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*HETEROGENEOUS EQUILIBRIA IN THE MnS — SrS SYSTEM**

SUMMARY. *The phase equilibria in the binary MnS — SrS system are studied by the methods of microstructural and thermal analyses. The phase diagram of the MnS — SrS system is referred to the eutectic type. According to the microstructure analysis of the samples, the eutectic composition is considered equal to 33.3(3) mol.% SrS. The Schroeder's, Efimov-Vozdvizhensky's, Cordes's empiric equations are used to calculate the coordinates of the eutectic point in the binary system. The melting temperatures of the eutectic crystals calculated by the Schroeder's, Efimov-Vozdvizhensky's, and Cordes' equations are 1,518 K, 1,534 K, 1,487 K, respectively. The solution composition change equation is used, according to it the composition and eutectic temperature are calculated: 22 mol.% SrS, 1,519 K. According to the thermal sample analysis of MnS — SrS system, the melting point of eutectic crystals is 1,523 K, which is well correlated with the Schroeder's and Efimov-Vozdvizhensky's equations and the solution composition change one. The approximate phase diagram of MnS — SrS system is presented. On the basis of the original sulfides, narrow areas of solid solutions can be formed by substitution type. The liquidus line position in the area of 0-33.3 (3) mol.% SrS is calculated according to the Schroeder's equation.*

KEY WORDS. Phase equilibria, sulfides, eutectics, physicochemical analysis.

Introduction. There are no data published on the phase equilibria study and the construction of the MnS — SrS system phase diagram. Strontium sulfide (SrS) and manganous sulfide (MnS, α-modification) have a cubic structure (the structure of NaCl-type, the Fm_3m space group) with the unit cell parameter (u.c.) of 0.6020 nm and 0.5224 nm, respectively. The congruent melting point is 2,590 K for SrS and 1,883 K for MnS. The difference in the effective ionic radii of rMn^{2+} = 0.0830 nm (CN = 6) and rSr^{2+} = 0.1180 nm (CN = 6) [1] is equal to 29.7%, which, in accordance with the Hume-Rothery rule, does not predetermine the formation of extensive solid solution ranges in the system. The difference in electronegativity of the manganese and strontium atoms (χMn = 1.90, χSr = 0.92) is equal to 51.6% [2].

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The construction of phase diagrams is a long and time-consuming process requiring much time to reach the state of equilibrium in the system formed by condensed components. As a result, it is continuously attempted to make an experimental procedure easier through the use of computational methods to predict the type of the phase diagram and its construction. The development of the theoretical basis is an important scientific objective, gaining of it enables broadening the field for the thermodynamic analysis application, to determine the essential properties, the experimental determination of which is difficult and sometimes impossible, and to distinguish the most promising directions for further experimental studies.

The purpose of this paper is to study the phase equilibria in the MnS — SrS system, to calculate the coordinates of the eutectic point and the liquidus curve position.

The experiment and data processing. Manganous sulfide was derived from manganic sulphate by the indirect method in the sulfiding chemical flow. The synthesis method is described in detail in [3]. The X-ray phase analysis (RPA) was carried out using the *DRON-7* diffractometer (CuKα-radiation, $\lambda_{avg.}$=1.54184 Å, Ni-filter). The microstructure analysis (MSA) was carried out using the *METAM LV-1* optical microscope in reflected light. The melting points for test samples were determined using the *NETZSCH (STA 449 F3)* simultaneous thermal analyzer, at the sample weight of 110-120 mg.

To calculate the coordinates of the eutectic point, the following equations were used [4-6]:

1. The Schröder's equation: $ln\, x_A^L = \frac{\Delta H_m^A}{R}\left(\frac{1}{T_m^A} - \frac{1}{T}\right)$, (1)

x_A^L Where e is the mole fraction of A component;

ΔH_m^A is the melting heat of A component, kJ/mol;

T_m^A is the melting point of A component, K;

R is the universal gas constant.

The formula (1) for calculating a eutectic point is as follows:

$$T_E = \frac{1}{\left[\frac{1}{T_m^A} - \frac{R}{\Delta H_m^A} ln\, x_A^E\right]} \quad (2)$$

where T_E is the eutectic temperature, K;

x_A^E — is the mole fraction of A component in the eutectic point.

