Conducting Ceramic Anodes Based on Titanium Oxides

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Abstract

A method has been developed for producing electroconductive ceramics based on titanium oxides using a reaction TiO_2 + Ti with preliminary mechanical activation of the mixture and subsequent thermal treatment under hydrogen and argon at 1060–1080 °C. X-ray phase analysis data are given to support the formation of the compounds, and conductivity data (160–630 S/cm) are presented. The anodic behavior of Ti_3O_5 and Ti_4O_9 has been studied, and anodic volt-ampere relationships are given.

INTRODUCTION

One of important challenges in electrochemical materials science is the search for inexpensive materials for insoluble anodes possessing stability in the range of oxygen evolution potentials, for example, in sulfuric acid solutions. Solving this problem involves improvement of the economic parameters of many important technological processes in hydrometallurgy (production of Cu, Zn, Ni, Co, Mn, *etc*.), electrode position, and desalting of ocean water by electrodialysis [1]. The greatest stability under these conditions is exhibited by anodes based on platinum metals (Pt, IrO_2) and other composites based on noble and nonferrous metal oxides. However, they are very expensive and cannot be used in a number of processes due to economic reasons, therefore, seeking less expensive and reasonably stable anodic materials has become a crucial problem.

One of practical ways of its solving is the employment of nonstoichiometric titanium oxides. It was demonstrated [2, 3] that some of these oxides (Ti_4O_7, Ti_5O_9 and Ti_6O_{11} Magneli phases) show high enough conductivity and good chemical stability. The transition metal cations in oxidation states higher than +4 incorporated in the structure of such oxides reduce overvoltage of the oxygen evolution reaction on electrodes made from these materials, raising their electrocatalytic activity. Thus, good results were reported in a study of electrodes based on the Magneli phases doped with Group V elements (vanadium and niobium) [4]. These electrode materials correspond to the composition $Ti_{3.95}M_{0.05}O_7$, where M = Nb or V; they were prepared from a stoichiometric mixture of TiO_2 and Nb_2O_5 or V_2O_5, respectively. However, the solid-phase sintering procedure with subsequent reduction takes more than a day and requires a change in the composition of the gaseous atmosphere.

The present work reports synthesis of electroconductive ceramics from titanium oxides, its doping with the vanadium and niobium cations, and using solid-phase reduction of titanium dioxide with metallic titanium both in reductive and neutral atmospheres. It also studies some electrochemical properties of this ceramics. A distinctive feature of this research is using preliminary mechanical activation of the starting mixture of components in the grinding machines. Previously, we demonstrated that mechanical activation promotes synthesis of the Magneli phases of titanium oxides [5].

EXPERIMENTAL

To prepare ceramic materials from titanium oxide, we used commercial reagents: TiO_2

(rutile) of "extrapure" grade intended for glassmaking, metallic titanium, Nb_2O_5, and V_2O_5 of "chemically pure" grade. From these reagents we prepared a fusion mixture containing TiO_2 and Ti each taken in a molar ratio of 50 % (62.5 % TiO_2 and 37.5 % Ti), 92.1 % TiO_2, and 7.9 mass % Ti based on the stoichiometric composition of Ti_4O_7, and $Ti_{3.95}M_{0.05}O_7$ samples, where M = Nb or V; the mixture was prepared from a stoichiometric mixture of TiO_2, Ti, Nb_2O_5, and V_2O_5, respectively.

Mechanical activation was performed with EI and AGO type mills (rotating speed of the rolls 700 rpm, acceleration 40 *g*; activation time 1–15 min). Titanium rolls with titanium carbonitride balls and steel rolls with steel balls were used.

The samples in the form of disks 18 mm in diameter and 5 mm thick and rectangular samples sized 40×15×5 mm were pressed from the activated powder. The press power was 200 kg/cm^2; an aqueous solution of glycerine with 25 % glycerine and 75 % water was used as a binder.

The samples obtained were dried for 4 h at a temperature of 200 °C.

