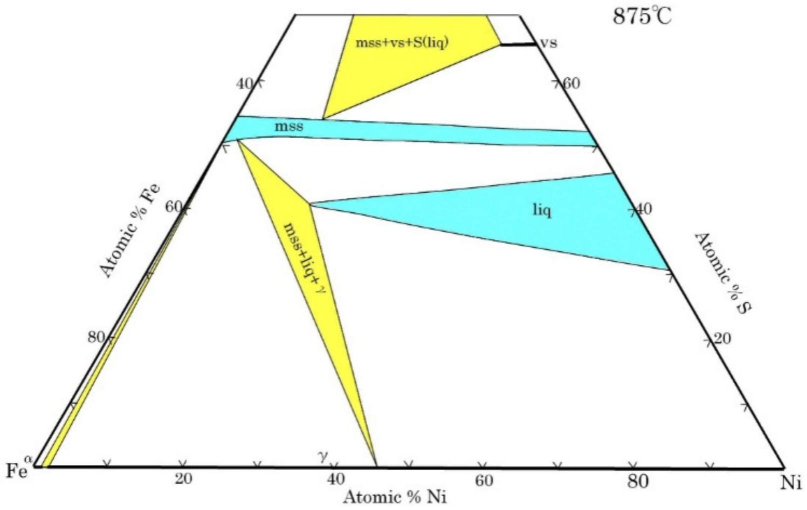


Fig. 4. Isothermal section in central portion of Fe-Ni-S system at 875°C (modified diagram after Kitakaze *et al.* [6])

Phase relation at 850℃

The phase relations based on the data of the equilibrium experiments and the EPMA at 850℃ are shown in Fig. 5 (modified diagram after Kitakaze *et al.*[6]). H-pn with $Fe_{4.93}Ni_{4.06}S_{8.01}$ first appears as stable at 870±3℃as a result of pseudoperitectic reaction between mas ($Fe_{0.89}Ni_{0.11}S_{1.00}$) and liquid ($Fe_{0.43}Ni_{0.17}S_{0.41}$).

The stable phases such as S(l), vs, mss, h-pn, sulfide liquid, α and γ are found in the figure. At 850℃, h-pn appears with a limited SS from $Fe_{5.08}Ni_{3.93}S_{7.99}$to $Fe_{3.81}Ni_{5.24}S_{7.96}$including $Fe_{4.50}Ni_{4.50}S_{8.00}$. Liquid phase occupies a wide field extending from the Ni-S join toward the inside of the ternary composition. H-pn coexists with mss and/or liquid. The α coexists with γ and mss. The Fe-rich ends of the h-pn and liquid are more Fe-rich than those by them.

Two univariant assemblages are found as h-pn + mss + γ and h-pn+ mss + S(l). The sulfide liquid on the metal-rich side coexists with mss and γ as a univariant assemblage. Most Fe-rich mss (～FeS) can coexist with α and γ as a univariant assemblage.

Vs coexists with mss and S(l) as a univariant assemblage. No pyrite is found at this temperature.

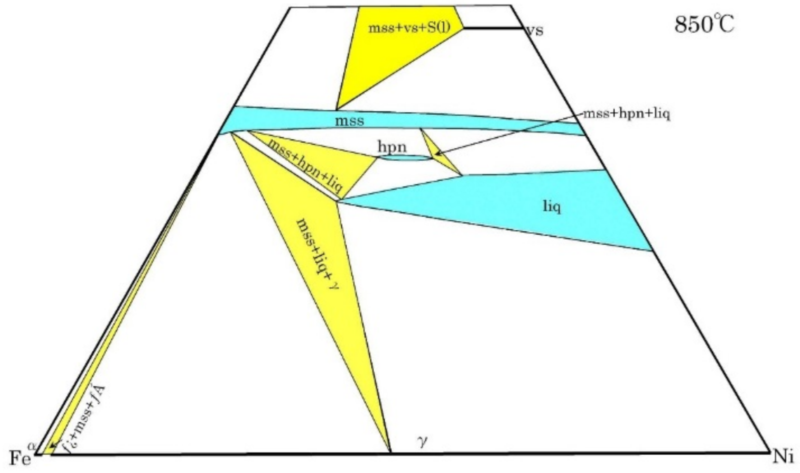


Fig. 5. Isothermal section in central portion of Fe-Ni-S system at 850°Cby dry method (modified diagram after Sugaki & Kitakaze, 1996; Kitakaze *et al.* [6]).

Phase Relations at 800℃

From the equilibrium run and EPMA data for the phases produced, the phase relations at 800℃ were obtained and shown as Fig. 6 (modified diagram after Kitakaze *et al.*6)).

H-pn ($Fe_{5.29}Ni_{3.74}S_{7.97}$) extends its field rapidly toward the Ni-rich side with decreasing temperature below 850℃, and reaches the Fe-free β_2 (44.7 atomic % S) in the Ni-S join at 806±3℃, at which β_2 crystallizes (Lin *et al.*20)). As seen in the figure, h-pn is formed continuous SS from h-pn ($Fe_{5.29}Ni_{3.74}S_{7.97}$) to β_2 at 800℃. The Fe-rich end composition of the SS ($Fe_{5.29}Ni_{3.74}S_{7.97}$) at 800℃ contains slightly Fe-rich than that at 850℃. Phase β_1 with the S-richest composition (～42.9 atomic % S) just appears by peritectic reaction between β_2 and liquid in the Ni-S join at 800℃. The liquid phase still occupies an extensive field but retreats its field toward the Ni-S join at 800℃. The continuous mss is present as at 850℃. The h-pn-β_2 SS coexists with the mss and/or liquid.

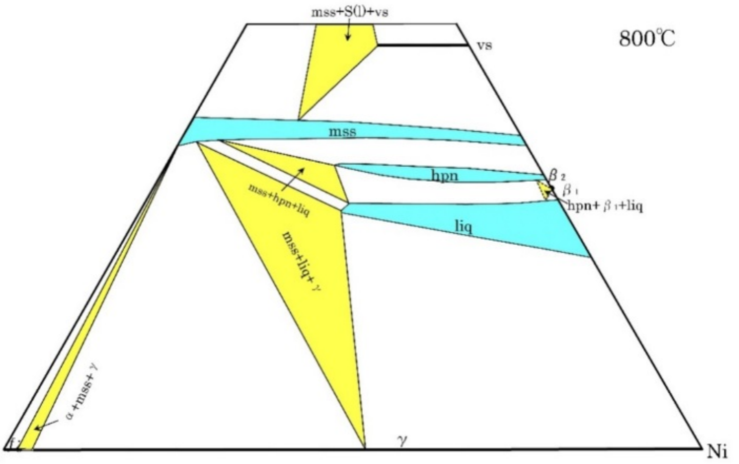


Fig. 6. Phase relations in the central portion of the Fe-Ni-S system at 800°C (modified diagram after Kitakaze *et al.*6)).

Five univariant assemblages are found in the isotherm at 800℃ as follows: h-pn + mss + liquid, mss + liquid + γ, mss + α + γ and β 1 (42.9 atomic % S) + h-pn + liquid and vs + mss + S(l).

Phase relation at 750℃

On cooling from 800℃, the liquid phase furthermore retreats toward the Ni-rich side. The tie-lines between mss and liquid are replaced by those between h-pn and γat 762±3℃ (invariant). The reaction is reversible.

