Study of the system V_2O_5—Na_2O. II.
Physicochemical properties of the molten V_2O_5—$NaVO_3$ mixtures

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The density, viscosity, and specific electrical conductivity of the molten V_2O_5—$NaVO_3$ mixtures in the temperature range $650-900°C$ were measured. It was found that in the range of the existence of vanadium bronze, $Na_{0.235}V_2O_5$, a stable redox system V^{IV}/V^V is formed in the investigated system which brings about a partial electronic conductance of the melt.

The mechanism of the vanadium corrosion and the influence of the electronic conductivity on the corrosion process are discussed.

The vanadium corrosion appears as a concomitant phenomenon in the combustion of liquid fuels containing vanadium and alkali in the production of the electrical energy in gas turbines. The corrosion is effected by the action of fused remnants of combustion on the construction materials of turbines and steam preheaters [1]. At the interface between the gaseous phase (gaseous products of combustion) and the construction material, the molten ash forms an inter-layer which by its chemical and transport properties participates in the corrosion process and provides the transport of the corrosion products from the melt/metal interface into the melt. Therefore the transport properties of these mixtures are of primary importance with respect to the rate and mechanism of the corrosion process.

The main components of these ashes were found to be vanadium(V) oxide and sodium oxide forming the system V_2O_5—Na_2O. The study of the phase equilibria in this system and of the physicochemical properties, mainly of the density, viscosity, and the specific electrical conductivity of the respective mixtures furnishes the fundamental information for the investigation of the transport properties of these melts.

The catalytic activity of V_2O_5 in the solid state in the oxidation reactions is well known. At melting, vanadium(V) oxide dissociates according to the reaction scheme

$$V_2O_5 \rightleftarrows V_2O_4 + 1/2O_2. \qquad (1)$$

The equilibrium of this reaction depends on the partial pressure of oxygen and on the temperature. On the basis of the experimentally determined temperature dependence of the equilibrium constant, *Pantony* and *Vasu* [2] calculated the value of 25.6 kcal for the heat of reaction (*1*). The theoretic value of the heat of reaction calculated on the basis of the thermodynamic data is 7.8 kcal. The difference 17.8 kcal represents

the partial molar heat of solution of V$_2$O$_4$ in V$_2$O$_5$. The high value of the heat of solution indicates the formation of vanadylvanadates in the melt. This is responsible for the properties of molten V$_2$O$_5$, which appears to be a semi-conductor of the type n. According to *Wickens* [3], at a partial pressure of oxygen of 0.055 atm the electronic conductance is predominant if compared with the ionic conductivity. The electronic conductance is stipulated by the increased concentration of V$_2$O$_4$ in the quasi-crystalline structure of V$_2$O$_5$ and its existence is confirmed also by the small change in the conductivity at the solid → liquid phase transition of V$_2$O$_5$. The hypothesis on the electronic conductance is further supported by the negative value of the Hall's coefficient which indicates that negatively charged particles take part in the transport of the current [4].

An addition of Na$_2$O or of other alkali and alkaline earth oxides favours the dissociation of V$_2$O$_5$ and consequently also the formation of the defects in its quasi-crystalline structure, thus facilitating the transport of oxygen across the layer of molten V$_2$O$_5$ [2]. The compounds formed by V$_2$O$_5$ and alkali oxides are known as "vanadium bronzes" and their crystalline structure is close to that of V$_2$O$_5$ [5]. Vanadium bronzes, M$_x$V$_2$O$_5$, represent a series of non-stoichiometric compounds with univalent M atoms localized in the distorted structure of V$_2$O$_5$. The valence electron of the metal M is trapped by a vanadium atom of the V$_2$O$_5$ matrix so that V^{IV} atoms with a tetragonal distortion with moderate spin-orbit coupling are formed [6]. The trapped electron is equivalent to the small polaron of Holstein, the conductivity of such a system being exponentially dependent on the temperature [7].

The present work deals with the study of the physicochemical properties of the system V$_2$O$_5$—Na$_2$O. In this context it should be pointed to the fact that, as a consequence of the equilibrium V^{IV}/V^{V}, in the range of the existence of vanadium bronzes the ternary system V$_2$O$_5$—V$_2$O$_4$—Na$_2$O is formed. However, with regard to the low concentration of V$_2$O$_4$ [1] and for the sake of simplicity the system is considered as a binary one. In the previous part of this work, the phase equilibria in the partial system V$_2$O$_5$—NaVO$_3$ have been studied [1]. In this part, the density, viscosity, and electrical conductivity of the melts of the investigated system were measured in the temperature range 650— —900°C in order to obtain the fundamental information for determining the mechanism of the vanadium corrosion and of possible influence of the electronic conductance on the corrosion process.

