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EXPERIMENTAL STUDIES OF THE TERNARY Fe-Co-S SYSTEM IN THE TEMPERATURE RANGE 500—700°C

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A b s t r a c t. The Fe-Co-S system is a part of the five-component Fe-Co-Ni--Cu-S system. Its thorough study is essential for the interpretation of the conditions of formation of some liquid-magmatic deposits which are important both from the geological and economic point of view.

Incomplete solid solution FeS_2 — CoS_2 occurs in the Fe-Co-S system. The solubility of CoS_2 in FeS_2 is very limited (below 2 wt. %) whereas that of FeS_2 in CoS_2 is significant, increasing evidently with temperature ($500°C$ — 37 wt. % FeS_2, $600°C$ — 60 wt. % FeS_2, $700°C$ — 75 wt. % FeS_2). The solubility of FeS_2 in CoS_2 attains a maximum value of 80 wt. % at 735 $±3°C$. At this temperature, an invariant reaction also takes place: $py + ct + V \rightleftarrows po + L + V$. In contradistinction to this, the solubility of iron sulphide in Co_3S_4 decreases with temperature. With an increase in temperature, the solubility of cobalt sulphide in iron monosulphide along the FeS — Co_9S_8 join increases substancially. At $500°C$ FeS takes 16 wt. % Co_9S_8 in its structure, at $600°C$ — 30 wt. %, and at $700°C$ — 38 wt. %. On the other hand, the solubility of FeS in Co_9S_8 does not change with temperature, amounting to app. 20 wt. % FeS. A precise determination of the phase boundaries in the metal-rich portion of the Fe-Co-S system by means of X-ray, microscopic and thermal methods is impossible and requires further investigations.

INTRODUCTION

The Fe-Co-S system is a part of the five-component Fe-Co-Ni-Cu-S system. Its thorough study is essential for the interpretation of the conditions of formation of some liquid-magmatic deposits which are important both from the geological and economic point of view. Earlier works (Wyszomirski 1976a, 1976b) as well as the present one, together with Lamprecht's studies (1975a, 1976) of the Co-Ni-S system, should yield data comparable with those on the Outukumpu ores. Ore mineralization of this type also occurs in the basic rocks of NE Poland, being characterized by a high Co content in pentlandite (Kucha, Salamon 1973).

PHASES IN THE Fe-Co-S SYSTEM

Figure 1 shows the minerals and synthetic phases present in the Fe--Co-S system.

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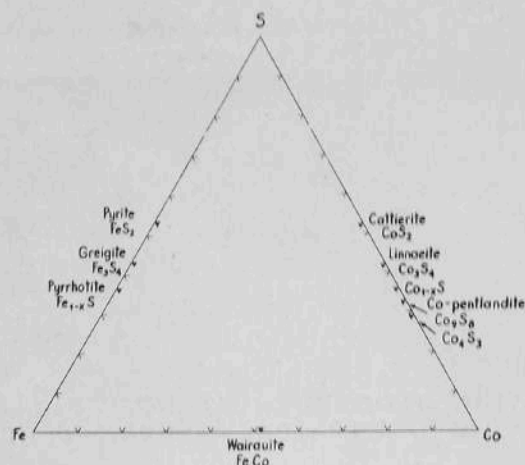
Fig. 1. Minerals and synthetic phases in the ternary
Fe-Co-S system (in wt.%)

Sulphur appears in nature in native state, forming concentrations of high purity in several deposits.

Pyrite, FeS_2, is the most common sulphide. It crystallizes in the cubic system, representing the Pa3 structure. Pyrite is stable up to 734°C, at which temperature, due to peritectic reaction, it decomposes into 1C hexagonal pyrrhotite and sulphur (Kullerud, Yoder 1959).

Cattierite, CoS_2, represents the type of structure identical with pyrite. It is stable up to 950°C; at this temperature it dissociates into $Co_{1-x}S$ and gaseous sulphur (Kužnecov et al. 1965).

Linnaeite, Co_3S_4, crystallizes in the cubic system, forming spinel structure. At 630°C it decomposes into $Co_{1-x}S$ and CoS_2 (Kužnecov et al. 1965).

