Study of the system V_2O_5–Na_2O. I.
Phase diagram of the system V_2O_5–$NaVO_3$

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The phase diagram of the system V_2O_5—$NaVO_3$ was studied. It was found that in the above system the congruently melting compound $2Na_2O \cdot 17V_2O_5$ and the incongruently melting compound $2Na_2O \cdot 5V_2O_5$ are formed. The congruently melting $2Na_2O \cdot 17V_2O_5$ belongs to the group of the vanadium bronzes. At solidifying, this compound releases oxygen. In the partial system V_2O_5—$2Na_2O \cdot 17V_2O_5$, there is an eutecticum with a composition 3 mole % $NaVO_3$ + 97 mole % V_2O_5, the eutectic temperature being 653°C. In this system, the existence of a narrow area of solid solutions of V_2O_5 in the vanadium bronze is assumed. In the partial system $2Na_2O \cdot 17V_2O_5$—$NaVO_3$, there is a peritectic point with a composition 39 mole % V_2O_5 + 61 mole % $NaVO_3$, the temperature of the peritectic reaction is 581°C, and an eutectic point, the eutectic composition being 71 mole % $NaVO_3$ + 29 mole % V_2O_5 and the eutectic temperature 541°C.

In the course of combustion of fuels containing vanadium and alkali in the gas turbines, the fused ionic mixtures consisting mostly of vanadium and sodium oxide are formed as undesirable side-products of the combustion. These melts exhibit a corrosive influence on the construction material of turbines and of the steam preheaters and lead to the formation of sediments of the corrosion products on the heating surfaces [1]. Regarding the study of the chemism of this corrosion, the knowledge of the phase diagram of the basic system V_2O_5—Na_2O appears to be of prime importance.

From the literature data it follows that in the system V_2O_5—Na_2O, the compounds with a general formula $Na_xV_2O_5$, denoted as vanadium bronzes, are formed. During solidifying, these compounds release oxygen whereas they bind it during melting [2]. So far, the chemism of this process is not entirely cleared up [3—5]. According to *Flood* and *Sørum* [6], besides the non-stoichiometric compound $Na_xV_2O_5$, where x varies in the region 0.13—0.31, another compound, $Na_{0.9}V_3O_8$, is formed in the system V_2O_5—Na_2O, whereas according to *Ozerov* [7] and *Illarionov et al.* [8], in the above system there exists a stable compound $Na_{0.33}V_2O_5$ and still another compound which could not be unambiguously identified.

In the study of the interaction of the components in the system V_2O_5—Li_2O, *Reisman* and *Mineo* [9] determined that in this system three compounds are formed: the incongruently melting compounds $2Li_2O \cdot 17V_2O_5$ and $2Li_2O \cdot 5V_2O_5$ and the congruently melting lithium metavanadate $Li_2O \cdot V_2O_5$. The existence of metavanadates of the alkali

metals of the type $MeVO_3$ was determined also in systems containing Na_2O and K_2O [7, 8]. Reisman and Mineo assumed that also in the system $V_2O_5-Na_2O$ most probably the incongruently melting compound $2Na_2O$ $5V_2O_5$ would be formed. The existence of an analogous incongruently melting compound $2K_2O$ $5V_2O_5$ was determined by *Illarionov et al.* [10].

The aim of this study was to re-examine the phase diagram of the partial system $V_2O_5-NaVO_3$ on which conflicting opinions were presented in the above-cited works.

Experimental

The phase equilibria in the system $V_2O_5-NaVO_3$ were studied using the thermal analysis method (TA) and the newly formed compounds were identified by means of the X-ray phase analysis.

For the preparation of samples, the following chemicals were used: V_2O_5 prepared by thermal decomposition of NH_4VO_3, reagent grade (Labora), the degree of decomposition being controlled gravimetrically, and Na_2CO_3, reagent grade (Lachema). In the preparation of samples, vanadium oxide and sodium carbonate were mixed in such a ratio that after the reaction was finished and CO_2 removed from the sample, its composition would correspond to the desired concentration of $NaVO_3$. Thus prepared sample was previously heated for 2 hours at $700-750°C$ and after cooling it was remelted in order to remove the last traces of CO_2.

The phase diagram was designed on the basis of the recorded cooling curves and of the X-ray analysis of the powdered quenched samples. The samples were melted in Pt crucibles in a Kanthal resistance furnace. The temperature was measured using a Pt/Pt10Rh thermocouple with an accuracy of $\pm 2°C$. The cooling rate in the TA did not exceed $6°C/min$.

The quenched samples were analyzed using an X-ray diffractograph Philips with a goniometer PW 1050. In this analysis, the CuK_α radiation with 15 mA and 35 kV was used.

