Titanium powder prepared by a rapid exothermic reaction

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ABSTRACT

In this paper, a combustion process (CS) to produce titanium powder from titanium oxide and magnesium exothermic mixture (TiO_2 + Mg) was developed successfully. The precursor material (TiO_2) mixed with variable amounts of reducing reagent (Mg), were charged into a metallic cup, and a self-sustaining combustion was initiated by an electrically heated metallic wire, in an argon atmosphere. Depending on the reaction parameters (magnesium concentration, inert gas pressure and sample diameter) the thermocouples registered temperature between 1200 and 1750 °C. The slightly sintered solid, consisted of MgO, Mg and Ti phases, were obtained after the combustion reaction, and titanium powder was recovered by leaching the combustion product with acid. The size of Ti particles was controlled by Mg concentration: at $2.0 \leq \alpha \leq 3.0$ (here α is mole number of Mg) titanium particles between 1 and 5 μm were obtained, whereas homogenous fine powder with a particle size less than 1 μm was synthesized from 3.5 to 4.0 mol Mg containing mixture. Depending on the synthesis conditions the amount of oxygen in purified titanium powder was 2.0–7.6 wt%.

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1. Introduction

Due to its light weight, high specific strength, corrosion resistance and biocompatibility, titanium is an attractive material for aerospace and terrestrial systems, chemical processing industries, and biomedical applications [1–3].

The commercial production of titanium metal involves the chlorination of natural or synthetically produced rutile (TiO_2) in the presence of carbon [4]. The resulting tetrachloride is then reduced to a titanium sponge by the Kroll magnesium process [5] or the Hunter sodium process [6], and also by the reduction of TiO_2 with calcium hydride [7]. However, the use of titanium has been restricted because of its high processing cost. Currently, several studies on a new titanium production process are being conducted in order to replace the current titanium production process. Chen et al. [8] carried out the direct electrochemical reduction of TiO_2 to titanium metal in molten $CaCl_2$. Despite low current efficiency, their process, which was named the Fray-Farthing-Chen (FFC) Cambridge Process, has been reported as successful at the laboratory scale and is currently being scaled up [9]. This technique is simple and its advantage is that it makes the process semi-continuous. The FFC process, however, has some disadvantages: impurities, such as carbon and iron, tend to accumulate in the titanium deposits because the feed electrode is largely electronegative. Since it is difficult to achieve high current efficiency, the energy efficiency

of the FFC process will also be a key factor affecting its commercial use. Ono and Suzuki are engaged in developing a commercial process, based on the calciothermic reduction of TiO_2 powder in a molten $CaCl_2$ salt [10]. In this process called OS from the authors names, reductant calcium is produced by electrolysis, and titanium powder is obtained by metallothermic reduction using the calcium produced electrochemically. This OS process like FFC one, is sensitive to carbon and iron contamination. Abiko et al. have developed a new titanium reduction process, in which titanium powder was prepared from TiO_2 through an electronically mediated reaction (EMR) using calcium as a reductant [11]. In Abiko's process the reduction is carried out in a molten $CaCl_2$ salt at 900 °C. Titanium powder with a purity of 99.5% was prepared by this technique in optimized reaction conditions.

Combustion synthesis (known also as Self-Propagating High Temperature Synthesis, SHS) is one of the simplest and cost-effective techniques which can be applied for a large scale production of Ti powder. A first attempt to produce Ti powder from TiO_2 + 2Mg precursor mixture via combustion technique has been reported by Frolov and Fetzov in early 1980 [12]. In this investigation the principal opportunity for the synthesis of Ti powder by the combustion of a TiO_2 + 2Mg mixture has been demonstrated. Unfortunately, no details are available in the literature regarding the powder characteristics. Recently, the synthesis of nanosized titanium particles having an average size between 50 and 100 nm have been reported by present authors [13]. The synthesis was performed from TiO_2 + 2Mg reactive mixture diluted with NaCl.

The purpose of the present paper is to further study the combustion process in TiO_2 + αMg system for the economical production of