Below 762±3℃, mss cannot crystallize from liquid by a pseudeutectic reaction. Phase β_1 grows and quickly extends as a SS from the Ni-S join within the ternary field with decreasing temperature, forming a SS with fairly large area.

The phase relation from the data for equilibrium studies and EPMA is shown in Figure 4 at 750℃ (modified diagram after Kitakaze *et al.* 6)).

There are five univariant assemblages in the system as follows: 1) mss + h-pn + γ; 2) h-pn + liquid + γ; 3) h-pn + β_1 + liquid; 4) mss + α + γ. 5) mss + vs + S (l).

A continuous SS from h-pn ($Fe_{5.44}Ni_{3.60}S_{7.96}$) to β_2 is formed at 750℃.

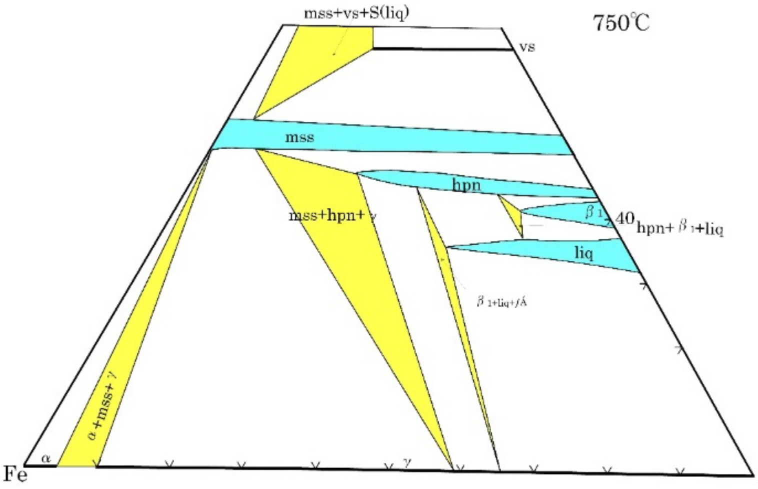


Fig. 7. The phase relations in the Fe-Ni-S system at 750℃ (modified diagram after Kitakaze *et al.* [6]).

Phase Relations at 700℃

Below 750℃, pyrite (py) appears in the system at 742±1℃ (Kullerud and Yoder[37], Barton and Skinner[38], Kubaschewski[35]) and assembles with vs and mss. And other tie-line change from h-pn and liquid to β_1 and γ at 739±3℃ was ascertained. Below this temperature, no crystallization of h-pn from liquid as pseudeutectic is found.

The isothermal phase diagram at 700℃, obtained from the equilibrium run data and EPMA data for the phases produced, is shown in Figure 5 (modified diagram after Kitakaze *et al.*, 2011). H-pn ($Fe_{5.07}Ni_{4.03}S_{7.90}$) continues as an elongated SS to phase β_2 in the Ni-S join. Liquid field shrinks toward the Ni-rich side but persists as a small field reaching the Ni-S join. Fe-rich portion of the metal-rich side of the h-pn SS coexists with γ, whereas its Ni-rich portion coexists with β_1SS.

Four univariant assemblages are found in the metal-rich portion of the system as follows: 1) mss + α+γ, 2) h-pn + mss +γ, 3) h-pn +β_1+γ, 4) β_1 + liquid +γ.

In the S-rich portion of the system, pyrite forms a limited SS at 700℃. Vs also has a limited SS. Both disulfides coexist separately with S (liquid) or mss and both SS coexist each other and form two univariant assemblages with mss or S (liquid).

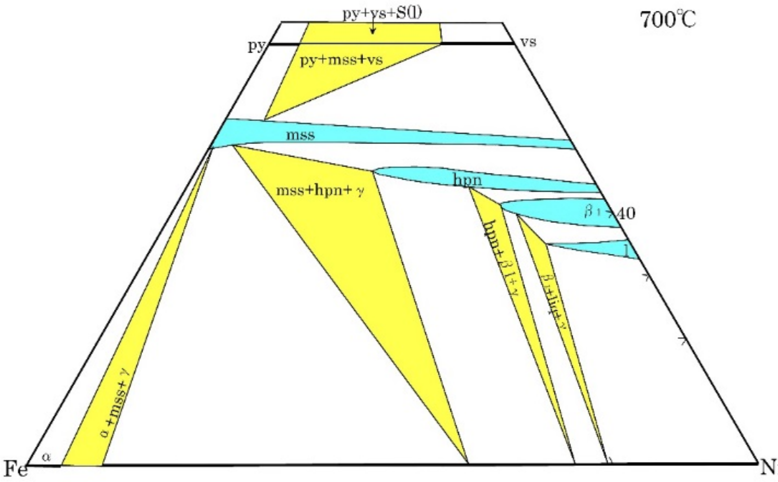


Fig. 8. The isothermal diagram in the Fe-Ni-S system at 700℃ (Modified diagram after Kitakaze et al., 2011).

Phase Relations at 650℃

The isothermal phase diagram at 650℃ is shown in Fig. 9. H-pn SS field grows slightly longer and wider (Sugaki & Kitakaze[13,14.39]), Kitakaze *et al*.[5.6]). The mss still exists and retains the complete SS. The field of phase β_1 contracts to become smaller than that at 700℃. The metal-rich side of h-pn SS ($Fe_{5.41}Ni_{3.65}S_{7.94}$), except the Ni-rich portion, coexists with γ as at 700℃. Phase β_1, except for its Ni-rich portion, can coexist with γdue to retreat of liquid field.

In the metal rich portion, four univariant assemblages are found as follows: 1) mss + α+ γ, 2) h-pn + mss + γ, 3) h-pn + β_1 + γ, and 4) β_1 + liquid + γ.

Also, in the S-rich portion of the system, two univariant assemblages of py ($Fe_{0.91}Ni_{0.09}S_{2.00}$) + vs ($Fe_{0.19}Ni_{0.81}S_{2.00}$) + mss ($Fe_{0.65}Ni_{0.20}S_{1.00}$) or S(l) also exist similar to those of 700℃.

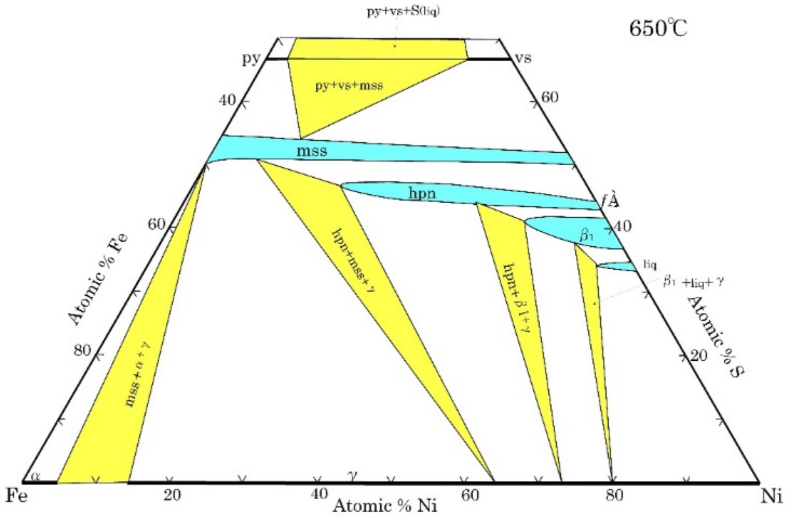


Fig. 9. The isothermal diagram in the Fe-Ni-S system at 650℃ (modified diagram after Kitakaze *et al*. [5,6]).

