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The Result Of The Study Of Eutectics In The System Sm_2O_2S-Sm_3S_4.

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ABSTRACT: *The preparation process is divided into two main groups depending on the phase composition of the polycrystalline reaction product: the formation of Ln_2O_2S as the only polycrystalline phase and the preparation of several polycrystalline Ln_2O_2S phases. Based on the established chemistry of the interaction of metallic samarium with sulfur in a sealed ampoule, phase equilibria in the Sm – Sm_2S_3 – Sm_2O_3 system, the synthesis parameters of a mixture containing more than 98.5 mol.% Solid solution are determined $Sm_{1+x} S_{1-x} ([Sm])_{1-y} [\ ]_x)_{2x}$ (x = 0–0,035, y = 0–1), saturated with excess samarium. According to the results of MSA, the composition of the eutectic was 65 mol% Sm_3S_4. The composition of the double eutectic has coordinates 0.65 Sm_3S_4, - 0.35 Sm_2O_2S and a calculated melting point of 1700K. As a result, the goal of the work was achieved.*

KEYWORDS: REE, X-ray diffraction patterns, Van Laar equation, diffractometer, kinetic properties, oxysulfide, double eutectic, phases, phase equilibria, polycrystalline.

I. INTRODUCTION

The preparation process is divided into two main groups depending on the phase composition of the polycrystalline reaction product: the formation of Ln_2O_2S as the only polycrystalline phase and the preparation of several polycrystalline Ln_2O_2S phases [7]. The formation of REE diethyl sulfate in an amount exceeding the detection limit by the XRD method occurs at a temperature of 530-570 ° C. In a single-phase state, a compound sample was obtained in the following temperature range: La_2O_2S -600-950 ° C; Pr_2O_2S -610-920 ° C; Nd_2O_2S -630-900 ° C; Sm_2O_2S -630-800° C; Eu_2O_2S -700-900° C. At higher temperatures, the formation of Ln_2O_3 compounds occurs simultaneously with the reaction. $Ln_2(SO_4)_3 + 9H_2 = Ln_2O_3 + 3S + 9H_2O$ (0)[1] The treated material was placed in a reactor consisting of an external quartz tube with a sealed bottom. The reactor has a gas outlet, an inner quartz glass and a quartz tube for supplying gas.

$$Sm_2(SO_4)_3 + 2H_2 = Sm_2O_2SO_4 + 2SO_2 + 2H_2O. \qquad (1)$$

$$Sm_2O_2SO_4 + 4H_2 = Sm_2O_2S + 3SO_2 + 4H_2O. \qquad (2)$$

This line limits the region of homogeneity of the Sm_2O_2S phase.

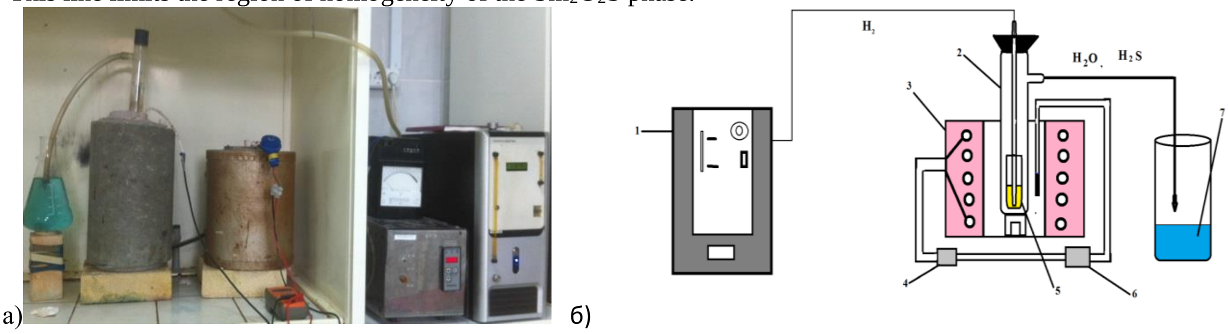


Figure:1. a) Photo of a hydrogen generator; b) Installation diagram for heat treatment of substances in a hydrogen stream: 1- hydrogen generator, 2- quartz reactor, 3- electric heating furnace, 4- power control unit for electric power supplied to the furnace 5- processed substance, 6- thermocouple, 7- water tank .