Experimental

For the preparation of samples the following chemicals were used: V$_2$O$_5$, prepared by thermal decomposition of NH$_4$VO$_3$, reagent grade (Labora) and Na$_2$CO$_3$, reagent grade (Lachema). The samples were previously heated for 2 hrs at 700—750°C and after cooling remelted in order to remove the last traces of CO$_2$.

The density of the molten V$_2$O$_5$—NaVO$_3$ mixtures was determined by the hydrostatic method described in detail in [8]. The total weighted-in amount was 70 g. The diver consisted of a Pt sphere ($d = 20$ mm) suspended on a Pt file. The temperature was measured with a Pt/Pt10Rh thermocouple.

The viscosity of the studied melts was determined with the aid of the torsion pendulum method described in [9]. The pendulum consisted of a Pt10Ir sphere ($d = 20$ mm) suspended on a molybdenum file.

In the determination of the specific conductivity, a transformer bridge, type Wayne Kerr, fed by a tone generator at the frequency of 50 kHz was used. A nanovoltmeter, type Unipan, served as the zero indicator. The measurement was carried out with a cur-

rent of 10 mA. The conductivity cell consisted of a Pt crucible and two disc electrodes ($d = 5$ mm) of bright platinum. The detailed description of the measuring scheme was presented in [10].

Results and discussion

In Fig. 1 the isotherms of the density of the molten $V_2O_5 - NaVO_3$ mixtures are presented. From the course of the isotherms it is evident that the density is only slightly changing with the increasing concentration of Na_2O in the melt. On the other hand, the temperature dependence of the density of mixtures close to the composition corresponding to vanadium bronze, $Na_{0.235}V_2O_5$, seems to be of definite interest. The coefficient of the thermal expansion of these melts appears to be markedly smaller than of any other mixtures over the entire investigated concentration range, this indicating a qualitative difference in the structure of the melt. It can be assumed that the combination of V_2O_5 groups in vanadium bronze is more pronounced, this leading to a relative decrease of the free volume of the melt indicated by the decrease of the coefficient of thermal expansion.

This assumption is confirmed also by the course of the viscosity isotherms of the molten $V_2O_5 - NaVO_3$ mixtures (Fig. 2). The maximum on the viscosity isotherms corresponds to the formation of vanadium bronze, $Na_{0.235}V_2O_5$. Such a maximum on the isotherms of viscosity can be explained only by the formation of the big structural entities in the melt.

The isotherms of the specific electrical conductivity are presented in Fig. 3. Also in this case the maximum on the isotherms corresponds to the composition of vanadium bronze. The coincidence of these maxima, on the isotherms of both the viscosity and
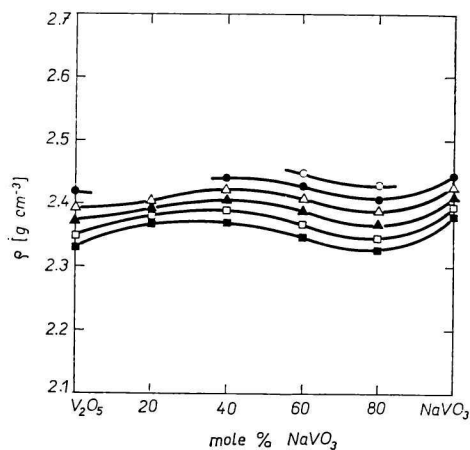

Fig. 1. Isotherms of the density of molten $V_2O_5 - NaVO_3$ mixtures.

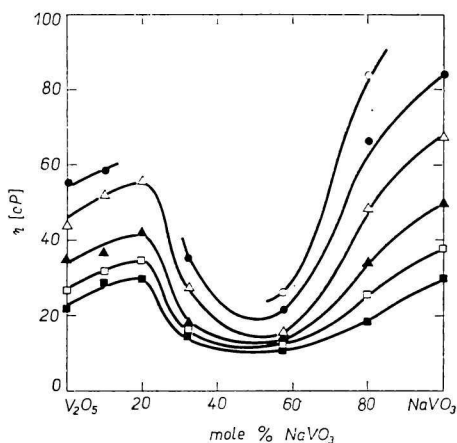○ 650°C; ● 700°C; △ 750°C; ▲ 800°C; □ 850°C; ■ 900°C.

Fig. 2. Isotherms of the viscosity of molten $V_2O_5 - NaVO_3$ mixtures.