Another spinel, greigite Fe_3S_4, also crystallizes in the Fe-Co-S system. Skinner et al. (1964) report that this phase decomposes into pyrrhotite and sulphur between 238° and 282°C in the conditions of experiments of short duration. They state, however, that this temperature range may be non-representative of the equilibrium conditions considering the small reaction rate. According to other investigators (Uda 1967; Berner 1971; Scott, Kissin 1973), greigite is a metastable phase appearing under low-temperature conditions.

Pyrrhotite, $Fe_{1-x}S$, is the most frequently investigated sulphide phase. This issues primarily from experimental difficulties due to sluggish, particularly at low temperatures, reaction kinetics. From the melting point (1190°C) down to 308°C only hexagonal pyrrhotite with the structure of the NiAs (1C) type occurs. This phase, though in a more limited composition range, also appears at lower temperatures. Disordered 1C pyrrhotite cannot be quenched (Corlett 1968), and crystals cooled from its phase field acquire one or more superstructures.

$Co_{1-x}S$, like $Fe_{1-x}S$, crystallizes in the hexagonal system. Within the homogeneous $Co_{1-x}S$ solid solution, a transformation of the NiAs structure ($a_0 = 3.384$ Å, $c_0 = 5.196$ Å) into a superstructure of the same type has been noted, the latter being characterized by a threefold increase in the values of the lattice parameters ($a_0 = 10.10$ Å, $c_0 = 15.48$ Å) (Kužnecov et al. 1965). The stoichiometric phase, CoS, has been described as jaipurite, though its existence is rather doubtful. $Co_{1-x}S$ is a stable phase from 360—475°C to 1195°C. A decrease in the temperature of eutectoidal decomposition of this phase from 475°C down to 360°C with an increase in sulphur content in the solid solution indicates that sulphur has a stabilizing effect on $Co_{1-x}S$ (Kužnecov et al. 1965).

Co-pentlandite is a phase whose chemical formula has raised much controversy among metallographists and mineralogists. Thus, Guertler and Schack (1923) claim that its formula is Co_5S_4, Cagliotti and Roberti (1932) — Co_4S_3, Hülsmann and Weibke (1936) — Co_6S_5, whereas Curlook and Pidgeon (1953) maintain that it is $Co_{15}S_{13}$. The correct formula, Co_9S_8, has been determined by Linqvits, Lundqvist and Westgren (1936) and confirmed by Kužnecov et al. (1965). Co-pentlandite also occurs as a mineral in nature (Stumpfl, Clark 1964). It crystallizes in the cubic system, representing the pentlandite structure. The phase in question is stable up to 830°C.

Co_4S_3 is a high-temperature phase which exists only in the temperature range of 785 — 930°C (Kužnecov et al. 1965). Thorough studies carried out by Lamprecht (1975b) have revealed that the beginning of the reaction of Co_4S_3 formation takes place in the temperature range from 785 ±3°C to 802 ±5°C. The same author states that Co_4S_3 crystallizes in the cubic system, representing face-centered lattice. Below the stability temperature, it decomposes into Co_9S_8 and metallic cobalt.

Native cobalt has not been reported so far from nature. This metal crystallizes in two modifications. Below 420°C, hexagonal α-modification is stable, which above that temperature is transformed into cubic γ-modification. The transformation is not, however, spontaneous; therefore, the two modifications coexist at room temperature. The melting point of pure cobalt is 1495°C.

Pure iron is very rare in nature. It appears in three allotropic modifications: as α-iron with body-centered cubic lattice, stable below 910°C; as γ-iron with face-centered cubic structure, stable in the range from 910° to 1400°C; and as δ-iron with body-centered cubic lattice, stable up to the melting point (1534°C).

The FeCo solid solution forms from the corresponding alloy due to the transformation disorded ⇌ order. It is stable below 730°C (Hansen, Anderko 1958). This phase is known in nature as wairauite (Challis, Long 1964).

PREVIOUS EXPERIMENTAL STUDIES

The Fe-S system

The Fe-S system has been studied by Kullerud and Yoder (1959) at temperatures above 400°C. Below 350°C, the phase relations in this system are very complicated because of the presence of some $Fe_{1-x}S$ superstruc-

tures. At those temperatures, the Fe-S system has been investigated by Scott (1974). In the temperature range studied here, the system contains, besides the end-members of sulphur and iron, two binary phases described earlier in this paper.

