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PHASE RELATIONS IN THE Fe-Co-S SYSTEM AT 800 C

UKD 541.123.33Fe-Co-S

A b s t r a c t. CoS_2, the only stable disulphide at 800°C in Fe-Co-S system, takes in solid solution about 33 wt. % FeS_2. Such a phase is in equilibrium with liquid sulphur and $(Fe, Co)_{1-x}S$ containing 10 wt. % $Co_{1-x}S$. In the central part of Fe-Co-S system exists a homogeneous field of Fe- and Co-monosulphide. Along the join FeS — Co_9S_8 the Fe-monosulphide takes up to about 20 wt. % FeS to its structure. At 752 ±3°C the metal-rich part of this system a ternary phase $(Co,Fe)_4S_3$ occurs. The composition of this phase lies on the FeS — Co_4S_3 „*join*" a point of approximately 16 wt. % FeS and 84 wt. % Co_4S_3.

INTRODUCTION

This paper contains the results of further investigations on the Fe-Co-S system. Phase relations in the temperature range 500—700°C have been discussed in the earlier publication (Wyszomirski 1976). The syntheses were performed in rigid, evacuated sealed silica glass tubes using the technique as described by Kullerud (1971). The samples were heated in controlled, horizontal furnaces with continuously recorded temperatures with an occuracy of ±3°C. The quench products were investigated as polished sections by means of the reflected light microscope, as well as by X-ray diffraction method in the room temperature and by DTA. The appearance of the ternary, nonquenchable high temperature phase $(Co,Fe)_4S_3$ made the necessity of use of high temperature powder X-ray diffraction technique. For this purpose the Guinier Simon high temperature X-ray camera was employed. These samples designed for X-ray high temperature investigations were prepared in evacuated silica glass capillaries as described by Moh and Taylor (1971).

The results of investigations of ternary Fe-Co-S system at 800°C are shown in Figure 1. The only stable disulphide under these conditions is cattierite CoS_2. Pyrite FeS_2 had decomposed, however, earlier at 743 ±3°C into hexagonal 1C pyrrhotite and liquid sulphur in peritectic reaction

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(Kullerud, Yoder 1959). At 800°C CoS_2 takes in solid solution about 33 wt. % FeS_2. Such a phase is in equilibrium with liquid sulphur and (Fe, Co)$_{1-x}$S containing 10 wt. % Co$_{1-x}$S. This value has been determined microscopically because the analitical X-ray (*10$\bar{1}$2*) peak is very diffused. This observation is in agree with data of Arnold (1958). The central part of Fe-Co-S system takes a large, homogeneous field of Fe- and Co-monosulphide phase. The composition of $Fe_{1-x}S$ varies from stoichiometric FeS to

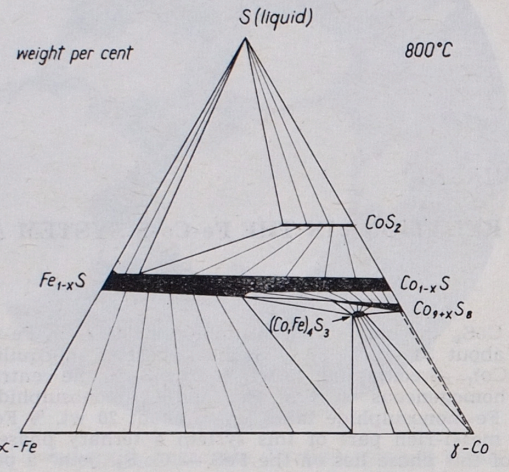

Fig. 1. The ternary Fe-Co-S system at 800°C

Fe-monosulphide with the content of 41.2 wt. % S (Arnold 1962). The other end-member of (Fe,Co)$_{1-x}$S solid solution, Co$_{1-x}$S possesses the area of homogeneity from 36.0 to 38.9 wt. % S (Kužnecov *et al.* 1965). The solubility of Co_9S_8 in FeS is very remarkable. So, FeS takes in solid solution about 47 wt. % Co_9S_8. This monosulphide makes a large, divariant field with α-Fe, which takes about 74 wt. % Co into its structure (Hansen, Anderko 1958). On the other hand the solubility of FeS in Co_9S_8 is remarkably less and amounts to about 20 wt. % FeS. This result is comparable with the values of solubility of FeS in Co_9S_8 at 500, 600 and 700°C (Wyszomirski 1976). At 752 ±3°C in the metal-rich part of the Fe-Co-S system a ternary phase (Co, Fe)$_4S_3$ occurs. In the presence of vapour the following invariant reaction takes place:

$$(Fe, Co)_{1-x}S + (Co, Fe)_9S_8 + Co_{ss} = (Co, Fe)_4S_3 + V.$$

The composition of the ternary (Co, Fe)$_4S_3$ phase lies on the FeS — Co_4S_3 "join" in a point of approximately 16 wt. % FeS and 84 wt. % Co_4S_3. With the increase of temperature the field of (Co, Fe)$_4S_3$ extends towards the binary Co-S side and the solid solution series become complete above 806°C. As known, above this temperature in binary Co-S system pure Co_4S_3 is stable (Lamprecht 1976). (Co, Fe)$_4S_3$ coexists with γ-Co taking up to about 17 wt. % Fe (Hansen, Anderko 1958). At 839 ±3°C the ternary eutectic with approximately 20 wt. % Fe, 55 wt. % Co and 25 wt. % S occurs. The binary eutectic of the Co-S system at 872°C lies between Co

and Co_4S_3 at 26.6 wt. % S (Kužnecov *et al.* 1965). The solubility of sulphur in the metallic phases as well as that of the metals or their sulphides respectively in liquid sulphur are too small to be detected by used method.

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ZALEŻNOŚCI FAZOWE W UKŁADZIE Fe-Co-S W TEMPERATURZE 800°C

Streszczenie

Kattieryt CoS_2 jest jedynym, trwałym dwusiarczkiem w układzie Fe-Co-S w temperaturze 800°C. Tworzy on roztwór stały z FeS_2 maksymalnie przyjmując do swojej struktury około 33% wag. tego połączenia. Taka faza występuje w równowadze z ciekłą siarką i (Fe, Co)$_{1-x}$S zawierającym 10% wag. Co$_{1-x}$S. Środkową część układu Fe-Co-S zajmuje jednorodne pole monosiarczku żelaza i kobaltu. Wzdłuż przekroju FeS — Co_9S_8 monosiarczek żelaza tworzy roztwór stały z Co_9S_8 maksymalnie przyjmując 47% wag. tego połączenia do swojej struktury. W roztworze stałym FeS w Co_9S_8 może zaś występować co najwyżej około 20% wag. monosiarczku żelaza.

W temperaturze 752 ±3°C w metalicznej części układu Fe-Co-S pojawia się faza trójskładnikowa $(Co, Fe)_4S_3$. Skład tej fazy leży na linii łączącej FeS i Co_4S_3 w punkcie, któremu odpowiada zawartość 16% wag. FeS i 84% wag. Co_4S_3.

OBJAŚNIENIE FIGURY

Fig. 1. Układ trójskładnikowy Fe-Co-S w temperaturze 800°C

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ФАЗОВЫЕ ЗАВИСИМОСТИ В СИСТЕМЕ Fe-Co-S ПРИ ТЕМПЕРАТУРЕ 800°C

Резюме

Каттиерит CoS_2 является единственным стабильным соединением серы в системе Fe-Co-S при температуре 800°C. Даёт он твёрдый раствор с FeS_2, принимая в свою структуру максимально около 33% по весу этого соединения. Такая фаза проявляется в ровновесии с текучей серой и $(Fe, Co)_{1-x}S$, содержащим 10% по весу $Co_{1-x}S$. Среднюю часть системы Fe-Co-S занимает однородное поле моносернистого железа и кобальта. Вдоль разреза FeS-Co_9S_8 моносернистое железо даёт твёрдый раствор с Co_9S_8 принимая максимально 47% по весу этого соединения в свою структуру. В твёрдом растворе FeS в Co_9S_8 может, с другой стороны, присутствовать в конечном счёте около 20% по весу FeS. При температуре 752 ±3°C в металлической части системы Fe-Co-S появляется трёхэлементная фаза $(Co, Fe)S_3$. Состав этой фазы лежит на линии соединяющей FeS и Co_4S_3 в точке, которой соответствует содержание 16% по весу FeS и 84% по весу Co_4S_3.

ОБЪЯСНЕНИЕ К ФИГУРЕ

Фиг. 1. Трёхэлементная система Fe-Co-S при температуре 800°C