Phase relations from 650°to 600˚C

The liquid field disappears entirely at the 637˚C and 33.2 atomic % S eutectic on the Ni-S boundary. Pentlandite (low-form; pn) first appears as a stable phase at 625°±3˚C due to a polymorphic phase-transition from h-pn SS of the most Fe-rich composition $Fe_{5.60}Ni_{3.40}S_{7.82}$. This reaction is reversible. The phase-transition was ascertained by high-temperature X-ray powder diffraction, DTA, EPMA and microscopic examination (Sugaki & Kitakaze 1998). It proceeds toward the more Ni-rich and/or S-poor portions of the SS with decreasing temperature successively, and as a result pn is formed as another SS. Meanwhile Fe-rich extremity of h-pn retreats toward the Ni-rich and S-poor sides with decreasing temperature.

The Fe-rich extremity of the pn SS grows a little to the Fe-rich side by peritectoid and pseudoperitectoid reactions between mss and Fe-rich extremity of h-pn SS with decreasing temperature from 625℃. Because of the retreat of the h-pn SS and a slight growth of the Fe-rich extremity of pn SS with decreasing temperature, new tie-lines between the most Fe-rich end of pn and γ occur at or below 617°±3˚C replacing those between mss and the Fe-rich end of h-pn SS which were stable above this temperature.

On the other hand, the Ni-rich extremity of pn

SS grows to the more Ni-rich side by a peritectoid reaction between mss ($Fe_{0.40}Ni_{0.57}S_{1.00}$) and h-pn ($Fe_{3.25}Ni_{5.75}S_{7.92}$) immediately after leaving from the S-rich boundary of h-pn at 603 ℃ and by a pseudoperitectoid reaction between them down to 568℃ successively.

Phase relations at 600˚C

The phase relations based on the data of the equilibrium experiments and the EPMA data at 600˚C are shown in Fig. 10 (modified diagram after Kitakaze *et al.*, 2016). H-pn SS still remains stably in the elongated field with compositions from $Fe_{5.28}Ni_{3.72}S_{7.54}$ to $Ni_{2.56\sim2.75}S_{3.00}$ (β_2) although it retreats toward the Ni-S boundary compared to its composition at 650˚C. Pn forms a limited SS with a composition range from $Fe_{5.64}Ni_{3.36}S_{7.82}$ to $Fe_{3.25}Ni_{5.75}S_{7.92}$ including $Fe_{4.50}Ni_{4.50}S_{8.00}$ at 600˚C. Therefore, both high- and low-from pentlandites coexist. The S-rich side of pn SS coexists with mss. Its metal-rich side coexists mostly with the high-form SS. Only the Fe-rich portion of the pn can coexist with γ because of the retreat of the field of the high-form SS.

The field of β_1 becomes smaller at 600˚C than that at 650˚C by shrinking and retreating toward the Ni-S boundary. It coexists with Ni-rich high-form pentlandite SS and/or γ.

In the metal-rich portion of the system, there are five univariant assemblages as follows: 1) mss + α+ γ; 2) mss + pn + γ; 3) pn + h-pn + mss; 4) pn + h-pn + γ and 5) h-pn +β_1 + γ. The univariant assemblage of 3) pn + h-pn + mss suggests that the last two phases participate in a pseudoperitectoid reaction extending the Ni-rich end of the pn SS. The 2) univariant assemblage indicates that the Fe-rich end of pn SS extends slightly to the more Fe-rich side by means of a pseudoperitectoid reaction between mss and γ on cooling, not h-pn, because of the tie-line change from mss-h-pn (Fe-rich end) assemblage to the Fe-rich pn -γ assemblage at 617℃ as mentioned above. H-pn cannot participate the reaction below this temperature. However, the 4) univariant assemblage h-pn + pn +γ indicates that the Fe-rich extremity of h-pn retreats toward the Ni-rich side due to its breakdown into a mixture of h-pn with a little Ni-rich composition + pentlandite +γ as a pseudoeutectoid reaction with decreasing temperature below 617℃ successively.

On the S-rich portion of the system, the compositions of py and va SS retreat toward the Fe-S and Ni-S boundaries, respectively. Despite this, both py and vs still form two univariant assemblages separately with mss or S (liq) as those at 600˚C.

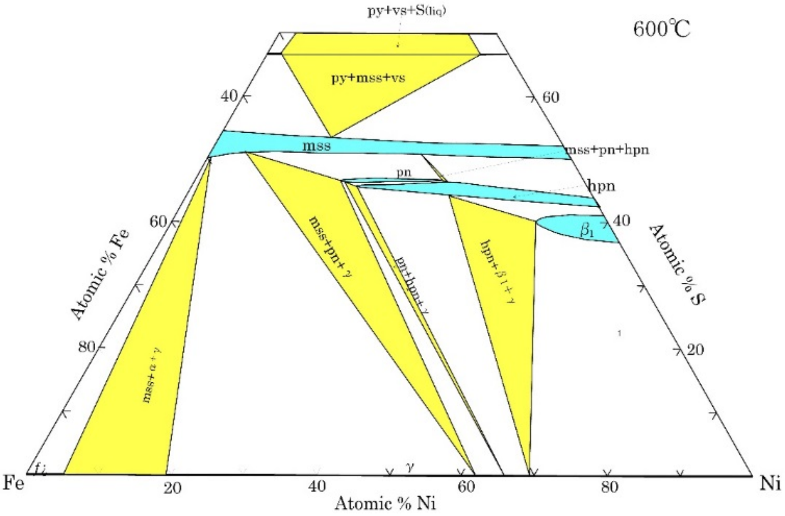


Fig. 10. The isothermal diagram in the Fe-Ni-S system at 600℃ (Modified diagram after Kitakaze et al., 2011).

Phase relations from 600° to 550˚C

The h-pn SS retreats rapidly toward the Ni-S boundary with decreasing temperature from 600˚C breaking down to a mixture of h-pn + pn + γ as its pseudoeutectoid reaction product. New tie-lines between pn and $\beta_1$replace those between h-pn and γ at or below 579°±3˚C. The This tie-line change is reversible. As a result, a new univariant assemblage of h-pn + pn + β_1 instead of the univariant assemblage of h-pn + pn + γ appear below this temperature. The Fe-rich extremity of h-pn furthermore retreats to more the Ni-rich side breaking down into a mixture of h-pn with a little Ni-rich composition + pn + β_1 as another pseudoeutectoid reaction with decreasing temperature from 579° to 503°±3˚C (ternary eutectoid of h-pn).

The Ni-rich extremity of the pn SS grows to the Ni-rich side by peritectoid and pseudoperitectoid reactions between mss and h-pn with decreasing temperature from 603 to 568℃. The compositions of the Ni-rich extremity of pn and mss and h-pn as pair of reactors as the pseudoperitectoids at temperatures from 600 to 570 ℃ are as follows.

The tie-lines between mss and h-pn are replaced by those between h-gd and pn SS at 568°±3˚C.