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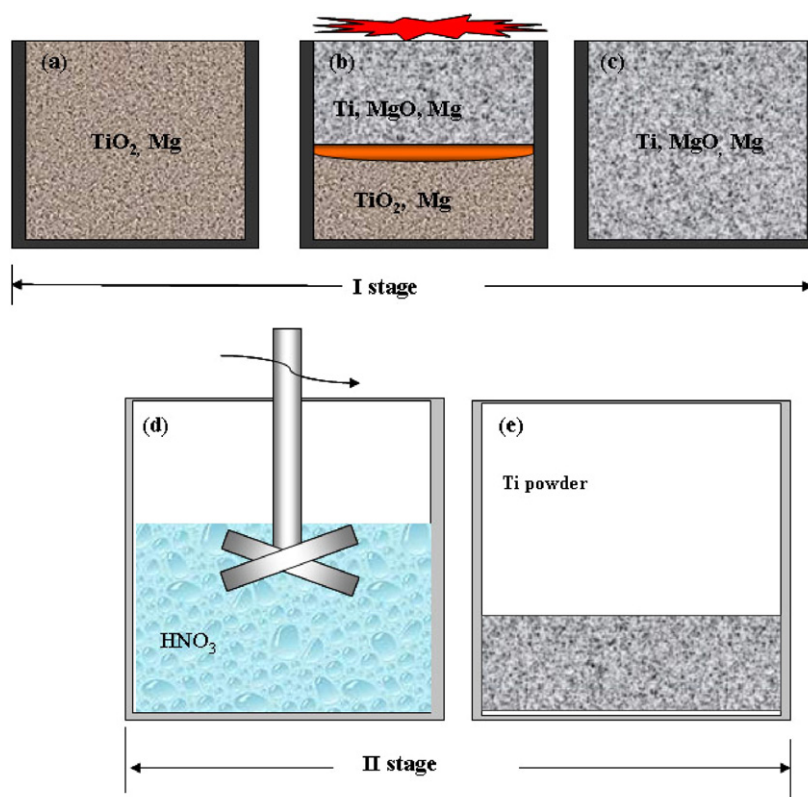E-mail address: haykrasom@hotmail.com (H.H. Nersisyan).

Fig. 1. Concepts of Ti production by rapid exothermic reaction: (a) $TiO_2 + \alpha Mg$ mixture compacted into metallic cup; (b) combustion process and reaction wave propagation; (c) combustion product with metallic cup; (d) acid leaching and water purification of product; (e) final titanium powder.

micrometer-sized titanium powder. Here, some basic experimental evidence at the laboratory scale is illustrated by this concept. The authors think that the technical aspects may be useful for industrial application.

2. Experimental

Titanium oxide powder (99.0% purity, and particle size $\leq 0.5\ \mu m$, Terrio Corporation, China), and magnesium powder (98.5% purity, and particle size 50–125 μm, Daejung Chemical and Metals Co., Ltd., South Korea) were used in the experiments.

Our concept for Ti powder preparation using TiO_2 and Mg is illustrated in Fig. 1. The main process consists of two major steps. In the first step, a controlled amount of TiO_2 and Mg powders was dry mixed and hand compacted into a metallic cup of 3–8 cm in diameter (Fig. 1a); and combusted by resistivity heated nickel–chromium wire in an argon atmosphere (Fig. 1b). The TiO_2 particles react with Mg and an excess of Mg is required for the complete reduction of TiO_2 to Ti:

$$TiO_2 + \alpha Mg = Ti + 2MgO + (\alpha - 2)Mg \tag{1}$$
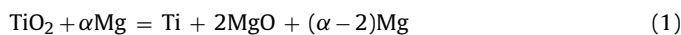
The product particles, consisting of Ti, MgO and residual Mg phases (Fig. 1c) were obtained by reaction (1).

In the second step MgO and residual Mg were drown off by acid leaching of combustion product. This process was performed with the dilute nitric acid solution using a stirring technique (Fig. 1d). During this process MgO and Mg were converted to water soluble $Mg(NO_3)_2$:

$$Ti + MgO(Mg) + 2HNO_3 + nH_2O \rightarrow Ti + Mg(NO_3)_2 + (n+1)H_2O \tag{2}$$
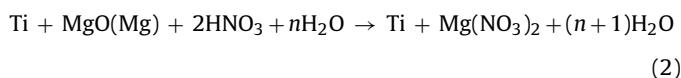
Then, the remaining powder was rinsed in water, alcohol and dried in a laboratory oven at 60–80 °C (Fig. 1e).

During the combustion process the data acquisition system (DASTC, Keithley) continuously recorded the thermocouples' time histories. Two tungsten–rhenium thermocouples (W/RE-5 versus W/Re-20, 100 μm in diameter) were previously inserted into the reaction pellet for temperature measurements. The combustion parameters examined were the combustion temperature (T_c) and the combustion wave velocity (U_c). The combustion velocity was calculated as $U_c = x/t$ (t is the time interval between temperature profiles and x is the distance between thermocouples) (Fig. 2).
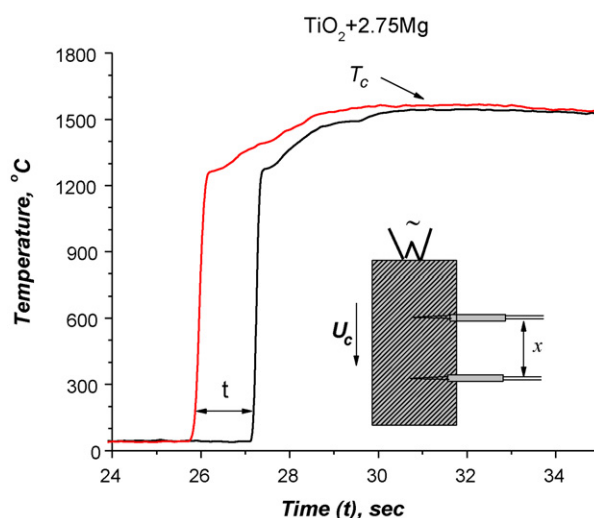

