Solid Solutions of the System \( \text{V}_2\text{O}_5 - \text{V}_2\text{O}_4 - \text{TiO}_2 \) in Air

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Abstract—Gravimetry in combination with X-ray phase analysis, X-ray crystallography, and X-ray densitometry were used to determine the contents of \( \text{V}^{5+} \), \( \text{V}^{4+} \), and \( \text{Ti}^{4+} \) ions and vacancies in solid solutions formed by the reaction of \( \text{V}_2\text{O}_5 \) with \( \text{TiO}_2 \) in air at atmospheric pressure.

Solid solutions formed by the reaction of \( \text{V}_2\text{O}_5 \) with \( \text{TiO}_2 \) in air at atmospheric pressure are well documented [1–5]. The oxides \( \text{V}_2\text{O}_5 \) and \( \text{TiO}_2 \) at reduced oxygen pressures form a continuous series of solid solutions [6] that exist in five different modifications [7]. In air these solutions are metastable and undergo gradual oxidation. Numerous studies of the phase composition of products of the reaction of \( \text{V}_2\text{O}_5 \) with \( \text{TiO}_2 \) of different modifications ruled out formation of any chemical compounds and revealed partial mutual dissolution of the starting components [2] accompanied by oxygen evolution [5]. Treatment of \((1 - x)\text{VO}_{2.5} + x\text{TiO}_2 \) (anatase) mixtures, where \( 0 \leq x \leq 1 \), with oxalic acid and their keeping at 400°C followed by heating to 550–600°C gave a \( \text{Ti}_{1-x}\text{V}_x\text{O}_{2.5+x/2} \) (0 \( \leq x \leq 0.12 \)) solid solution with the rutile structure [4]. Calcination of such mixtures at 530°C without pretreatment with oxalic acid gives samples comprising phases with the anatase and \( \text{V}_2\text{O}_5 \) structures [1]. According to [2, 8], this system (synthesis temperature 450°C) at room temperature have the same \( g \) factor as \( \text{V}_2\text{O}_5 \). This finding suggests presence of \( \text{V}^{4+} \) ions in the anisotropic environment. Solid solutions \( \text{Ti}_{1-x}\text{V}_x\text{O}_4 \) [6] at room temperature give no EPR signal [2], which allows all \( \text{V}^{4+} \) ions detected by EPR to be related to \( \text{V}_2\text{O}_5 \)-based solid solutions, whereas the other \( \text{V}^{4+} \) ions, to \( \text{TiO}_2 \)-based solid solutions. Assuming that the reaction of \( \text{V}_2\text{O}_5 \) with anatase results in exclusive formation of a \( \text{TiO}_2 \)-based solution in equilibrium with \( \text{V}_2\text{O}_5 \), we previously [2] correlated the amount and composition of the phases formed with the \( \text{V}:\text{Ti} \) ratio in the starting mixture. In [1] we performed qualitative chemical phase analysis of products of the calcination of \( \text{V}_2\text{O}_5 \) with \( \text{TiO}_2 \) (anatase) at 530°C, with account for the possible incorporation of \( \text{V}^{5+} \) into \( \text{TiO}_2 \)-based solid solutions and of \( \text{V}^{4+} \) and \( \text{Ti}^{4+} \) into \( \text{V}_2\text{O}_5 \)-based solid solutions. An unexpected result of the cited work was that the compositions of co-equilibrium solid solutions are not invariable and depend on the \( \text{V}:\text{Ti} \) ratio in the starting mixture even beyond their homogeneity regions, i.e. in those sections of the phase diagram that should relate to a mixture of boundary compositions of these solid solutions. This fact suggests that the system in hand lacks boundary compositions. Thus, it was found that, as the vanadium content in the starting mixture increases, its content in the solid solution with the \( \text{TiO}_2 \) structure increases, reaching formally ca. 100%, even though the fraction of such solid solution in the reaction product correspondingly decreases to reach zero in pure \( \text{TiO}_2 \).

One of the possible explanations for this phenomenon might be fluctuations of partial oxygen pressure caused by local temperature fluctuations. Another explanation follows from the consideration of the system as ternary (Ti–V–O). The oxides \( \text{TiO}_2 \) and \( \text{V}_2\text{O}_5 \) have homogeneity regions with respect to oxygen; connods drawn from different points of the \( \text{TiO}_2 \) homogeneity region intersect the \( \text{TiO}_2 - \text{V}_2\text{O}_5 \) line in different figurative points of the diagram. However, each of these points corresponds to chemical equilibrium of phases with various \( \text{V}^{4+} \) contents, which is actually observed experimentally. The reason of course can be sought in errors in the fractional analysis used in [1, 2]. However, taking into account that the \( \text{V}_2\text{O}_5 \) and \( \text{TiO}_2 \) homogeneity regions with respect to oxygen and atmospheric temperature and pressure fluctuations are extremely small, while the errors in the chemical analysis have their inherent limitations, these factors cannot affect the principal conclusion in [1]. We suggest that the actual reason for this phenomenon is as follows. It is known that the kinetic energies of gaseous molecules obey the Maxwell distribution. According to this distribution, the more the kinetic energies of molecules differ from the mean energy, the less abundant are such molecules. However, the total number of such molecules is still considerable. The dissociation process and, as a result, mutual solubility of the starting components depend...
on the kinetic energies of oxygen molecules in the surrounding gas medium. For this reason, the composition of solid solutions formed at any temperature in any chemical system should have quite a definite distribution that depends, on the one hand, on the Maxwell speed distribution for gaseous molecules and, on the other hand, on peculiar features of the system (dissociative ability of the components of the system, their mutual solubility, etc.). It is clear from the aforesaid that the compositions of solid solutions formed at a specific temperature and starting component ratio should obey and do obey (see [1]) a corresponding distribution that is a function of the Maxwell kinetic energy distribution for oxygen molecules. The composition distribution of the solid solutions formed has its maxima for each starting component ratio and corresponds to mean velocities for the given temperature. The compositions of solid solutions, corresponding to these maxima, where, in addition, are points of the maximum mutual solubility of the starting components, are reasonable to be treated as boundary compositions of the corresponding solid solutions. The aim of the present work was to find the boundary compositions formed by solid-phase reaction of V₂O₅ with TiO₂.