The samples were annealed in an argon atmosphere and in a hydrogen atmosphere in furnaces under the following conditions: exposure time at the required temperature 4 h, heating and cooling time 1 h. The annealing temperature was 1060–1080 °C unless stated otherwise.

In the case of steel rolls and steel balls used for activation, we determined the amount of iron formed during grinding in the powder and the effect of iron on the conductivity of the sintered samples.

To determine the yield of milled iron during mechanical activation, the spectral method of chemical analysis was used along with X-ray measurements for samples taken 1, 3, 5, 10, and 15 min after the start of activation.

X-ray measurements were conducted on a DRON-3 device with a copper anode.

To study the anodic behavior of oxides we employed a specially designed electrochemical cell.

RESULTS AND DISCUSSION

To study the effect of Group V *d*-elements of the periodic system on the properties of ceramics obtained, we at first prepared a mixture of TiO_2 and Ti taken in a stoichiometric ratio on Ti_4O_7. Then the required quantity of vanadium oxide was added to form a compound with a composition $Ti_{3.95}V_{0.05}O_7$. In the second case, a mixture of only TiO_2 and V_2O_5 was made for this compound. In order to rule out the emergence of iron in the activated powder, mechanical activation was carried out in titanium rolls with titanium carbonitride balls. The samples were annealed both in hydrogen and in argon.

As noted in [5], the interplane distances in the lattices of Magneli phases are close in magnitude; therefore, the majority of reflections on the diffractograms overlap one another. However, in the range of small angles, there are (rather intense) reflections of compounds of interest to us, which do not overlap and which unambiguously point to the existence of the given phase: θ =10.39° for Ti_4O_7, θ = 11.01° for Ti_5O_9, and θ =11.42° for Ti_6O_{11}.

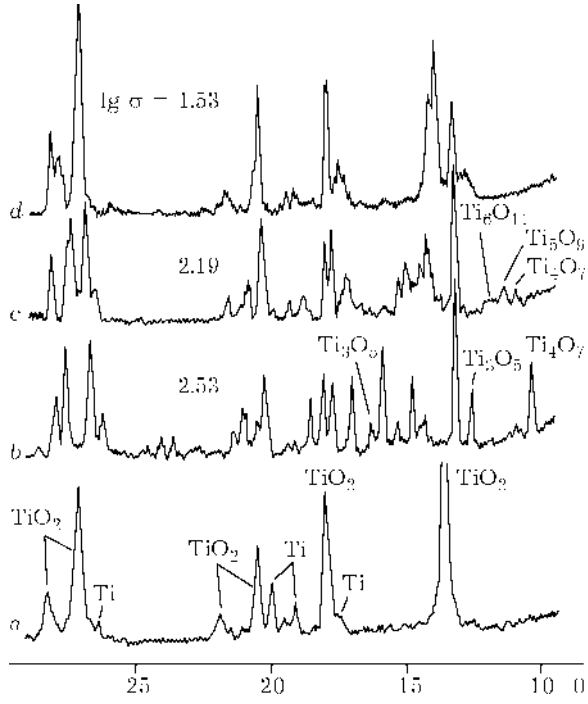

Fig. 1. Diffractograms of the vanadium-containing samples with a composition $Ti_{3.95}V_{0.05}O_7$: *a* – the starting mechanically activated powder is TiO_2 + Ti + V_2O_5; *b* – TiO_2 + Ti + V_2O_5, annealing in hydrogen; *c* – the same, annealing in argon; *d* – TiO_2 + V_2O_5, annealing in hydrogen.