H-gd (αNi_7S_6 of Kullerud & Yund[40]), Misra & Fleet[41])) first appears in the ternary field close to the Ni-S boundary by a peritectoid reaction between mss and h-pn. It gets to the Ni-S boundary at 573°±3℃ (Kullerud & Yund[40])), and also grows to the Fe-rich side conversely as a limited at 568℃ with decreasing temperature by a pseudoperitectoid reaction between mss and h-pn at temperatures from 596° to 568℃, and furthermore extends continuously to the composition by pseudoeutectoid reactions of mss or h-pn at temperatures from 568 to 503℃.

Heazlewoodite first appears by inversion of β_1 (Ni_3S_2) at 565°±3˚C, and then by exsolutions subsequently from the β_1 and β_2 solid-solutions on cooling from 565° to 533˚C and from 564 to 524˚C, respectively, at the Ni-S boundary. This phase also occurs together with β_2 at a S-rich eutectoid of β_1 at 564˚C on the boundary, and grows as a small solid-solution within the ternary, coexisting with Ni-rich h-pn (Fe-bearing β_2) and β_1 (Fe-bearing β_1) as a limited SS below this temperature.

Phase relations at 550˚C

An isothermal phase-diagram obtained from the experimental data at 550℃ is shown in Fig. 11

(modified diagram after Kitakaze *et al.*⁵⁾). Due to the tie-line changes at 579° and 568°C and the appearances of h-gd at 596°C and hz at 565°C on cooling as described above, the phase relations in the Ni-rich portion of the metal-rich field of the diagram become more complicate than those at 600°C (Fig. 10).

Pn grows as a SS from $Fe_{5.68}Ni_{3.32}S_{7.84}$ to $Fe_{2.44}Ni_{6.56}S_{7.85}$ at 550°C and coexists with mss, h-pn. h-gd, β_1 and γ. However, an assemblage of pn and hz is unable to be formed because of the stable tie-lines between h-pn and β_1 at this temperature. Elongated h-pn SS retreats furthermore to the Ni-rich side, but still persists in a reduced field. It coexists with h-gd, β_1 and/or hz besides pn. A β_1 field shrinks and deforms, but its Ni-rich portion still connects with the Ni-S boundary. H-gd appears as a limited SS.

New five univariant assemblages of 1) mss + pn + h-gd; 2) pn + h-pn + h-gd; 3) pn + h-pn + β_1; 4) h-pn + pn h + β_1 and 5) pn + β_1+ γ appear in comparison with the isotherm at 600℃. Other univariant assemblages of 6) mss + α + γ and 7) mss + pn ($Fe_{5.68}Ni_{3.32}S_{7.84}$) + γ in the metal-rich portion and of 8) py+ vs + mss or S (liquid) in the S-rich portion still exist stably as the same as those at 600°C, but the composition of each phase of the assemblages differ with those at 600°C.

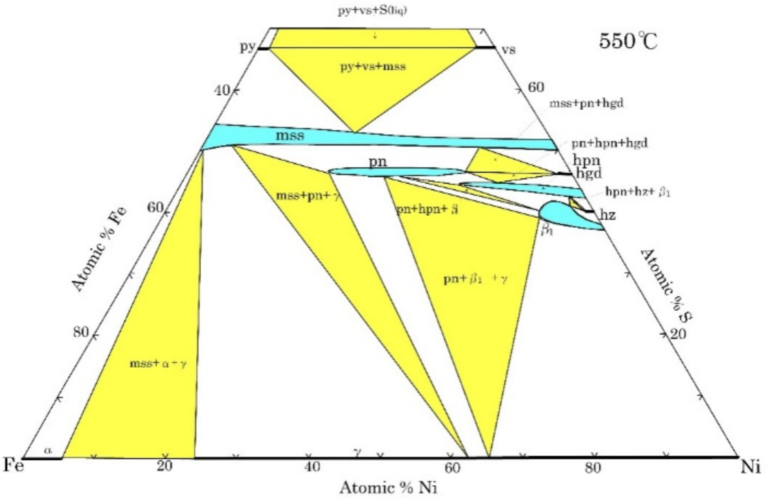


Fig. 11. The phase diagram in the system Fe-Ni-S at 550℃ (modified diagram after Kitakaze et al., 2011).

Phase relations from 550° to 500°C

Phase β_1 disappears at 533°±3°C to break down to a mixture of hz and Ni on the Ni-S boundary. However, it persists stable as a ternary phase away from the Ni-S boundary at 520°C. The β_1 coexists with pn, h-pn, h-pn, hz and/or γ. Phase $\beta_2$breaks down to a mixture of hz and h-gd at 524°±3°C of an eutectoid on the Ni-S boundary. but its SS (h-pn) remains as a Ni-rich ternary phase within a small thin field coexisting with hz, β_1, h-gd and/or pn. Pn coexists separately with mss, h-gd, β_1, and/or γ in addition to h-pn SS.

Awaruite appears due to an order–disorder transformation of γ at 517°C and has a limited SS extending along the Fe-Ni boundary with decreasing temperature (Kubaschewski³⁵⁾, Swartzendruber⁴²⁾). It coexists with hz and/or γ below 517°C.

The tie-lines between h-pn and hz are replaced by those between h-gd and β_1 at 512°±3°C or below.

The h-pn SS finally breaks down to a mixture of pn, β_1 and h-gd at 503°±3°C. The composition of the h-pn at the eutectoid 503°C is almost the same as composition ($Fe_{1.04}Ni_{7.96}S_{6.93}$), and the compositions of its breakdown products also are very close to $Fe_{2.44}Ni_{6.56}S_{7.85}$ for pn, β_1 and h-gd at 500˚C.

Phase relations at 500˚C

At 500˚C, h-pn disappears, and pn is present as an elongated SS extending from $Fe_{5.68}Ni_{3.32}S_{7.85}$ to $Fe_{2.43}Ni_{6.57}S_{7.85}$, and coexists with mss, h-gd, β_1 and/or γ as shown in Fig. 13. The mss field becomes narrower but still extends continuously across the entire diagram. H-gd coexists with β_1 and/or hz in addition to mss and/or pn. Hz coexists stably with γ and/or awaruite as well as β_1 and/or h-gd. Awaruite coexists only with hz and/or γ at 500℃.

There are nine univariant assemblages in the system as follows: 1) mss + α+ γ; 2) pn ($Fe_{5.68}Ni_{3.32}S_{7.85}$) + mss + γ; 3) pn + mss + h-gd; 4) pn + h-g + β_1; 5) h-gd + β_1 + hz; 6) pn + β_1 + γ; 7) hz + β_1 + γ; 8) hz +γ+ awaruite and 9) hz + awaruite + γ.

Meanwhile, in the S-rich portion of the system, py and vs at 500˚C still form two univariant assemblages with 10) mss or S (liquid) as they do at higher temperature although their SS fields have shrunk.