The pure starting components V₂O₅ and TiO₂, subjected to 610°C for 1000 h, showed no weight changes. This funding agrees with data in [9]: The vapor pressure over even melted V₂O₅ (mp 675°C) is as low as 3.4×10⁻² mm Hg, which almost secures against the influence of V₂O₅ vaporization on the sample weight even over such a long synthesis time.

The V⁴⁺ contents of reaction products formed at specific synthesis temperatures could not be determined be means of known thermographic techniques (TG or DTG) under either increasing or decreasing sample temperature, as well as under any constant temperature. The reason lied in the impossibility to grind samples periodically, thus eliminating diffusion hindrances to the reactions that occurred; as a result, the reactions failed to come to completion during thermoanalytical measurements. Therefore, in the present work we applied our specially developed new gravimetric procedure [10] that allows us to grind samples during reaction and account for mechanical losses at each grinding. To this end, the samples were annealed in crucibles of known weight and periodically grinded and weighed after every annealing and every grinding. The total relative weight loss b (wt %) over the course of multiple annealing was calculated by Eq. (1) [10].

\[
b = \frac{100}{M_i} \left[ \sum_{i=1}^{n} (M_i - m_i) + (m_1 - M_2)(1 - m_2/M_2) + (1 - m_3/M_2)(1 - m_2/M_3) + (1 - m_4/M_3)(1 - m_3/M_4) \right] + (m_3 - M_4)(1 - m_4/M_4).
\]

Here \(M_i\) is the sample weight after the ith annealing and \(m_p\) sample weight after the ith annealing. Therewith, \(m_0 = M_1\), since the mechanical losses before the first annealing can be neglected.

From the annealing equation (2), where \(0 \leq p \leq \alpha \leq 1\), the molecular weight of the starting mixture \(M_0\) was taken to be 100 wt %, and then the relative molecular weight of evolved oxygen is \(b\) wt % [Eq. (3)], where \(M(O_2)\), \(M(TiO_2)\), and \(M(VO_{2.5})\) are the molecular weights of oxygen and titanium and vanadium oxides, respectively. The value \(\alpha\) was found from proportion (3) by formula (4).

\[
(1 - p)TiO_2 + pVO_{2.5} \rightarrow Ti_{1-p}V^{4+} + \alpha O_2 + 0.5(p - \alpha)\text{TiO}_2 + 0.25\alpha O_2.
\]

\[
M_0 = (1 - p)M(TiO_2) + pM(VO_{2.5})
\]

\[
+ 0.25\alpha M(O_2)\quad (100 \text{ wt }\%),
\]

\[
\alpha = \frac{b(1 - p)M(TiO_2) + pM(VO_{2.5})}{25M(O_2)}.
\]

The required relative content of vanadium(IV), wt %, was estimated from proportion (5), where \(M_T\) is the molecular weight of annealed mixture by Eq. (1), and \(M(Ti)\) and \(M(V)\), atomic weights of titanium and vanadium by Eq. (6).

\[
M_T = (1 - p)M(Ti) + pM(V)
\]

\[
+ \left[ 1 + 0.25(p - \alpha)M(O_2) \right] 100\text{ wt }\%,
\]

\[
\alpha = \frac{a}{100\text{ }\alpha M(V)/M_T}.
\]

The figure depicts the dependences of V⁴⁺ content on starting mixture composition over the course of synthesis [Eq. (6)]. As seen from these dependences, with all the compositions, the contents of V⁴⁺ ions in TiO₂-based solutions obtained with the use of anatase (solid solutions I) are higher than in those obtained with the use of rutile (solid solutions II). These dependences look like broken lines whose extremes correspond to the boundary compositions of solid solutions I and II: 19.2±0.5 and 11.8 ± 0.5 wt % VO₂₅, respectively. The inflection at 95 wt % VO₂₅ relates to the boundary composition of solid solution III with the V₂O₅ structure. The X-ray phase analysis of the synthesized samples gave evidence for the formation in the system in hand at 610°C in air of V₂O₅-based solid solutions containing 5±0.5 mol % TiO₂, as well as of solid solutions with the rutile