Based on the established chemistry of the interaction of metallic samarium with sulfur in a sealed ampoule, phase equilibria in the Sm – Sm_2S_3 – Sm_2O_3 system, the synthesis parameters of a mixture containing more than 98.5 mol.% Solid solution are determined $Sm_{1+x} S_{1-x} ([Sm])_{1-y} [\ ]_x)_{2x}$ (x = 0–0,035, y = 0–1), saturated with excess samarium. Technical ceramics in the form of a powder from crystalline formed particles of a fraction of 90–110 μm and a target in the form of a sintered pellet with a diameter of 75 mm were obtained from a batch. The use of solid solution particles during thermal explosion spraying ensures their preferential evaporation in the case of a directed fall in the thermal field of a tungsten heater with a temperature of 2570–2670 K.

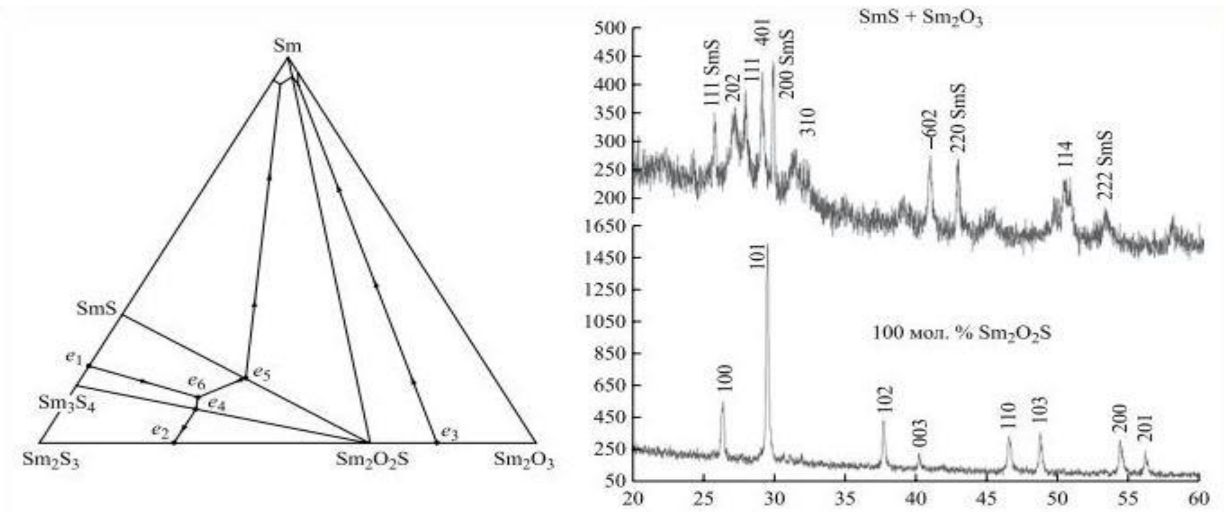


Fig. 1. The position of the conodes in the Sm_2S_3 – Sm – Sm_2O_2S system at 1070 K. ei (i = 1,2, ..., 6) are the eutectic compositions. X-ray diffraction patterns of a mixture of the starting materials 3SmS + 2 Sm_2O_3 and the products of their interaction — the Sm_2O_2S phase at annealing temperatures of 1670 K[13].

Sections of the Sm_2S_3 – Sm – Sm_2O_3 system have eutectic phase diagrams:

Sm_3S_4–SmS (e_1: 33 mol.% SmS; T_{mt} = 2140 K [3]), (3)

Sm_2S_3– Sm_2O_2S (e_2: 23 mol.% Sm_2O_3; T_{mt} = 1850 K), (4)

Sm_2O_2S – Sm_2O_3 (e_3: 80 mol.% Sm_2O_3; T_{mt} = 2290 K), (5)

Sm_3S_4– Sm_2O_2S (e_4: 34 mol.% Sm_2O_2S; T_{mt} = 1920 K), (6)

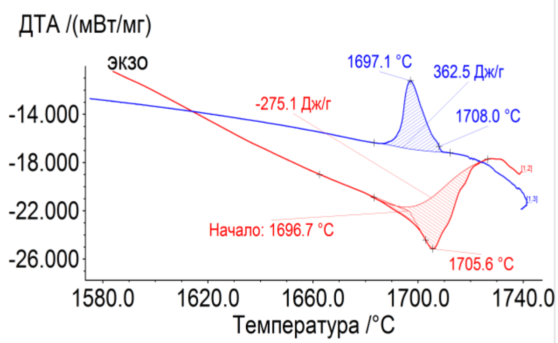
SmS– Sm_2O_2S (e_5: 53 mol.% Sm_2O_2S; T_{mt} = 2170 K) (Fig. 1.). (7)