2. The Efimov-Vozdvizhensky's equation. V.M. Vozdvizhensky proved the direct dependence of the eutectic interaction coefficient (C_i) on the temperature factor, only broken at the temperature factor close to one (0.8÷0.9):

$$C_I = C_E \frac{T_H - T_E}{T_H} \quad (3)$$

where C_E is the mole fraction of the low-melting component (the eutectic composition);

T_E is the eutectic temperature, K;

T_H is the melting point of the high-melting component;

$C_I + F_T = 1, F_T = \frac{T_L}{T_H}$

where F_T is the temperature factor; T_L is the melting point of the low-melting component.

Basing on these relations, the expression for each of the four variables is as follows:

$$Ce = \frac{T_H - T_L}{T_H - T_E} \quad (4)$$

$$T_E = \frac{T_L - T_H(1 - Ce)}{Ce} \quad (5)$$

$$T_L = T_H - Ce(T_H - T_E) \quad (6)$$

$$T_H = \frac{T_L - CeT_E}{1 - Ce} \quad (7)$$

3. The Kordes' equation: $\frac{x_A^E}{x_H^E} = \frac{T_H - T_E}{T_H} \div \frac{T_A - T_E}{T_A}$ (8)

4. The equation proposed in the paper on the change in solution properties [7]:

$$\Delta X = (1 - x_1)T_2 + x_1\left(\frac{(x_1T_1)^2 + ((1 - x_1)T_2)^2}{x_1T_1 + (1 - x_1)T_2}\right) \quad (9)$$

where T_1 is the melting point of the first (low-melting) eutectic component;

T_2 is the melting point of the second (high-melting) eutectic component;

ΔX — the change in solution property (the liquidus curve);

x_1 is the mole fraction of the first (low-melting) eutectic component.

Results and discussion. The difference between the effective ionic radii (Mn^{2+} and Sr^{2+}) by 29.7 % does not assume the formation of original sulfide-based extended solid solution ranges. Thus, the equations which allow calculating the eutectic point coordinates and the liquidus curve position close to perfect ones, can be applied to the systems. To calculate the eutectic point coordinates according to the equations

(1-8), it is required to use the data published or to determine experimentally one of the two coordinates: either the composition or the eutectic crystal melting point. As far as the experiment is concerned, the best way to determine the eutectic crystal composition is the microstructural analysis of the test samples. Based on the MSA study of the test samples containing 25, 30, 33.3(3), 35, 40 mol.% SrS crystallized from the melt and annealed at 1470 K, the eutectic composition is considered equal to 33.3(3) mol.% SrS. The melting point for the eutectic crystals is calculated by the empiric equations by Schröder (2), Efimov-Vozdvizhensky (5), and Kordes (8) (Table 1).

Table 1

Equations	Schröder's	Efimov-Vozdvizhensky's	Kordes'
Eutectic temperature, K	1,534	1,487	1,518

In [7] the authors offer the equation (9), according to which the deviation of the solution property from additivity is determined. The equation (9) allows calculating the eutectic point coordinates based on the original component melting point. The x_1 value is randomly given with a required step size; in this paper, the calculations were made with the step size of 0.02 within the interval of 0÷1 (Fig. 1).

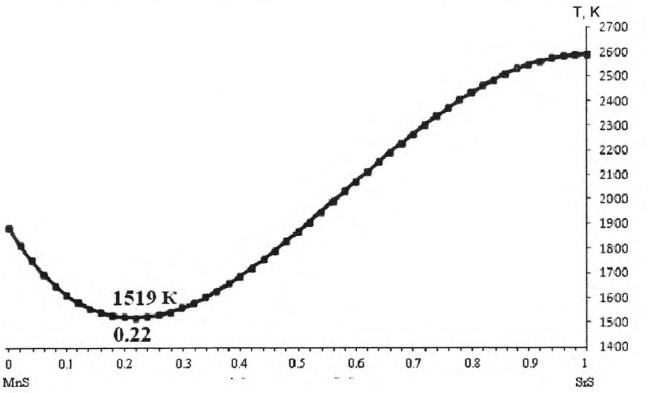


Fig. 1. The dependence of the melting point on the SrS mole fraction in the binary MnS — SrS system