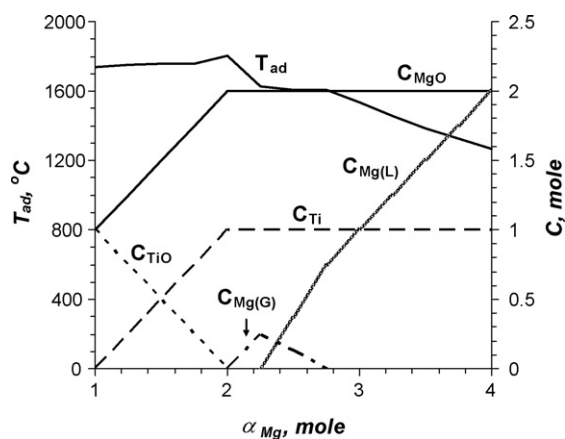**Fig. 2.** Typical temperature–time profiles for calculation of the combustion parameters.

Fig. 3. Thermodynamic analysis of TiO$_2$ + αMg system: P = 2.0 MPa.

Fig. 4. Combustion parameters as a function of Mg mole number.

After drying, the powder morphology and particle size was examined using a scanning electron microscope (SEM; JSM 5410, JEOL, Japan). The phases were identified by X-ray diffraction (XRD, Siemens D5000, Germany) measurement. The impurity magnesium in the reduced powder was analyzed by ICP-AES, and the oxygen and nitrogen concentrations were analyzed by using an ELTRA ON-900 Oxygen/Nitrogen Determinator.

3. Results and discussion

3.1. Thermodynamic analysis

Prior to the experiments, an adiabatic combustion temperature, T_{ad}, and equilibrium composition of reaction products of TiO$_2$ + αMg system was theoretically estimated using software "Thermo" which was specially designed for the combustion processes [13]. This program allows to calculate the thermodynamic equilibrium in complex multi-component hetero-phase systems and to analyze the phase composition of synthesis products (solid, liquid, and gaseous) and the adiabatic combustion temperature of a system. The calculation of equilibrium characteristics is based on minimization of the thermodynamic potential of the system. Fig. 3 shows the equilibrium phases and the corresponding adiabatic combustion temperatures (T_{ad}). The initial temperatures of the reagents and the reaction pressure were set to be 25 °C and 2.0 MPa, respectively. As shown in Fig. 3, the adiabatic combustion temperature of the TiO$_2$ + αMg system is predicted to be maximum (1806 °C) at the stoichiometric point ($α = 2$). In this point bi-phase reaction product consisting of Ti and MgO is obtained. With an excess of Mg ($α > 2$), the heat released per unit volume decreased. The reaction heat is partially consumed for the heating, melting, and evaporation of Mg, therefore, T_{ad} drops at $α > 2$. At that, an excess of Mg used remains in the final product. Below the stoichiometric point ($α < 2$) the reduction process of TiO$_2$ leads to the formation of TiO, MgO and Ti phases.

3.2. Combustion synthesis

Numerous factors could affect the combustion wave progress through the reactants. However, the initial reactant ratio is the most influential factor to determine combustion parameters (T_c and U_c). In the combustion process of TiO$_2$ + αMg system the concentration of Mg plays a key role and its effect on the combustion process was examined first. The reaction samples 3.0 cm in diameter and 1.1 g/cm^3 density were used in these experiments and the argon gas pressure was set to be 2.0 MPa. The results of the experiments are shown in Fig. 4. The tendency of T_c is similar to
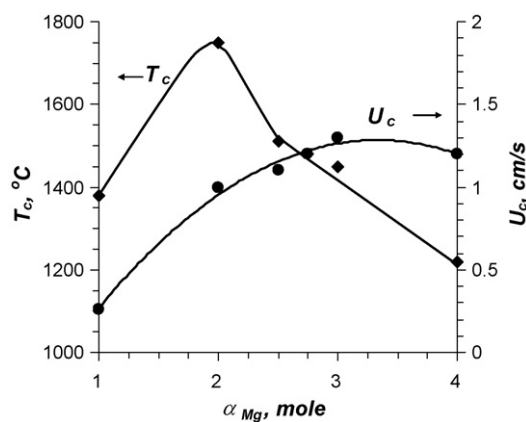
that of T_{ad}, i.e. maximum at the stoichiometric point (1750 °C), and almost linear temperature drops from the Mg concentration. However, in TiO$_2$ + αMg system experimentally measured values of T_c are comparatively low (<50–130 °C) from thermodynamically predicted one. The deviations between the temperature results are due to the fact that the short time of combustion is not sufficient to complete the reduction process of TiO$_2$. Typical temperature–time profiles of TiO$_2$ + 2.75Mg system shown in Fig. 1 clearly demonstrate that the combustion period for the reaction sample 3.0 cm in diameter is less than 5 s, and this time obviously is not sufficient yet to reach adiabatic combustion temperature. Within the concentration range of the tests the combustion velocity shows increasing tendency, and maximum value of U_c (1.3 cm/s) corresponds to $α = 3$. The relatively higher-propagation velocity observed at $α > 2$ may be due to the thermal conductivity change in the reaction zone conditioned by Mg concentration.