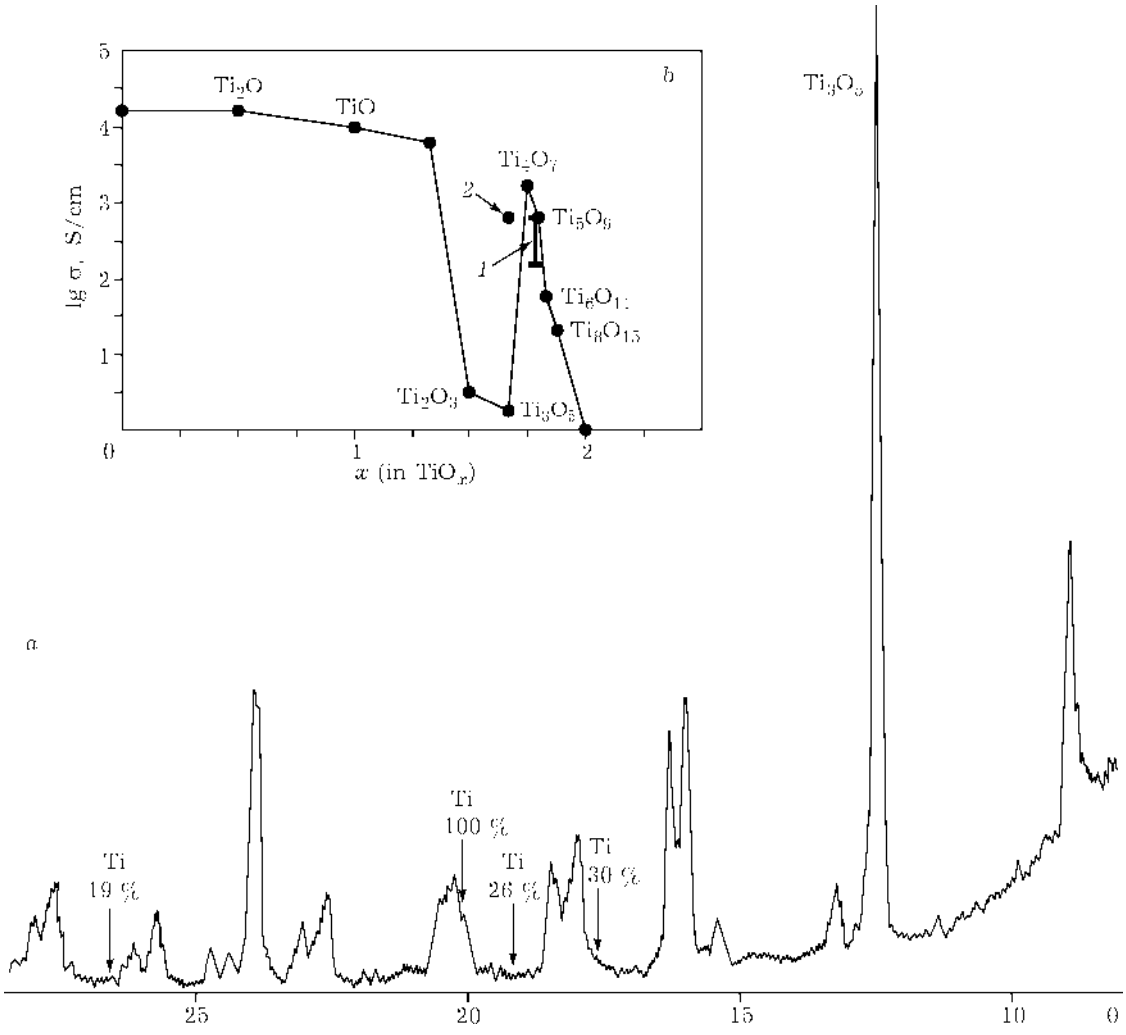

Fig. 2. Diffractogram of the Ti_3O_5 sample of the initial composition Ti + TiO_2 (*a*), and the diagram showing the conductivity of oxide systems *versus* the oxygen content (*b*) [6]: *a* – the molar ratio Ti : TiO_2 = 1 : 1, annealing in argon, the arrows point to the positions where the titanium reflections must be located, the figures indicate their relative intensities; *1* – the conductivity of the samples obtained in the present experiments; density 3.0–3.6 g/cm^3; *2* – the Ti_3O_5 sample; density 3.1 g/cm^3, conductivity σ = 630 S/cm.