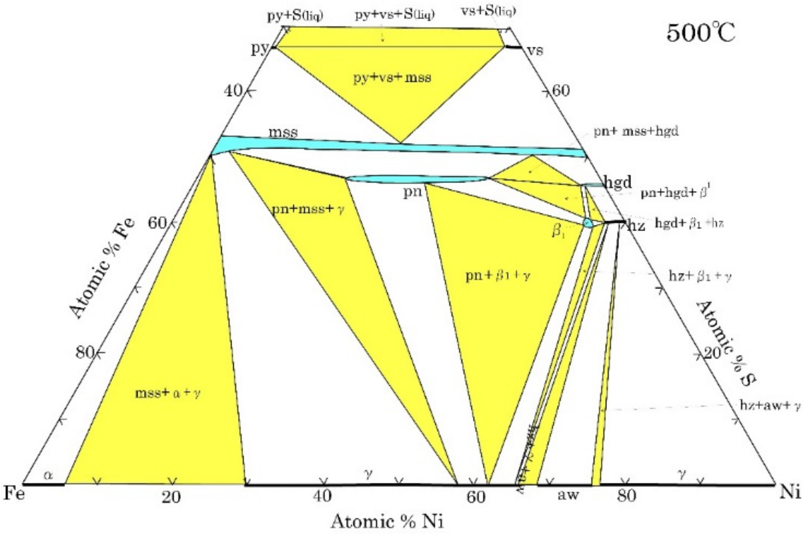


Fig.12. The phase diagram in the Fe-Ni-S system at 500℃(modified diagram after Kitakaze *et al.*, 2011).

Phase relations from 500˚ to 450˚C

The tie-lines between $\beta_1$and h-gd are replaced by those between pn and hz at 498°±3˚C. Pn is able to coexist stably with hz below this temperature. The β_1 field contracts with decreasing temperature, and finally disappears by its breakdown to a mixture of pn, hz and γ at 484°±3˚C of a ternary eutectoid. The composition of the β_1 at this eutectoid is very close to that of the β_1 ($Fe_{0.26}Ni_{2.87}S_{2.00}$) produced at 485°±3℃. Also, the compositions of the breakdown products at the eutectoid are close to those of pn, hz, and γ at 482℃.

Vl of composition $Fe_{0.70}Ni_{2.29}S_{4.00}$ at 455℃ appears independently as a ternary phase within the S-rich portion of the system as a product by a peritectoid reaction between mss and vs. This phase grows as a limited solid-solution to the Ni-rich side by a pseudoperitectoid reaction between vs and mss with decreasing temperature. The Fe-rich end of vl coexists with py, vs and mss as two univariant assemblages of py + vs + vl and py + mss + vl at 459℃ or below.

Phase relations at 450˚C

Because of disappearances of h-pn at 503˚C and β_1 at 484˚C, the phase relations at 450˚C become simpler than those at 500°C as seen in Fig. 14. Mss still maintains a continuous SS field as before but becomes thin. It coexists with py, vs and vl in the S-rich side and with pn, h-gd, α and γ in the metal-rich side. Pn is also found as a principal phase as before, and coexists with mss, h-gd, hz and γ. It forms an elongated SS of the composition range from $Fe_{5.73}Ni_{3.27}S_{7.92}$ to $Fe_{2.84}Ni_{6.16}S_{7.89}$ including $Fe_{4.5}Ni_{4.5}S_{8.0}$, but becomes thinner than that at 500°C.

Seven univariant assemblages as follows: 1) mss + α +γ; 2) mss + pn ($Fe_{5.73}Ni_{3.27}S_{7.92}$) + γ; 3) pn ($Fe_{2.84}Ni_{6.16}S_{7.89}$) + mss + h-gd; 4) pn ($Fe_{2.84}Ni_{6.16}S_{7.89}$) + h-gd + hz; 5) pn ($Fe_{3.61}Ni_{5.39}S_{7.73}$) + hz + γ; 6) hz + γ + awaruite and 7) hz + awaruite + γ are found in the metal-rich portion of the isotherm at 450°C. On the other hand, vl appeared at 459°C as above grows as a limited SS. There are four univariant assemblages of 8) py+ vl + vs; 9) py + vl + mss and 10) vs + vl + mss or 11) S (liquid) in the S-rich portion of the system. A limited SS of vl coexists with vs, py and mss, and forms two univariant assemblages of 8）and 9) in the Fe-rich side and a univariant assemblage of 10) in the Ni-rich side. No the coexistence of pentlandite and awaruite is found at 450°C, however, pentlandite appears in association with awaruite and/or γ below 431°± 3°C.

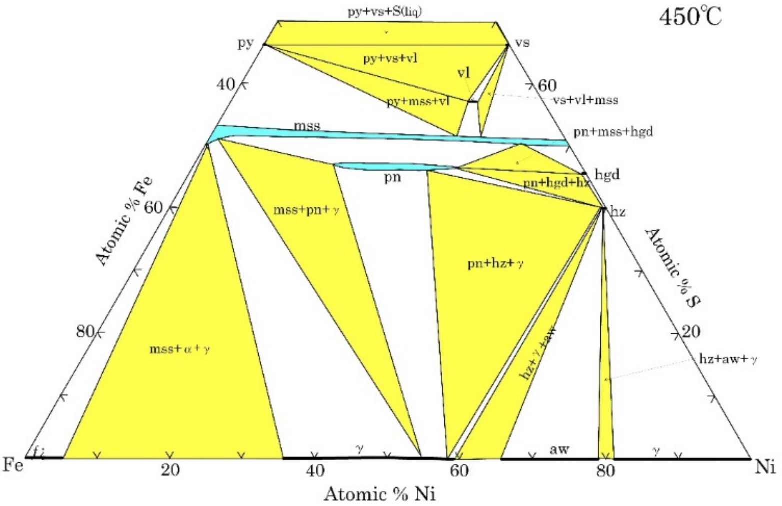


Fig. 13. The phase diagram in the system Fe-Ni-S at 450℃ (modified diagram after Kitakaze *et al.* [5])).

Phase relations of the $Fe_{4.5}Ni_{4.5}$-S and $Fe_{0.9}$-Ni_3S_2 joins in the system Fe-Ni-S

Phase relations along the $Fe_{4.5}Ni_{4.5}$-S join

The phase relations were investigated along the pseudobinary $Fe_{4.5}Ni_{4.5}$-S join at temperatures from 1,100° to 450°C using the evacuated silica tube method, with a particular focus on a limited composition range from 35 to 57 atomic % S in order to unravel the thermal stability ranges of high- and low-form pentlandites, coexisting with monosulfide solid-solution and γ.

The resulting phase diagram combined and modified with data after 1998; Kitakaze *et al.* [5,6])) is shown in Fig. 14. About same diagram was already reported by Sugaki & Kitakaze (1998), but there were some minor mistakes of phase assemblages for pseudoeutectoid, pseudoeutectic and pseudoperitectoid in consideration as ternary phase relations. From the diagram it is understood that h-pn transforms into pn (low-form) on cooling.

Pn of composition $Fe_{4.5}Ni_{4.5}S_{8.0}$ is cubic *Fm*3*m* with *a*=10.100 Å at room temperature. On the other hand, h-pn ($Fe_{4.5}Ni_{4.5}S_{7.95}$) is cubic *Pn*3*m* with *a*=5.194Å at 650˚C, corresponding to one half of the cell edge of pn. This high-low inversion is reversible. It is thought to be a transition of an order-disorder type from the supercell (low-form) to the sub-cell (Sugaki & Kitakaze[13,14]).