The Co-S system

The Co-S system has not been so far the object of so many comprehensive studies as the Fe-S system. The knowledge of the system, particularly of its high-temperature, sulphur-rich portion, is, therefore, incomplete. The first study of the Co-S system was made by Rosenquist (1954). Its fuller description was then given by Kužnecov et al. (1965) and by Lamprecht (1976b). Besides the cobalt and sulphur end-members, five binary phases, discussed earlier in this work, are present in the Co-S system.

The Fe-Co system

The works dealing with this system have been summarized by Hansen and Anderko (1958), Elliott (1965) and Shunk (1969). Apart from the iron and cobalt end-members, the phase FeCo has been identified in the Fe-Co system. These phases Fe_3Co and $FeCo_3$ have also been thought to occur in the system in question (Elliott 1965). Subsequent studies (Pokorna, Velišek 1973) have failed, however, to confirm this thesis.

Phase relations

As appears from the data cited in literature, the Fe-Co-S system has been studied only fragmentarily. Thus Klemm (1962) investigated the $FeS_2-CoS_2-NiS_2$ join, conducting the syntheses in the presence of LiCl-KCl mixture. He has found that the FeS_2-CoS_2 solid solution series is incomplete at 500°C and 600°C and that at 700°C those disulphides dissolve entirely. The FeS_2-CoS_2 join was also investigated by Bouchard (1968), who carried out the syntheses by hydrous method. His experiments performed over a temperature range from 650 — 700°C have revealed the existence of a complete solid solution series. This fact failed to be confirmed by the studies of Wyszomirski (1976c), which have shown that the FeS_2-CoS_2 solid solution is incomplete in the range of 75 — 98 wt. % FeS_2 at 700°C. His experiments were made, however, using dry method. It seems that the completeness of the $(Fe,Co)S_2$ solid solution noted in the experiments performed by hydrous method is of metastable character.

The $CoS_{1.95}-Fe_{12}S_{13}$ join in the monosulphide field of the Fe-Co-S system was investigated by Curlook and Pidgeon (1953). They have found that the minimum of the liquidus temperature is 1138°C with the $Fe_{12}S_{13}$ content in the monosulphide studied being 65%.

Moleva et al. (1958) have studied the pseudobinary $FeS-Co_4S_3$ join. Yet, as follows from their report, it is the $FeS-Co_9S_8$ join that was the object of their investigations. It appears therefore that these authors committed, after Cagliotti and Roberti (1932), an error of ascribing the formula Co_4S_3 to Co-pentlandite.

METHODS OF INVESTIGATION

Starting materials

Experimental samples were either synthetized from stable phases in the Fe-S and Co-S systems or obtained directly from elements using the following reagents:
— 3N iron powder from Koch-Light Laboratories LTD,
— 2N5 cobalt powder from Koch-Light Laboratories LTD,
— spectrally pure sulphur (99.999%) from American Smelting and Refining Company Denver, Colorado.

Techniques

Sulphides were synthetized in evacuated, sealed silica tubes with minimum vapour space as described by Kullerud (1971). Heating experiments were performed in electrically controlled horizontal furnaces with temperature accuracy ±3°C, and the temperature was recorded continuously. When required, individual samples were repeatedly ground in the presence of acetone and reheated at given temperature, sometimes over extended periods of time, until equilibrium was attained. Runs were quenched in ice water and the reaction products routinely identified at room temperature.

Identification of phases

Specimens were investigated by microscopic, X-ray and DTA methods. Small polished sections of the products were prepared for examination under a reflected light microscope, and the identification of the phases was aided by using oil immersion. X-ray powder diffraction patterns were obtained with a Philips diffractometer, using Mn-filtered FeK_α radiation. DTA experiments were carried out on mixtures with standard quartz from Lake Toxaway in sealed, evacuated silica tubes; heating and cooling rates were about 3°C/min.