II. EXPERIMENT TECHNIQUES.

The samples were studied by X-ray (RFA) (diffractometer DRON-6, CuKa radiation Fe filter), visual poly thermal (VPTA), microstructural (MSA) (Microstructural analysis was performed on a metallographic microscope AxioVert .A1MAT manufactured by ZEISS (Germany), resolution 0.5 µm. The image from the microscope was transmitted to a computer through a video camera[15]. Software complex AxioVision SE64) analysis was used for obtaining photos of grain sizing. Cell parameters are calculated using the High Score Plus program (data collection for the Drone-6 set; diffrac.file exchange. V5) with accuracy ± 0.001 and ± 0.0001 nm for rhombic and cubic structures, respectively. Mathematical processing of data of thermal methods of research and graphical constructions are performed in the program Edstate 2D. Evaluation of melting heat was carried out according to Van Laar equation [5].

III. RESULTS AND THEIR DISCUSSION.

The available data on upward deformation, kinetic properties of the process during the processing of REE sulfates in a hydrogen stream, sulfide gases, phase diagrams of Sm_2S_3 – Sm_2O_3 systems [6], kinetics of heterogeneous reactions and kinetics of lanthanide oxysulfide synthesis are generalized. The phase change occurs when a sample of the $Sm_2O_2SO_4$ compound is processed at 700 ° C. First, the sample will be two-phase $Sm_2O_2SO_4$ + Sm_2O_2S, then single-phase Sm_2O_2S. With increasing temperature, the time to reach the homogeneous Sm_2O_2S state decreases[9]. The phase states of the samples in the diagram reflect the fields $Sm_2O_2SO_4$, $Sm_2O_2SO_4$ + Sm_2O_2S, Sm_2O_2S. Samarium sulfide Sm_3S_4 was carried out by prolonged annealing in a muffle furnace previously obtained Sm_2S_3, placed in a quartz ampoule. Synthesize Sm_3S_4 from elements of metallic samarium and sulfur. The interaction of the elements occurs in a vacuum and sealed quartz ampoule when the mixture is heated to 1300 K as a result of sequentially and parallel reactions (9,8,10) Sm + 2S = SmS_2 (8) 3SmS_2 + Sm = 2 Sm_2S_3; (9) Sm_2S_3 + Sm + Sm_3S_4 (10). In this synthesis method, it was very important to observe the temperature regime of annealing: gradual heating to 850K for 25 days, and subsequent exposure of the ampoule for a month at a constant temperature [5]. Thus, Sm_3S_4 was obtained in 4 stages, and the target phase in it was more than 98.5% according to the results of XRD. During the experiment, the calculated composition range was used. Samples obtained in the concentration range close to the literary composition of the eutectic were taken with an interval of 2%. According to the results of MSA, the composition of the eutectic was 65 mol% Sm_3S_4 (Fig. 1). The eutectic mixture is represented by elongated yellow crystals of Sm_3S_4 and black oxysulfide.

a) 

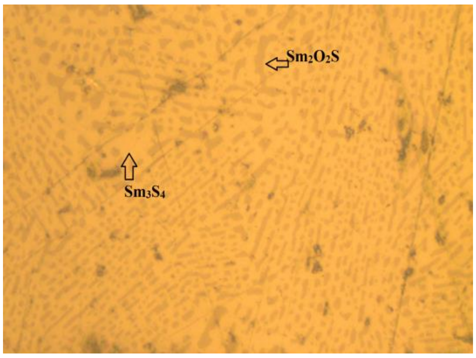
b) 

Fig. 1. a) Thermograms were obtained on the installation of synchronous thermal analysis STA 449 F3 Jupiter (company NETZSCH); b) a photo of the eutectic microstructure in the Sm_3S_4 - Sm_2O_2S system.

IV. CONCLUSIONS.

In accordance with the calculated coordinates on the basis of literature data, a sample of double eutectic was taken, but as a result of the analysis this composition was not eutectic. After obtaining a sample with a composition calculated on the basis of experimental data, a double eutectic point was not detected either, however, it turned out to be close to the desired microstructure. After adjusting the composition, based on the assumption that the position of the eutectic in the Sm_2S_3 – Sm_2O_3 system affects the position of the double eutectic in Sm_3S_4 - Sm_2O_2S, an exact eutectic composition was obtained containing all two components in the equilibrium state, which was confirmed by the MSA and XRD data. The composition of the double eutectic has coordinates 0.65 Sm_3S_4, - 0.35 Sm_2O_2S and a calculated melting point of 1700K. As a result, the goal of the work was achieved.

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