A S-less portion of the h-pn SS than 46 atomic % S cannot invert into the low-form, but successively exsolves pn from the SS along a solvus reducing its SS field with decreasing temperature. Finally, the h-pn SS gets to composition $Fe_{4.5}Ni_{4.5}S_{7.36}$ (44.98 atomic % S) at 587°±3˚C corresponding to the end of the exsolution and the beginning of the pseudoeutectoid of the high-form in the join. It breaks down into a mixture (univariant assemblage) of h-pn with a very little Ni-richer composition, pn and γ at 587℃, and changes successively to the divariant assemblage of pentlandite and γ at 585°±3℃on cooling. The appearance of this univariant assemblage was ascertained as a narrow field as a limited temperature range of only a few degrees such as 1°, 2°, 3° and 6℃ at 45.8, 45.0, 44.4 and 36.0 atomic % S, respectively. In the S-richer portion than 47 atomic % S as a bulk composition in the join h-pn or pn appear as the divariant assemblages with mss. These pentlandites play a phase-transition of the no mass-transfer type. In the cases, their inversion temperatures fall slightly from 615° to 611°±3˚C with increasing S content of the bulk composition because a composition of pentlandites in the divariant assemblages becomes more Ni-rich than Fe=Ni in atomic % so as to be off the join.

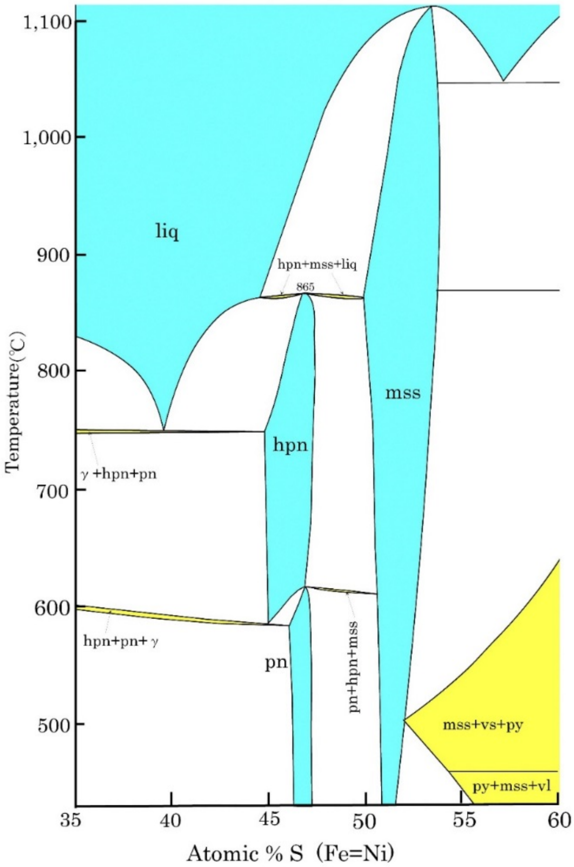


Fig. 14. The phase relations of the $Fe_{4.5}Ni_{4.5}$-S join in the composition range from 35 to 60 atomic % S at temperatures from 1,100 to 450℃ in the Fe-Ni-S system (redrawing diagram after Kitakaze *et al.*[5,6,13]).

Phase relations along the $Fe_{0.9}S$-Ni_3S_2 join

The pseudo binary phase diagram for the $Fe_{0.9}S$-Ni_3S_2 join (0 to 60 atomic % Ni), passing through the ideal composition $Fe_{4.5}Ni_{4.5}S_{8.0}$ of pentlandite, in the system at temperatures from 950 to 450°C was constructed in order to examine the thermal stabilities of both high- and low-form pentlandite solid-solutions, and to ascertain their intricate relations with coexisting phases such as mss, β_1、h-gd and hz below 600°C. As a result, the diagram was obtained as shown in Figure 10. This figure corresponds to that at the same position as a cross section shown by Kullerud (1962, 1963a), but the phase relations in this diagram really differ to those by him, because of the appearances of high-form pentlandite and β_1 as the new phases, their eutectoids and the tie-line changes among the phases as mentioned above already. The phase relations are especially complicated in the Ni-rich portions below 550°C.

The h-pn SS has a large wedge-like field, and coexists with mss, pn or β_1 as the divariant assemblages in the join. On the other hand, pn appears as limited SS from 26.5 to 31.6 atomic % Ni (561°C) below 614°C in the join、and coexists with mss, h-pn, β_1, h-gd, hz and/or γ as the divariant and univariant assemblages. This pn SS is principally formed by the phase-transition from the high-form SS on cooling. This phase-transition begins from h-pn with $Fe_{4.42}Ni_{4.58}S_{7.96}$ at 614°C as the non-mass-transfer inversion, continues as the mass-transfer inversion immediately and ends at 561°C and 31.6 atomic % Ni of pentlandite. The field of the high-form SS also reduces by exsolution along its solvus for pn addition to the phase-transition with decreasing temperatures down to 561°C. At this temperature the h-pn SS of a composition with 40.0 atomic % Ni breaks down by a pseudoeutectoid reaction into a mixture of h-pn with a little S-poorer composition, pn and β_1 as a univariant assemblage. However, h-pn of this univariant assemblage decrease its amount with descending temperature and disappears at 529°C, 40 atomic % Ni. Its field changes to the divariant assemblage of pn and β_1 below this temperature. H-pn (Fe-bearing β_2) is stable down to 503°C of its eutectoid in the system, but the fields of the univariant assemblage h-pn + pn + β_1 disappears at higher temperature (540° to 509°C) than 503°C because those are out of the

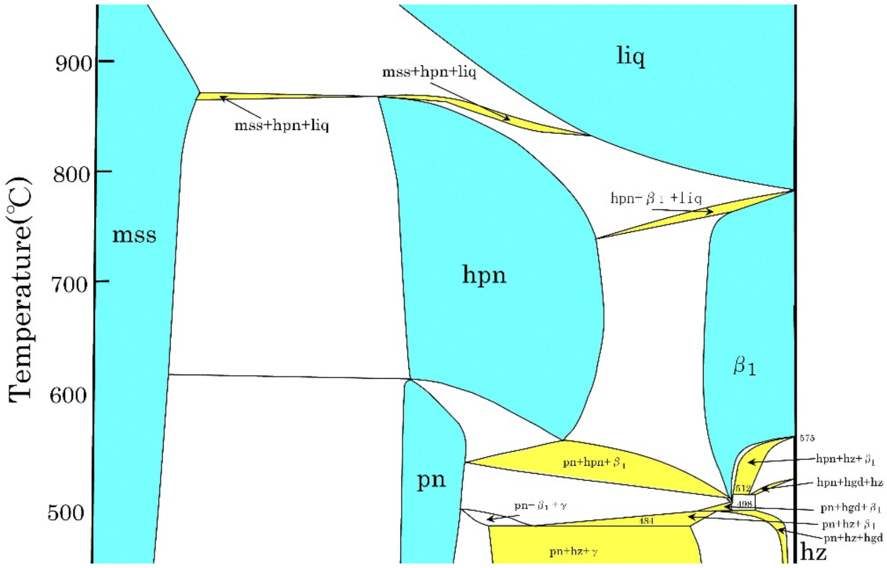


Fig. 15 The phase relations in the $Fe_{0.9}S$-$Ni_{3.0}S_{2.0}$ join of the system Fe-Ni-S at the temperatures from 950° to 450℃ in the composition from 0 to 60 atomic % Ni(redrawing diagram after Kitakaze et al.[5,6])).

join. Divariant assemblage h-pn + β_1 also disappears at 509℃.