EXPERIMENTAL RESULTS

The results of investigations of the ternary Fe-Co-S system at 500°, 600° and 700°C are shown in Figures 2 — 4. Incomplete solid solution occurs between disulphides FeS_2 and CoS_2 which coexist with liquid sulphur. In all cases, the solubility of CoS_2 in FeS_2 is very limited, its value being below 2 wt. %. In contradistinction to this, the solubility of FeS_2 in CoS_2 increases evidently with temperature. Thus, at 500°C CoS_2 takes up to 37 wt. % FeS_2 in solid solution; at 600°C this value increases to 60 wt. %, and at 700°C to 75 wt. % FeS_2. The solubility of FeS_2 in CoS_2 attains a maximum value of 80 wt. % at 735 ±3°C. Simultaneously, an invariant reaction takes place:

$$py + ct + V \rightleftharpoons po + L + V$$
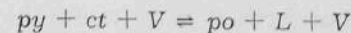
where:
py — pyrite,
ct — cattierite,
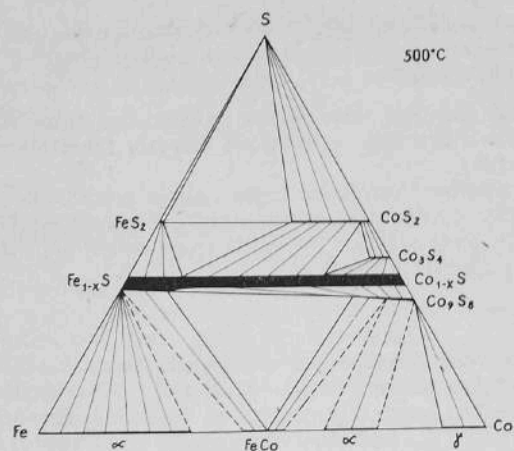po — pyrrhotite,
L — liquid,
V — vapour.

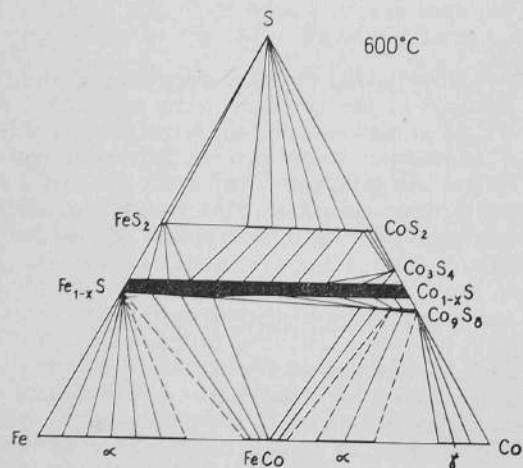Fig. 2. Isothermal join of the ternary Fe-Co-S system at 500°C (in wt.%)

Fig. 3. Isothermal join of the ternary Fe-Co-S system at 600°C (in wt.%)

Fig. 4. Isothermal join of the ternary Fe-Co-S system at 700°C (in wt.%)

22 wt. % (600°C) or 6 wt. % $Co_{1-x}S$ (700°C). At 500°C, $(Co,Fe)S_2$ solid solution with 5 to 37 wt. % FeS_2 forms a divariant field with the metal--deficient monosulphide solid solution containing from 20 to 72 wt. % $Co_{1-x}S$. At 600°C, a similar field has been noted between the $(Co,Fe)S_2$ solid solution taking 5 — 60 wt. % FeS_2 and the monosulphide containing 22 — 72 wt. % $Co_{1-x}S$. An increase in temperature makes Co_3S_4 incorporate less iron sulphide in its structure. At 500°C, Co_3S_4 takes 8 wt. % Fe_3S_4, the latter phase being, however, unstable at this temperature. At 600°C

Fig. 5. Relationship between the chemical composition of the $(Fe,Co)S_2$ solid solution and parameter a_0 of the unit cell