As can be seen from X-ray phase analysis data (Fig. 1, *b*), annealing of the activated mixture in hydrogen gives rise to a biphase product composed of Ti_4O_7 and Ti_3O_5, the Ti_4O_7 phase being dominant. The conductivity of these samples is within 340 S/cm, and their density amounts to 3.73 g/cm^3. The samples (see Fig. 1, *c*) were annealed in argon; each sample includes three phases. Their conductivity is somewhat lower (150–160 S/cm), and the density is 3.47 g/cm^3.

The samples obtained only from titanium and vanadium oxides (see Fig. 1, *d*) have a high density (3.74 g/cm^3). However, they have no developed Magneli phase structure, their conductivity being around 34 S/cm.

The samples containing niobium were prepared in the same manner as those with vanadium. The diffractograms for the niobium-containing samples are similar to X-ray data for the vanadium-containing samples. The diffractogram of the starting activated powder did not show any lines of niobium oxide. This is indicative of the fact that its quantity is insignificant and that it is uniformly distributed in the rest of the matrix.

Similar results were obtained during annealing. Annealing in hydrogen formed a two-phase structure of Ti_3O_5 and Ti_4O_7 with a conductivity of 320 S/cm and sample density of 3.63 g/cm^3; annealing in argon yielded a three-phase structure, the samples show lower

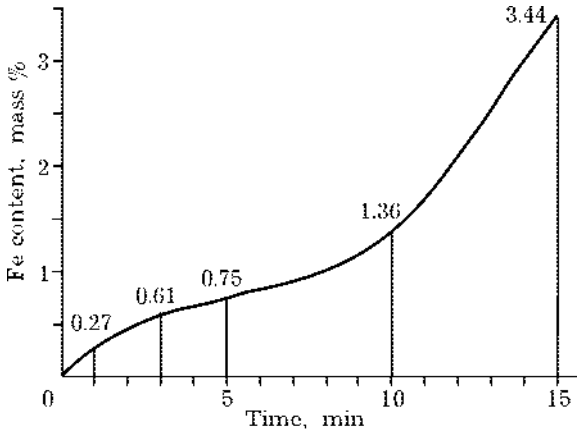

Fig. 3. Iron content in the powder *versus* activation time during activation with steel balls in an AGO-2 mill.

conductivity (200 S/cm), and the density is 3.48 g/cm^3. In samples containing no titanium additives, the density has the largest value (3.73 g/cm^3), while the conductivity is at the lowest level (30 S/cm). The crystal structure in this case is inconsistent with Magneli phases.

In the course of experiments we obtained samples (Fig. 2, *a*) with a Ti_3O_5 structure and without admixtures of other phases. They were obtained from the powder of the starting mixture of titanium and rutile each taken in a molar ratio of 50 %, and were annealed in argon. From the data of [6] it follows that the conductivity of Ti_3O_5 is low enough (see Fig. 2, *b)*, but the samples exhibit exceedingly high conductivity, 630 S/cm. This conflicts with the data presented by Clarke (and demands further rationalization); the density of these samples is 3.1 g/cm^3.

A reasonably large amount of powder is necessary for industrial manufacturing of ceramic details. Since the most productive mills operate with steel rolls and steel balls, we tried to find the amount of iron that emerges in the powder during grinding and to determine its effect on the conductivity and electrochemical properties of the sintered ceramics.

As can be seen from Fig. 3, the yield of milled iron was up to 1 mass % after the first 5 min of treatment and 3.44 % after 15 min. The starting products gradually amorphized, but iron reflections on the diffractograms did not appear even with the maximum quantity of iron. From XRPA data it follows that the early stages of sintering of iron-free samples (up to 1000 °C) somewhat differ from the sintering process for samples with an iron content of 3.44 %; however, the compounds corresponding to Magneli phases did not form in any case.