Heazlewoodite with Ni_3S_2 in the join first appears as a stably principal phase owing to the phase transition of β_1 at 565°C, and coexists with β_1 (565° to 484℃), high-form pentlandite (565° to 512°C), high-form godlevskite (524° to 397°C), pentlandite (below 498°C) and γ (below 484°C) as the divariant and univariant assemblages in the join. Among them, the assemblage of pn and hz occurs as a principal association due to the tie-line change at 498°C or below as illustrated already, sometimes in association with β_1, h-gd or γ. The univariant assemblage of pn + hz + β_1 among them only appears at limited temperature range between 498 and 484°C.The univariant assemblages of pn + hz + h-gd or γ is stable below 498° or 484°C, respectively. As mentioned above, the phase relations in the Ni-rich portion of the join below ～550°C are complicate because of the occurrence of two tie-line changes at 512° and 498°C and two eutectoid of high-form pentlandite and β_1 at 503° and 484°C, respectively. So, an enlarged figure of that portion is given supplementary.

Pentlandite ss

The compositional ranges of the pn SS at temperatures from 625to 450°C in this study are shown in comparison with those obtained by Shewman & Clark[43], Misra & Fleet[41,44] and Ueno *et al.*[45] in Fig. 16. These SS ranges overlap in a principal portion each other except for both the Fe- and Ni-rich extremities of the solid-solutions as seen in the figure. There also is a tendency roughly that the solid-solution range moves gradually to the Fe-richer side with decreasing temperature. A compositional range from $Fe_{5.68}Ni_{3.32}S_{7.85}$ to$Fe_{2.43}Ni_{6.57}S_{7.85}$ (46.59 atomic % S) including $Fe_{4.5}Ni_{4.5}S_8$ at 500°C by us is approximately the same as those obtained by these authors except Shewman & Clark[43]. The pn SS retreats its Ni-rich extremity to the inside of the ternary so as to reduce its field below 500°C (Shewman & Clark[43], Ueno *et al.* [45], this study).

According to the previous papers (Kullerud[46], Naldrett *et al.* [47], Kullerud *et al.* [9], Shewman & Clark[43], Fedorova & Sinyakova[15]), pentlandite cannot coexist with γ at temperatures from 575° to 600°C because the FeS-$(Ni,Fe)_{3\pm x}S_2$tie-lines are stable. However, no such tie-lines were found in this study. Pentlandite can coexist with γ in a wide temperature range from 617° to 450℃ or below. The assemblage of most Ni-rich pn and hz as seen in Ni-Cu ores appears first at 498°±3°C by the tie-line change as mentioned already. This is in good agreement with of approximately 500°C estimated by Kullerud[46].

Pn is also produced by exsolution from the h-pn SS and β_1 SS of ternary compositions with decreasing temperature and by those breakdowns at 503° and 484°C, respectively, of eutectoids as stated above already.

Kitakaze & Sugaki[49] reported that a single phase of pentlandite of the compositions with $Fe_{3.0}Ni_{6.0}S_{8.0}$ and $Fe_{2.5}Ni_{6.5}S_{8.0}$ shows phase transition of non-mass-transfer type at 603° and 597°±3°C, respectively.

Bell *et al.* [48], who studied physical stability of pn by the high-pressure DTA method, found that breakdown temperature of synthetic pentlandite ($Fe_{4.5}Ni_{4.5}S_8$) into a mixture of pyrrhotite and high (α) or low (β) hz h falls to 535°C at 14 kb and 425°C at 25 kb. However, these temperatures may correspond to those of the high-low inversion of pn. If so, it is thought that the inversion temperatures of h-pn and low-form pn decrease significantly with increasing pressure, but we have now no such a data about its pressure effects.

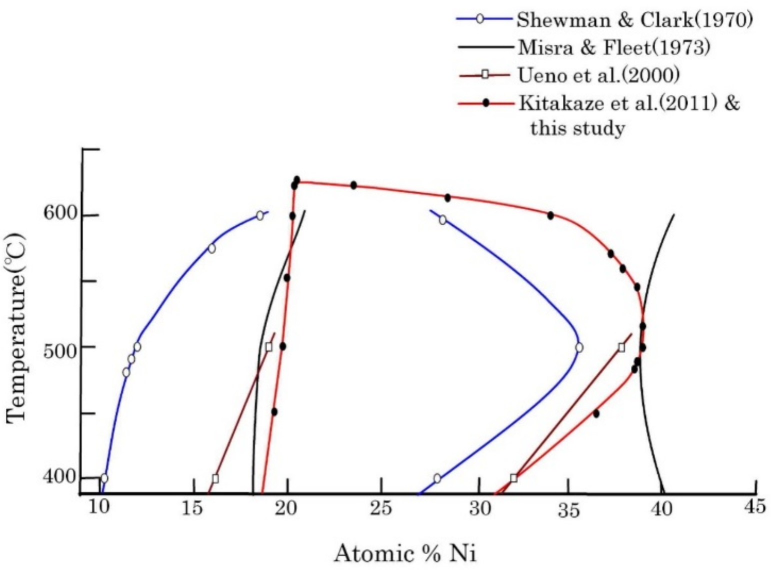


FIG. 16. A composition range in the maximum and minimum values of the Ni-content of pentlandite solid-solution at temperatures from 625to 400℃ in comparison to that by Sewman & Clark[43], Misra & Fleet[41] and Ueno *et al.* [45] (modified diagram after Kitakaze *et al.* [5]).

DISCUSSION

Pentlandite stability

No phase corresponding to h-pn SS including $Fe_{4.5}Ni_{4.5}S_{8.0}$ was found at temperatures above 610°C by Kullerud[8,46], Kullerud *et al.*[9] and Hsieh *et al.*[27]. However, Sugaki *et al.*[2,3] found an extensive field for h-pn with more Fe-rich compositions than $Fe_{4.5}Ni_{4.5}S_{8.0}$ to $Ni_{3\pm x}S_2$ of the Ni-S boundary at 800 and 650°C. Hayashi *et al.* [50] and Hayashi[29] also recognized existence of the same SS as above in the equilibrium runs of the quaternary Cu-Fe-Ni-S at 850°C, and 800, 650 and 600°C, respectively. Fedorova and Sinyakova1[5] investigated the isothermal phase relations in the Fe-Ni-S system at 900, 820 and 600°C, and reported an extended hz SS $(Fe_xNi_{1-x})_{3\pm y}S_2$ at 820 and 600°C at which limited pn SS. Karup-Møller & Makovicky[16] showed an elongated field of $(Fe,Ni)_{3\pm x}S_2$ in the phase diagram at 725°C. Both the SS correspond to h-pn-$Ni_{3\pm x}S_2$ SS of Sugaki *et al.*[2,3] and Kitakaze *et al.*[5,6].

Ni-rich ternary phase $Ni_{3\pm x}S_2$ in the Ni-rich portion of the system was found at 862°C by Kullerud[8] and Kullerud *et al.*[9]. Also, a ternary phase β with a limited SS at 850°C was described by Hsieh *et al.*[27]. However, these phases are in the liquid field or along its S-rich boundary at 850°C in this study except a small S-rich part of phase β.

H-pn with composition $Fe_{4.94}Ni_{4.06}S_{8.00}$ appears earliest at 870±3°C by the pseudoperitectic reaction between mss and sulfide liquid in the system. This precipitation by the pseudoperitectic reaction terminates when the high-form solid-solution extends composition to reach the Ni-S join to include phase β_2 at 806±3°C. It is noticeable that the appearance of the high-form is so fast as to form the extensive SS on cooling for only 64°C from 870 to 806°C. After the pseudoperitectic reaction, the crystallization of the high-form from the liquid by pseudeutectic reaction continues with decreasing temperature down to 739±3°C, at which the tie-line of the liquid-high-form pentlandite changes into those of the β_1-γ. Fedorova & Sinyakova[15] also stated that hz SS (h-pn SS) is formed by a peritectic reaction between mss and sulfide liquid below 876°C.