X-ray powder method proved very useful in the investigations of the $(Fe,Co)S_2$ solid solutions (Wyszomirski 1976c) since, as can be seen from Fig. 5, the relationship between the chemical composition of the $(Fe,Co)S_2$ solid solutions and the respective unit cell parameters, which has been established basing on the author's studies and the data cited in literature (Bouchard 1968), is in good agreement with Vegard's law. Pyrite coexists with the metal-deficient monosulphide up to 20 wt. % (500°C),
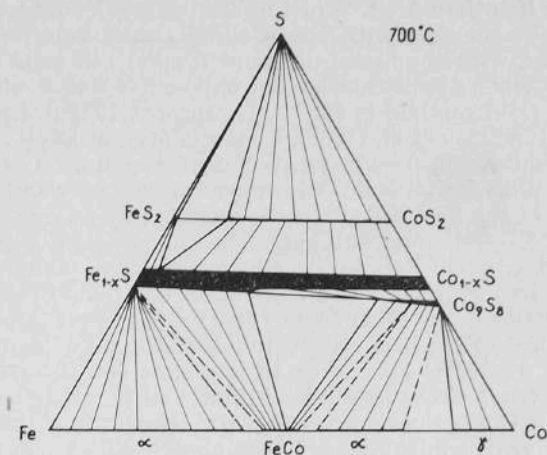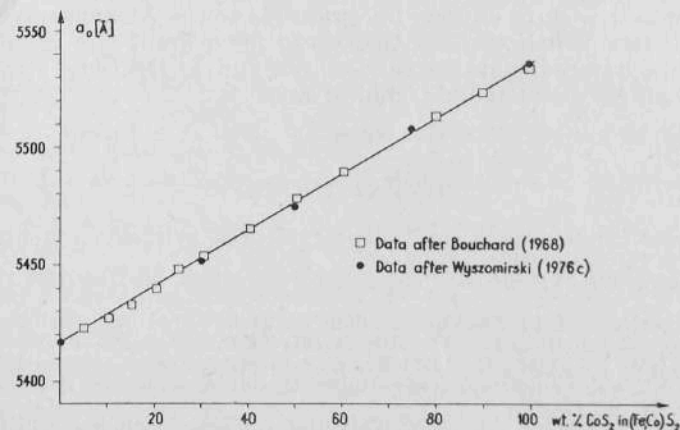
Co$_3$S$_4$ dissolves less than 2 wt. % of this iron sulphide. Both at 500°C and 600°C, (Co,Fe)$_3$S$_4$ coexists with the (Co,Fe)S$_2$ solid solution with up to 5 wt. % FeS$_2$ and with the metal-deficient (Co,Fe)$_{1-x}$S solid solution containing 0 — 28 wt. % Fe$_{1-x}$S. The decomposition temperature of Co$_3$S$_4$ determined by DTA method is 692°C (Lamprecht 1976b), i.e. higher than that given by Kužnecov et al. (1965). Consequently, at 700°C the (Co,Fe)S$_2$ solid solution containing 0 — 75 wt. % FeS$_2$ forms only a large divariant field with the (Co,Fe)$_{1-x}$S solid solution with 0 — 94 wt. % Fe$_{1-x}$S. The central portion of the Fe-Co-S system is occupied by a large, homogeneous field of iron and cobalt monosulphide. The composition of pyrrhotite varies from stoichiometric FeS to Fe$_{1-x}$S according to Arnold (1962). The other end-member of the (Fe,Co)$_{1-x}$S solid solution, Co$_{1-x}$S, possesses the region of homogeneity from 36.0 to 38.9 wt. % S (Kužnecov et al. 1965). The solubility of Co$_9$S$_8$ in iron monosulphide increases evidently with temperature. Thus, at 500°C FeS takes 16 wt. %, at 600°C — 30 wt. %, and at 700°C — 38 wt. % Co$_9$S$_8$ in solid solution. On the other hand, the solubility of FeS in Co$_9$S$_8$ does not vary with temperature, being about 20 wt. % FeS. Similar dependences have been observed by Moleva et al. (1958), though these authors have interpreted erroneously Co$_9$S$_8$ as Co$_4$S$_3$. Both (Fe,Co)S and (Co,Fe)$_9$S$_8$ form divariant fields with the FeCo solid solution. Yet, a precise determination of the phase boundaries in the metal-rich portion of the Fe-Co-S system by means of X-ray, microscopic and thermal methods is impossible and requires further investigations. Finally, FeS coexists with the Fe-Co melt and Co$_9$S$_8$ forms a divariant field with the Co-Fe alloy. The size of those fields is in good agreement with the data presented by Hansen and Anderko (1958) and by Elliott (1965).