Figure 4 presents the diffractograms of the samples annealed at a temperature of 1060–1080 °C for 4 h both in hydrogen and argon atmospheres. The starting composition of the powders is, mass %: Ti 7.9 and TiO_2 92.1.

As can be seen from Fig. 4, *a*, the iron-free sample annealed in argon is a three-phase product of high specific conductivity (200 S/cm, density 3.4 g/cm^3). The samples containing iron and annealed in hydrogen show a monophase structure, while the sample with 3.44 % iron content (see Fig. 4, *b)* has low conductivity (20 S/cm, density 2.73 g/cm^3). The sample with an iron content of 1.36 % iron (see Fig. 4, *c)*, on the contrary, has higher conductivity than the three-phase sample (280 S/cm) and higher density (3.45 g/cm^3). The same samples annealed in argon and having 1.36 % iron (see Fig. 4, *d)* have no developed

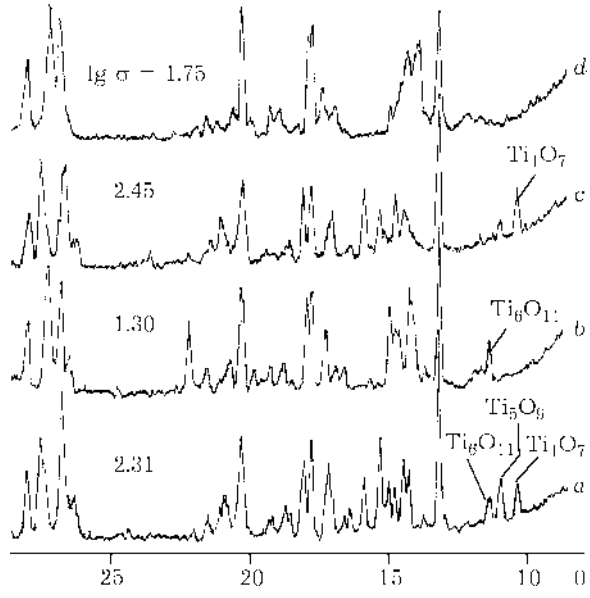

Fig. 4. Diffractograms of samples: *a* – Ti + TiO_2; annealing in argon; three-phase product with Ti_4O_7, Ti_5O_9, and Ti_6O_{11}; conductivity σ = 202 S/cm, density 3.4 g/cm^3; *b* – Ti + TiO_2 + Fe, annealing in hydrogen, Ti_6O_{11} product, σ = 20 S/cm, density 2.73 g/cm^3; *c* – Ti + TiO_2 + Fe, annealing in hydrogen, σ = 280 S/cm, density 3.45 g/cm^3; *d* – Ti + TiO_2 + Fe, annealing in argon, σ = 14.5 S/cm, density 2.91 g/cm^3.

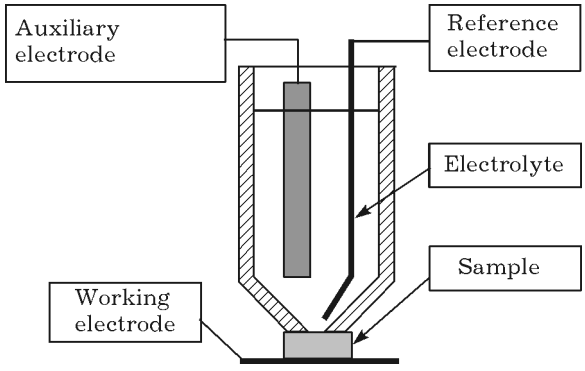

Fig. 5. Schematic diagram of a clamping electrochemical cell for studying the anodic behavior of ceramics based on titanium oxides.

Magneli phase structure; they possess low conductivity (14–15 S/cm) and low density. Hence the low iron content promotes the formation of the Ti_4O_7 phase, which is the best conductor, during annealing in hydrogen.

The Ti_3O_5 and Ti_4O_7 phases, which exhibit maximum electric conductivity among the synthesized titanium oxides, are of greatest interest for use as materials for insoluble anodes applied in a number of electrochemical industries.