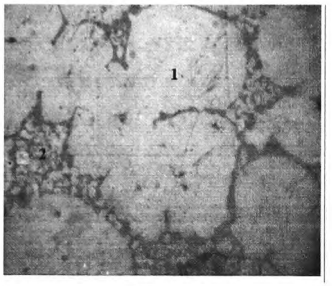
The composition — temperature dependence has a minimum attributable to the composition of 22 mol.% SrS (Fig. 1), which conflicts with the experimentally determined eutectic crystal composition of 33.3(3) mol.% SrS.

The liquidus curve position, which is estimated using the equation (1), yields the approved results in the hypoeutectic range (0 — 33.3(3) mol.% SrS) (Fig. 1). Within the range of 33.3(3) — 100 mol.% SrS compositions, to calculate the liquidus curve position by the equation (1), the melting heat value for SrS is required. There are no

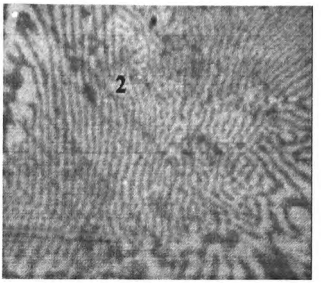
data on this value in the reference literature. In [9] the melting heat values are calculated as follows: $\Delta H_{melt}(SrS)$ = 88 kJ/mol, $\Delta H_{melt}(BaS)$ = 57 kJ/mol, basing on the experimentally constructed phase diagrams for sulfide systems. The values for magnesium and calcium sulfides are 63 and 67 kJ/mol, respectively [10, 11]. The liquidus curve calculated by the equation (1) within the range of 33.3(3) — 100 mol.% SrS is obtained with the overrated temperature values, which does not correspond to the general liquidus curve of the eutectic system and the thermal analysis data. The melting heat for strontium sulfide calculated by the Schöder's equation is 33.8 kJ/mol, which is an underrated value as compared to the melting heat values for alkaline-earth metal sulfides. To correct the melting heat values for strontium sulfide, it is required to continue constructing the liquidus curve experimentally in the high-temperature section and to make calculations by the Van-Laar.

There were 15 samples of various chemical compositions and preparation conditions studied in the MnS — SrS system. A total of 18 samples was studied by the physicochemical analysis methods (PCA). The samples were annealed at 1,470 K and 1,170 K. The reflexes of two phases of NaCl -type (MnS and SrS) were registered in all the samples containing from 2 to 95 mol.% SrS. The type of the two-phase range is eutectic (Fig. 2). When analyzing the test samples of the eutectic range by the MSA method, the initially crystallized round-shaped light-gray grains of MnS were observed. The linear size of grains was 20-80 μm; when approaching the eutectic point, the initial crystal size reached 7-10 μm (30 mol. % SrS). The eutectic was represented by the combination of 1-3-μm fine crystals of two phases (MnS and SrS). According to the MSA data, the eutectic composition was considered equal to 33.3(3) mol.% SrS. When analyzing the test samples of the hypereutectic region by the MSA method, the initially crystallized SrS grains in reflected light had an oval-oblong shape, the linear size was 30-100 μm, they were dark-gray; the eutectic was also observed in the intergranular space, the amount of it regularly decreased with the increase in the amount of strontium sulfide in the samples [8].

The differential thermal analysis (DTA) was carried out to study the samples containing 33.3(3) and 40 mol.% SrS. The melting peak of the test sample containing 33.3(3) mol.% SrS (annealed at 1,470 K) had a linear section beginning at 1,523 K. The peak shape demonstrates that the non-variant phase equilibrium correlates with the fixed melting process at 1,523 K. In the thermogram of the sample, containing 40 mol.% SrS (annealed at 1,470 K), the heat effect of eutectic crystal melting at 1,523 K and initial SrS crystal melting (1,790 K) were registered. Based on the methods of microstructural and thermal analyses, the phase diagram of the MnS —SrS system was constructed, its approximate view is given in Fig. 3. From the experimental MCA and DTA data, the eutectic point coordinates are considered equal to 33.3(3) mol.% SrS and 1,523 K.