REFERENCES

ARNOLD R. G., 1962: Equilibrium relations between pyrrhotite and pyrite from 325° to 743°C. *Econ. Geol.* 57, 72—90.
BERNER R. A., 1971: Principles of chemical sedimentology. McGraw-Hill, New York, 205.
BOUCHARD R. J., 1968: The preparation of pyrite solid solution of the type Fe$_x$Co$_{1-x}$S$_2$, Co$_x$Ni$_{1-x}$S$_2$ and Cu$_x$Ni$_{1-x}$S$_2$. *Mat. Res. Bull.* 3, 563—570.
CAGLIOTTI V., ROBERTI G., 1932: Ricerche roentgenografiche supra un sottosolfuro di cobalto adoperato come catalizzatore di idrogenazione del fenolo. *Gazz. chim. ital.* 62, 19—29.
CHALLIS G. A., LONG J. V. P., 1964: Wairauite — a new cobalt-iron mineral. *Mineral. Mag.* 33, 942—948.
CORLETT M., 1968: Low-iron polymorphs in the pyrrhotite group. *Z. Kristallogr.* 126, 124—134.

CURLOOK W., PIDGEON L. M., 1953: The Co-Fe-S system. *Can. Min. Met. Bull.* 46, 297—301.
ELLIOTT R. P., 1965: Constitution of binary alloys. 1st suppl. McGraw-Hill, New York, 319—320.
GUERTLER W., SCHACK H., 1923: Das ternäre System Nickel-Kobalt-Schwefel. *Metall u. Erz* 20, 367—371.
HANSEN M., ANDERKO K., 1958: Constitution of binary alloys. 2nd ed. McGraw-Hill, New York, 471—474.
HÜLSMANN O., WEIBKE F., 1936: Über die niederen Sulfide des Kobalts. Das Zustandsdiagramm des Systems Co — CoS. *Z. Anorg. u. Allgem. Chem.* 227, 113.
KLEMM D. D., 1962: Untersuchungen über die Mischkristallbildung im Dreieckdiagramm FeS$_2$-CoS$_2$-NiS$_2$ und ihre Beziehungen zum Aufbau der natürlichen „Bravoite". *N. Jb. Miner. Mh.*, 76—91.
KUCHA H., SALAMON W., 1973: Pentlandyt kobaltowy ze złoża „Krzemianka". *Spraw. Pos. Kom. Nauk. Oddz. PAN w Krakowie*, XVII/2, 479—480.
KULLERUD G., 1971: Experimental techniques in dry sulfide research. In, G. C. Ulmer, Ed., Research Techniques for High Pressure and High Temperature. Springer-Verlag, New York, 288—315.
KULLERUD G., YODER H. S., 1959: Pyrite stability relations in the Fe — S system. *Econ. Geol.* 54, 533—572.
[KUŽNECOV V. G., SOKOLOVA M. A., PALKINA K. K., POPOVA Z. V.] КУЗНЕЦОВ В. Г., СОКОЛОВА М. А., ПАЛКИНА К. К., ПОПОВА З. В., 1965: Система кобальт — сера. *Изв. АН СССР. Неорг. Мат.* I, 675—689.
LAMPRECHT G., 1975a: Kobalt-Nickellagerstätten und eine experimentelle Untersuchung innerhalb des Systems Co-Ni-S. *Chemiker Z.* 99, 441—445.