Results and discussion

Taking into account the method of preparation of the samples when sodium carbonate was used, the phase diagram of the investigated system in the concentration range $0-50$ mole % Na_2O was established, which corresponds to the partial system $V_2O_5-NaVO_3$. The samples with a higher Na_2CO_3 concentration would correspond to the system $NaVO_3-Na_2CO_3$.

In Fig. 1, the phase diagram of the system $V_2O_5-NaVO_3$ determined on the basis of the TA and X-ray phase analysis is shown. It was confirmed that in the above system one congruently melting compound of composition $2Na_2O$ $17V_2O_5$ and one incongruently melting compound, $2Na_2O \cdot 5V_2O_5$, are formed. At solidifying, close to the phase transition temperature $724°C$ the compound $2Na_2O$ $17V_2O_5$ releases oxygen, most probably according to the scheme

$$2Na_2O + 17V_2O_5 \rightleftarrows 17Na_{0.235}V_2O_5 + O_2 \qquad (1)$$
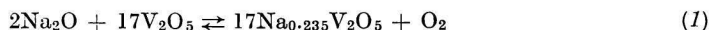
and it belongs to the group of the vanadium bronzes as stated by *Flood* and *Sørum* [6]. At melting, the reaction (1) runs in the opposite direction since below the melting point, the partial pressure of oxygen is evidently higher than it is above the m.p. The determined m.p., $724°C$, is by $14°C$ lower than the value reported by *Illarionov et al.* [8]. The higher value in the cited work is most probably due to an incorrect evaluation of the cooling curves. The release of oxygen at solidifying is accompanied by thermal effect which
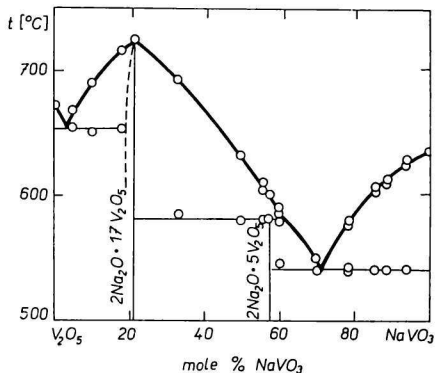
Fig. 1. The phase diagram of the system $V_2O_5 - NaVO_3$.

affects the thermographic record. The compound $2Na_2O \quad 17V_2O_5$ is analogous to the compound $2Li_2O \quad 17V_2O_5$ identified by *Reisman* and *Mineo* [9].

In the partial system $V_2O_5 - 2Na_2O \quad 17V_2O_5$, there exists most probably a narrow area of solid solutions of V_2O_5 in the vanadium bronze, $Na_{0.235}V_2O_5$, since the powder lines of vanadium oxide are absent in the diffraction pattern of samples with a composition close to the vanadium bronze. The co-ordinates of the eutectic point of this partial system are: 3 mole % $NaVO_3$, 97 mole % V_2O_5 and 653°C, these values being in good agreement with the data presented by *Illarionov et al.* [8] who determined the eutectic temperature of 655°C and assumed also the existence of solid solutions of V_2O_5 in the vanadium bronze.

The compound $2Na_2O \quad 5V_2O_5$ which is formed in the system $V_2O_5 - NaVO_3$ melts incongruently, the temperature of the peritectic reaction being 581°C. The identification of this compound confirmed assumption of its existence presented by *Reisman* and *Mineo* [9] who determined the analogous compound $2Li_2O \cdot 5V_2O_5$. No compound of this type was found by *Illarionov et al.* [8]. These authors established the existence of a congruently melting compound with m.p. of 614°C at 65 mole % $NaVO_3$; however, they did not identify the substance itself. The existence of this compound seems to be somewhat dubious and the erroneous conclusions of the above authors followed most probably from an incorrect interpretation of the results of thermal analysis. It is to be mentioned that the alleged eutectic temperature in the partial system formed by the vanadium bronze and the unidentified compound, 579°C, reported by *Illarionov et al.* [8], is practically identical with the temperature of the peritectic decomposition of $2Na_2O \quad 5V_2O_5$, 581°C, determined in this work.

The eutectic composition in the partial system $2Na_2O \quad 17V_2O_5 - NaVO_3$ is 71 mole % $NaVO_3$ and 29 mole % V_2O_5, the temperature of the eutectic crystallization is 541°C. This value is somewhat higher than the value of 530°C reported by *Illarionov et al.* [8], most probably owing to an inadequate degree of purity of $NaVO_3$ which was used in the above-cited work.

The measured melting point of sodium metavanadate was 634°C. The lower value of m.p. of $NaVO_3$, 627°C, determined in [8], is evidently also affected by the presence of impurities in metavanadate which was prepared by dissolution of V_2O_5 in a solution of NaOH and subsequent carbonatization. In the present work, $NaVO_3$ was prepared by melting V_2O_5 with an equivalent amount of Na_2CO_3. This method of preparation seems to be more appropriate than that mentioned above since there is always some carbonate present in NaOH.

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