A



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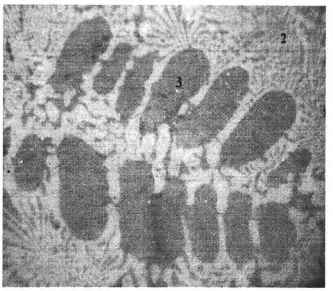

C

Fig. 2. The photographs of the microstructure of the MnS — SrS system samples (the samples are crystallized from the melt)
A — 10 mol.% SrS — 90 mol.% MnS; B — 33.3(3) mol.% SrS — 66.6(6) mol.% MnS;
C — 50 mol.% SrS — 50 mol.% MnS.
The following phases are registered: 1 — initial MnS crystals;
2 — the eutectic between the SrS and MnS phases; 3 — initial SrS crystals.

The samples containing 33.3(3), 50, 66.6(6) mol.% SrS and annealed at 1,170 K (during 3,300 hours), are two-phase, the arrangement of grains is eutectic. The formation of complex sulfides is not registered if the original component ratio is 2MnS:1SrS, 1MnS:1SrS, 1MnS:2SrS; the reflexes of two phases (MnS and SrS) are registered in the diffraction patterns of these samples.

Conclusion. The phase equilibria in the MnS - SrS system were studied. The phase diagram of the system is of eutectic type. The eutectic point coordinates are 33.3(3) mol.% SrS, T = 1,523 K. No complex sulfides are formed in the system. Based on the original sulfides, the narrow solid solution ranges may be formed by the substitution type. According to the experimental data on eutectic crystal composition, the melting point for eutectic crystals is calculated by the Schröder's, Efimov-Vozdvizhensky's, and Kordes' equations, it is 1,518 K, 1,534 K and 1,487 K, respectively. According to the equation of the solution property change, the coordinates of the eutectic point are 22 mol.% SrS, T = 1,519 K.

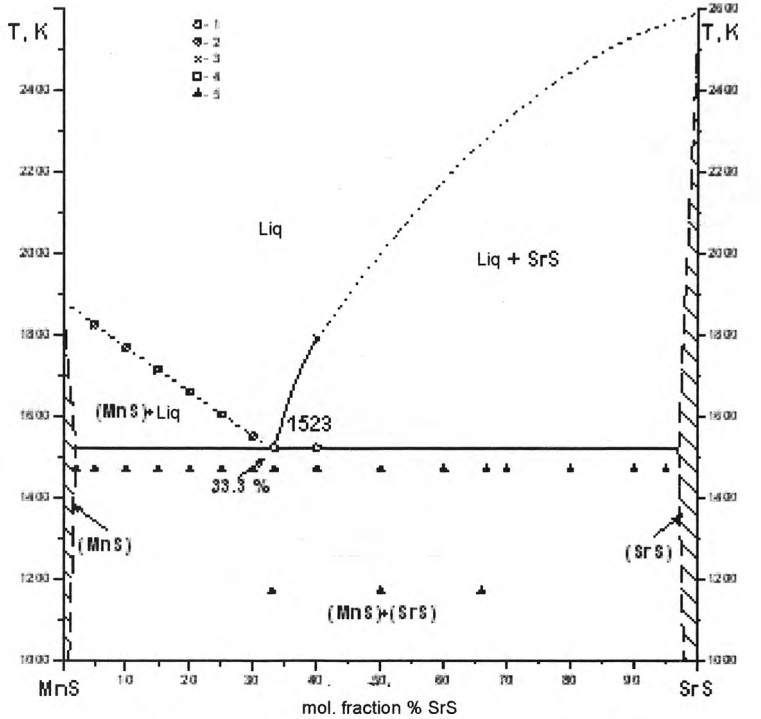

Fig. 3. The approximate phase diagram for the MnS — SrS system.
The key:
The DSC data: 1 — the incipient melting, the eutectic crystal melting,
3 — the complete melt of the sample, the completing of the initial crystal melt;
The MSA and RPA data: 4 — the two-phase sample;
2 — the computational data according to the Schröder's equation (1)

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