LAMPRECHT G., 1975b: Röntgenographische Untersuchung der nicht abschreckbaren Hochtemperaturphase Co$_4$S$_3$. *N. Jb. Miner. Mh.*, 288—289.
LAMPRECHT G., 1976a: The system Co-Ni-S. In: Ore Mineral Systems, Report 1975; by G. H. Moh. *N. Jb. Miner. Abh.* 126, 130—131.
LAMPRECHT G., 1976b: Some new data on the Co-S system. In: Experimental and descriptive ore mineralogy, Report 1976; by G. H. Moh. *N. Jb. Miner. Abh.* 128, 126—127.
LINDQVIST M., LUNDQVIST D., WESTGREN A., 1936: The crystal structure of Co$_9$S$_8$ and of pentlandite (Ni,Fe)$_9$S$_8$. *Svensk. Kem. Tidskr.* 48, 156—160.
MOH G. H., 1976a: Ore mineral systems; Report 1975 (with coworkers). *N. Jb. Miner. Abh.* 126, 134—145.
MOH G. H., 1976b: Experimental and descriptive ore mineralogy; Report 1976 (with coworkers). *N. Jb. Miner. Abh.* 128, 115—188.
[MOLEVA N. G., KUSAKIN P. S., VETRENKO E. A., DIEV N.P.] МОЛЕВА Н. Г., КУСАКИН П. С., ВЕТРЕНКО Е. А., ДИЕВ Н. П., 1958: К вопросу о диаграмме состояния системы железо—кобальт—сера. *Журн. Неорг. Хим.* 3, 904—910.
POKORNA A., VELIŠEK J., 1973: 550° anomaly in iron-cobalt alloys. *Czech. J. Phys.* 23, 1411—1412.
ROSENQUIST T., 1954: A thermodynamic study of the iron, cobalt and nickel sulphides. *J. Iron Steel Inst.* 176, 37—57.
SCOTT S. D., 1974: The Fe-S system. In, *Sulfide Mineralogy*, Miner. Soc. Am. Short Course Notes 1, CS21—CS40.
SCOTT S. D., KISSIN S. A., 1973: Sphalerite composition in the Zn-Fe-S system below 300°C. *Econ. Geol.* 68, 475—479.
SHUNK F. A., 1969: Constitution of binary alloys. 2nd suppl. McGraw-Hill, New York, 720.
SKINNER B. J., ERD R. C., GRIMALDI F. S., 1964: Greigite, the thiospinel of iron; a new mineral. *Am. Miner.* 49, 543—555.
STUMPFL E. F., CLARK A. M., 1964: A natural occurrence of Co$_9$S$_8$, identified by X-ray microanalysis. *N. Jb. Miner. Mh*, 240—245.
UDA M., 1967: The structure of synthetic Fe$_3$S$_4$ and the nature of transition to FeS. *Z. Anorg. u. Allgem. Chem.* 350, 105—109.
WYSZOMIRSKI P., 1976a: The system Fe-Co-S. In: Ore Mineral Systems, Report 1975; by G. H. Moh. *N. Jb. Miner. Abh.* 126, 129—130.
WYSZOMIRSKI P., 1976b: The Fe-Co-S system. In: Experimental and descriptive ore mineralogy, Report 1976; by G. H. Moh. *N. Jb. Miner. Abh.* 128, 127—129.
WYSZOMIRSKI P., 1976c: Badania rentgenograficzne roztworów stałych (Fe,Co)S$_2$. *Spraw. Pos. Kom. Nauk. Oddz. PAN w Krakowie* (in press).