○ 650°C; ● 700°C; △ 750°C; ▲ 800°C; □ 850°C; ■ 900°C.

the electrical conductivity, can be explained only by the existence of "free" electrons which are responsible for the partial electronic conductivity of these melts. Since the existence of the neutral sodium atoms in the presence of V^V atoms is highly improbable, the partial electronic conductance can be explained by the transfer of the valence electron
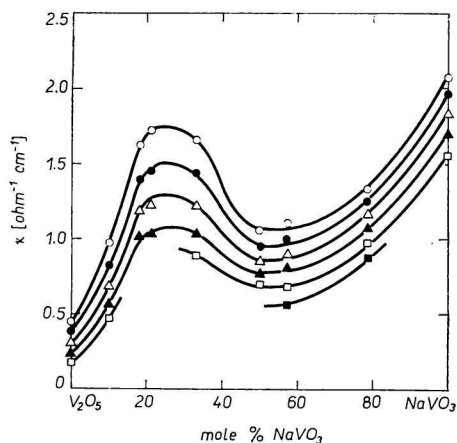

Fig. 3. Isotherms of the electrical conductivity of molten V$_2$O$_5$—NaVO$_3$ mixtures.

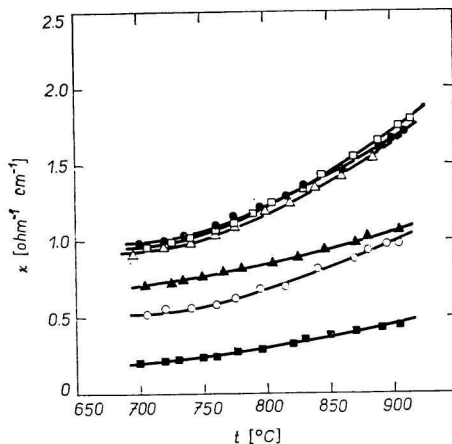■ 650°C; □ 700°C; ▲ 750°C; △ 800°C; ● 850°C; ○ 900°C.

Fig. 4. Polytherms of the electrical conductivity of molten V$_2$O$_5$—NaVO$_3$ mixtures.

■ V$_2$O$_5$; ○ 10% NaVO$_3$; △ 18% NaVO$_3$; □ 21% NaVO$_3$; ● 33% NaVO$_3$; ▲ 50% NaVO$_3$.

from the alkali metal to the free d-orbital of the vanadium atom. Such a "localized" group, *i.e.* the electron and the entrapping atomic displacement, denoted as a small polaron of *Holstein* [7], has only a small mobility and it can be easily described on the basis of the theory of diffusion. A direct evidence for the existence of the V^{IV} atoms and thus for the formation of the small polaron inside the array of V$_2$O$_5$ was delivered by the e.p.r. measurements, which were carried out by *Gendell et al.* [11] in the lithium bronzes. The exponential character of the temperature dependence of the electrical conductivity of the molten V$_2$O$_5$—NaVO$_3$ mixtures in the concentration range 10—50 mole % NaVO$_3$ (Fig. 4) indicates the existence of the small polaron in the above melts. With respect to the fact that in the process of melting of vanadium bronzes a rapid change of the electrical conductivity does not exist [4], the structure of molten vanadium bronze can be considered as a quasi-crystalline containing a large number of defects. Thus, vanadium bronze keeps its semi-conductor properties also in the molten state [2, 12].

The presence of a stable redox-system V^{IV}/V^V in the layer of the molten ash can be decisive with respect to the rate of the corrosion process since the corrosion reaction in this system can act as a depolarizing agent (electron acceptor), and simultaneously assuring the removal of the products of the corrosion from the surface of the metal.

Conclusion

The results of the study of the physicochemical properties of the molten $V_2O_5 - NaVO_3$ mixtures indicate the formation of a stable redox system V^{IV}/V^V in the above melts, this being responsible for the partial electronic conductance of the melt and for the formation of a galvanic cell with the separate places of the anodic and cathodic reactions at the interfaces melt/metal and melt/gaseous phase. In the corrosion of metals, the formation of such a galvanic cell affects substantially the mechanism of the corrosion. From this aspect, the formation of vanadium bronzes substantially increases the rate of the corrosion.

The molten V_2O_5 is able to oxidize all metals, even at a low partial pressure of oxygen. At a low partial pressure of oxygen, however, the degree of oxidation is lower, since V_2O_4, which is formed by the reaction

$$2M + V_2O_5 = M_2O + V_2O_4 \qquad (2)$$
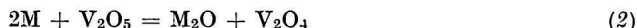
is not being re-oxidized according to the reaction

$$V_2O_4 + 1/2O_2 = V_2O_5 \qquad (3)$$

and the oxidizing ability of the melt is thus reduced. Under the oxidizing conditions, the oxidation of the metal proceeds till the rate of oxidation surpasses the rate of dissolution of oxides. In an opposite case, a layer of oxides is formed at the surface of the metal and the rate of oxidation is determined by the rate of dissolution of the corrosion products. Then the influence of sodium oxide becomes evident by an increased ability of the melt to absorb oxygen from the atmosphere, the increased electrical conductivity, the improved diffusion properties, and finally by an increased solubility of metal oxides in the melt.

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