Karup-Møller & Makovicky[16)] suggested that liquid (sulfide melt) -mss fractionation is replaced by liquid- $Ni_{3\pm x}S_2$ fractionation soon below 850℃, and this fractionation persists down to 635℃, at which the liquid in the Ni-S join solidifies (Kullerud & Yund[40)]). According to our study, the tie-line between liquid and high-form pentlandite persists at temperatures from 870±3℃ to 739±3℃, but no such tie-lines exist below 739±3℃. Similarly, liquid-monosulfide solid-solution tie-lines persist down to 762±3℃, but no such tie-lines are found below this temperature.

Pentlandite Ore Genesis

H-pn with Fe=Ni in atomic % can crystallize from liquid at temperatures from 865° to 746˚C in the system Fe–Ni–S (Sugaki & Kitakaze[14)]). This implies that Ni-Cu sulfide ores with h-pn can be formed by crystallization from sulfide magma in a geological process, as supported by many published observations and descriptions in the previous literatures (e.g. Lindgren[51,52)], Bateman[53)], Hawley[54)], Ramdohr[55)]). From our experimental data and referring to previous papers for pentlandite genesis, we propose that pentlandite is formed by the following genetic process: 1) a phase-transition (625° to 550˚C in the Fe-Ni-S system) from h-pn crystallized primarily from sulfide magma by successive peritectic and eutectic (and/or pseudoperitectic or pseudoeutectic) reactions (865° to 746˚C for Fe=Ni in the Fe-Ni-S system) (Sugaki *et al.*[1,2,3)], Fedorova & Sinyakova[15)], Karup-Møller & Makovicky[16)], Sugaki & Kitakaze[14)] Kitakaze *et al.*[5,6)]), 2) an exsolution from the S-rich extremity (boundary) of the h-pn SS consuming its large field with decreasing temperatures from 625° to 503℃ for the metal-rich boundary of the pn SS, 3) an exsolution of the metal-rich boundary of mss below 625 ℃ for the S-rich extremity of the pn SS as a narrow rim as a S-richer portion (Edwards[56)] , Hawley 1962[54)], Naldrett *et al.* [47)], Francis *et al.* [57)], Ramdohr[55)], Craig & Vaughan[12)], Fedrova & Sinyakova[15)], Kitakaze *et al.*[5,6)]), 4) an exsolution from a field of the β_1 SS, 5) a peritectoid at 603℃ and a pseudoperitectoid from 603° to 568℃ continuously between mss and h-pn for the growth of the Ni-rich extremity of pn with S (and Ni)-richer composition, 6) two pseudoperitectoids between mss and the Fe-rich extremity of h-pn at temperatures from 625° to 617℃ and between mss and γ at temperatures from 617° to 450℃ or below successively for a little growth of the Fe-rich extremity of pn (Fedorova & Sinyakova[15)], Kitakaze *et al.*[5,6)]), 7) two successive pseudoeutectoids of the Fe-rich extremity of h-pn breaking down to pn with the metal-rich extreme composition (and γ or β_1) at temperatures from 617° to 579℃and from 579° to 503℃, 8) pseudoeutectoid of h-pn at temperatures from 568° to 503℃ for the growth of the Ni-rich extremity of pn successively from 5) pseudoperitectoid reaction, 9) pseudoeutectoid of mss at temperatures from 568° to ～500℃ for the Ni-rich end of pn (and h-gz) an exsolution from Fe-bearing h-gd below 503℃ for the Ni-rich extremity of pn, 11) an eutectoid of h-pn ($Fe_{1.04}Ni_{7.96}S_{6.93}$) breaking down to the Ni-rich extremity of pn (h-gd and β_1)at 503℃and 12) an eutectoid of β_1 ($Fe_{0.26}Ni_{2.86}S_{2.00}$) breaking down to pn, hz and γ at 484℃.

Among these possibilities, pentlandite in magmatic Ni-Cu sulfide deposits is thought to have been formed principally by the reactions of 1) to 5). Pentlandite can also appear as a product by hydrothermal precipitation and replacement below ～600˚C (e.g. Lindgren[52)], Bateman[53)], Edwards[56)], Hawley[54)], Park & MacDiarmid[58)], Sugaki & Kitakaze[59)]). Fleet[60)] recently reviewed that high-form pentlandite (Fe=Ni) crystallizes from metal-rich liquid between 865° and 746℃ in a series of presentation extending from Sugaki *et al.*[1)] to Sugaki & Kitakaze[14)], noting that pentlandite in the magmatic sulfide ores in generally understood to form by segregation or phase separation from mss in the subsolidus.

Pentlandite from the magmatic Cu–Ni ore deposits commonly assembles with pyrrhotite and chalcopyrite and sometimes cubanite and bornite. Accordingly, to study the pentlandite ore genesis, it is sure to furthermore ascertain the phase relations in the quaternary system Fe–Ni–Cu–S in addition to those of the ternary Fe–Ni–S. For such a purpose the phase–equilibrium studies of the quaternary Fe–Ni–Cu–S in relation with the ore genesis of the Cu–Ni deposits were already carried out by Craig & Kullerud[26)], Hill[61)], Hayashi[29)] and Peregoedova & Ohnenstetter[19)]. Although they reported the divariant and univariant assemblages among the phases on the Fe–Ni–S, Cu–Ni–S, Cu–Fe–S and Cu–Fe–Ni faces of the quaternary tetrahedron, there are found no a four component phase independently within the Cu–Fe–Ni–S tetrahedron except for such a limited quaternary solid-solution grown fat slightly within the tetrahedron from the Fe–Ni–S or Cu–Fe–S faces as monosulfide solid-solution, pentlandite and heazlewoodite or bornite and intermediate solid-solution, respectively.

While Kitakaze[62)] found three sulfide phases, X:$(Fe,Cu)_6Ni_3S_8$, Y:$CuFe_6Ni_2S_8$ and Z:$Cu_2Fe_5Ni_2S_8$, in the Fe-Ni-Cu-S system as unknown minor minerals in lherzolite of the Horoman peridotite massif in the southern mountains of Hidaka, Hokkaido, Japan. These phases were approved by the Committee for New Minerals and Mineral Names of the International Mineralogical Association and named as sugakiite $Cu(Fe,Ni)_8S_8$ for phase Y (Kitakaze[63)]), and horomanite $(Fe,Ni,Co,Cu)_9S_8$ and samaniite $Cu_2(Fe,Ni)_7S_8$ for phases X and Z (Kitakaze[64)], Kitakaze *et al.* [65)]), respectively. Peregoedova & Ohnenstetter[19)] recently reported that a complete quaternary SS between hz SS $(Ni, Fe)_{3\pm x}S_2$ and intermediate SS $Cu_{1\pm x}Fe_{1\pm x}S_2$ (their terminology) in the quaternary system Fe–Ni–Cu–S at 760˚C. Recentry, Kitakaze et al.[66)] found Ni-rich horomanite associating chalcopyrite in the Kouyama gabbroic body, Hagi, Japan.

These facts suggest a possibility that the phase relations in the quaternary system Fe–Ni–Cu–S will be more complicate than those by the authors of the previous literatures as above.

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