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BADANIA UKŁADU TRÓJSKŁADNIKOWEGO Fe-Co-S W ZAKRESIE TEMPERATUR 500—700°C

Streszczenie

System Fe-Co-S jest częścią układu pięcioskładnikowego Fe-Co-Ni-Cu-S. Całkowite opracowanie tego układu jest istotne z punktu widzenia interpretacji warunków tworzenia niektórych, ważnych zarówno w sensie geologicznym jak i gospodarczym, magmowych złóż typu likwacyjnego.

W układzie Fe-Co-S występuje nieciągły roztwór stały FeS_2-CoS_2. Rozpuszczalność CoS_2 w FeS_2 jest bardzo ograniczona i przyjmuje wartość poniżej 2% wag. Z drugiej strony rozpuszczalność FeS_2 w CoS_2 jest znaczna i wyraźnie zwiększa się ze wzrostem temperatury (500°C — 37% wag. FeS_2, 600°C — 60% wag. FeS_2, 700°C — 75% wag. FeS_2). Rozpuszczalność FeS_2 w CoS_2 osiąga maksimum w temperaturze 735 $\pm3°$C, przyjmując wartość 80% wag. W tej temperaturze zachodzi również reakcja zerozmienna:

$$py + ct + V = po + L + V$$
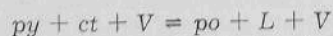
W przeciwieństwie do tego rozpuszczalność siarczku żelaza w Co_3S_4 maleje ze wzrostem temperatury. Podwyższenie temperatury wyraźnie wpływa na wzrost rozpuszczalności siarczku kobaltu w monosiarczku żelaza wzdłuż przekroju FeS—Co_9S_8. W temperaturze 500°C FeS przyjmuje do swojej struktury 16% wag., w 600°C — 30% wag., zaś w 700°C — 38% wag. Co_9S_8. Z drugiej strony rozpuszczalność FeS w Co_9S_8 nie zmienia się ze wzrostem temperatury i wynosi około 20% wag. FeS. Dokładne określenie granic fazowych w bogatej w metal części układu Fe-Co-S jest niemożliwe przy zastosowaniu metody rentgenograficznej, mikroskopowej oraz termicznej i wymaga dalszych badań.

OBJAŚNIENIA DO FIGUR

Fig. 1. Minerały i fazy syntetyczne występujące w układzie trójskładnikowym Fe-Co-S (w % wag.)
Fig. 2. Przekrój izotermiczny układu trójskładnikowego Fe-Co-S w temperaturze 500°C (w % wag.)
Fig. 3. Przekrój izotermiczny układu trójskładnikowego Fe-Co-S w temperaturze 600°C (w % wag.)
Fig. 4. Przekrój izotermiczny układu trójskładnikowego Fe-Co-S w temperaturze 700°C (w % wag.)
Fig. 5. Zależność pomiędzy charakterem chemicznym roztworu stałego (Fe,Co)S_2 a parametrem a_0 komórki elementarnej

Петр ВЫШОМИРСКИ

ИССЛЕДОВАНИЯ ТРОЙНОЙ СИСТЕМЫ Fe-Co-S В ПРЕДЕЛАХ ТЕМПЕРАТУР 700—500°C

Резюме

Система Fe-Co-S является частью пятикомпонентной системы Fe-Co-Ni-Cu-S. Полное изучение этой системы существенно с точки зрения интерпретации условий образования некоторых, важных так в геологичес-ком как и экономическом смысле, магматических месторождений ликвационного типа.

В системе Fe-Co-S существует прерывистый твердый раствор FeS_2-CoS_2. Растворимость CoS_2 в FeS_2 очень ограничена и величина ее составляет ниже 2 вес. %. С другой стороны, растворимость FeS_2 в CoS_2 очень значительна и отчетливо увеличивается с температурой (500°C — 37 вес. % FeS_2; 600°C — 60 вес. % FeS_2; 700°C — 75 вес. % FeS_2). Растворимость FeS_2 в CoS_2 достигает максимум в температуре 735 $\pm3°$C, составляя 80 вес. %. В этой температуре также имеет место обратная реакция

$$py + ct + V \rightleftharpoons po + L + V$$
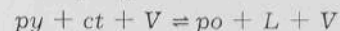
Наоборот, растворимость сульфида железа в Co_3S_4 с увеличением температуры уменьшается. Рост температуры отчетливо влияет на увеличение растворимости сульфида кобальта в моносульфиде железа вдоль сечения FeS-Co_9S_8. В температуре 500°C FeS принимает в свою структуру 16 вес. %, в 600°C — 30 вес. % а в 700°C — 38 вес. % Co_9S_8. С другой стороны растворимость FeS в Co_9S_8 с увеличением температуры не изменяется и составляет около 20 вес. % FeS. Точное определение фазовых границ богатой металлом части системы Fe-Co-S рентгенографическим, микроскопическим и термическим методами невозможно и требует дальнейших исследований.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Минералы и искусственные фазы тройной системы Fe-Co-S (в вес. %)
Фиг. 2. Изометрическое сечение тройной системы Fe-Co-S в температуре 500°C (в вес. %)
Фиг. 3. Изометрическое сечение тройной системы Fe-Co-S в температуре 600°C (в вес. %)
Фиг. 4. Изометрическое сечение тройной системы Fe-Co-S в температуре 700°C (в вес. %)
Фиг. 5. Взаимозависимость химического характера твердого раствора (Fe,Co)S_2 и параметра a_0 элементарной ячейки