Apart from high chemical resistance to the action of electrolyte and electrolysis products, these materials should ensure high rate of anodic processes, *i.e.*, they should endure significant anode current densities without surface passivation. The anodic behavior of Ti_3O_5 and Ti_4O_7 was studied using a clamping three-electrode electrochemical cell (Fig. 5). The special design of the cell enables one to carry out an electrochemical study with a selected site of the sample 0.2 cm^2 in area. A solution of 100 g/l of H_2SO_4 was used as an electrolyte.

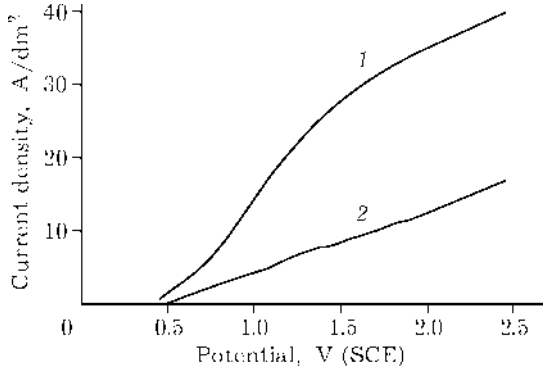

Fig. 6. Anodic volt-ampere relationships obtained with electrodes made from Ti_3O_5 *(1)* and Ti_4O_7 *(2)* in an H_2SO_4 solution (100 g/l). Potential scanning speed is 10 mV/s (the potential was measured relative to the saturated calomel electrode as the reference electrode).

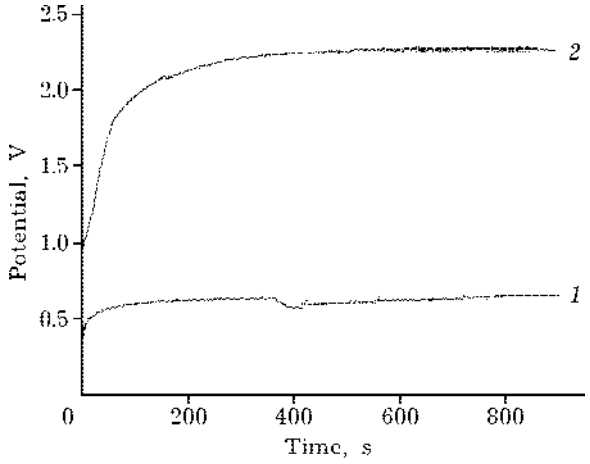

Fig. 7. Time profiles of the anode potential of the electrodes made from Ti_3O_5 *(1)* and Ti_4O_7 *(2)*. Anodic current density 5 A/dm^2; the electrolyte is a solution containing 100 g/l of H_2SO_4.

Figure 6 presents anodic volt-ampere relationships $I = f(E)$, based on which one can draw tentative conclusions to the effect that obtainable current densities with Ti_3O_5 and Ti_4O_7 anodes suffice to carry out large numbers of commercial electrochemical processes using insoluble anodes.

The relationships $E - t$ (Fig. 7) obtained with the same samples at anodic current density of 5 A/dm^2 indicate that the behavior of the alive anodes of titanium oxides under study is stable enough to afford prolonged electrolysis without passive film formation.

CONCLUSIONS

A procedure has been developed for synthesizing conducting phases from titanium oxides by means of titanium oxide reduction with titanium using preliminary mechanical activation. This procedure enables the use of an atmosphere of inert gases, in particular, argon atmosphere instead of the explosive hydrogen reductive medium. The annealing time of ceramic products is reduced considerably.

Both mono- and multiphase materials with high conductivity have been obtained. The ef-

fect of dopants and milled iron yield on the conductive properties of the ceramics has been demonstrated.

The anodic behavior of Ti_3O_5 and Ti_4O_7 has been studied. It follows from the volt-ampere and $E - t$ relationships that the materials under discussion hold much promise for the production of insoluble anodes.

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