More parametric optimization of the synthesis conditions has been performed using Ti + 2.75Mg reaction mixture. As will be shown below, the mixture of given composition produces Ti powder with lowest oxygen content and can be chosen for optimum. The influence of initial sample diameter (d) and inert gas pressure P_{Ar} on combustion parameters (T_c and U_c) has been investigated. A noticeable increase in T_c (from 1450 to 1580 °C) is found when sample diameter changes from 1.0 to 5.0 cm (Fig. 5a). This increase is due to longer reaction time, and higher conversion degree of reactants. As for the combustion velocity, after a linearly increase, it reaches to maximum point (1.2 cm/s) at $α = 2.75$, and then a decrease follows. Fig. 5b shows the effect of argon pressure on the combustion parameters for the mixtures with $α = 2.75$. The temperature slightly is increased in a qualitatively similar way to the decrease in wave velocity. In the pressure interval from 0.5 to 3.0 MPa the change of the temperature is less than 100 °C, and the velocity change is from 1.1 to 1.25 cm/s. The relative stability of the combustion parameters in a wide diapason of the pressure indicates about minor degassing of Mg during the processes and the perspectives of the given system for a large scale design.

3.3. Combustion products characterization

XRD investigation have revealed successful reduction of TiO$_2$ by Mg in the $1.0 \leq α \leq 4.0$ interval of α (Fig. 6). Under the stoichiometric point ($α = 1$) the combustion product is consisted of TiO and MgO (Fig. 6a). At the stoichiometric point ($α = 2$) bi-phase combustion product consisting of MgO and Ti is obtained. Above stoichiometric point residual Mg also remains in the final product (see $α = 3$). The aforesaid combustion products were purified by using acid leaching to eliminate MgO and Mg, followed by washing with distilled water to get rid of surplus acid. Fig. 6b shows the XRD patterns of acid puri-
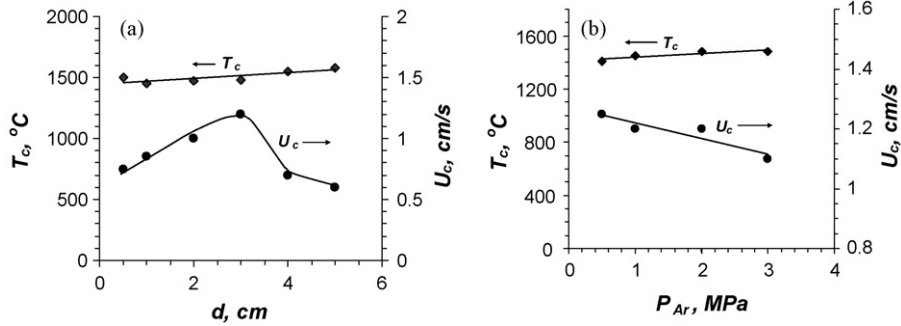
Fig. 5. Combustion parameters of $TiO_2 + 2.75Mg$ system as a function of the sample diameter (a) and argon gas pressure (b).

fied samples synthesized at different α levels. The main diffraction peaks on XRD patterns are identified as α-Ti. However, some background noises and undefined small peaks also can be seen on XRD. These may be related with tiny amount of Ti low oxides (TiO, Ti_2O_3, Ti_3O_5, etc.) formed during the combustion process.

The oxygen concentration in the recovered Ti powder analyzed by Oxygen/Nitrogen Determinator is shown in Fig. 7. In the investigated interval of α, the lowest oxygen contents were obtained for the samples with 2.75 mol of Mg. Moreover, in this point the content of oxygen is reduced from 3.9 to 2.0 wt% by increasing the sample diameter from 3.0 to 8.0 cm. Other impurities, such as nitrogen and magnesium are within 0.1–0.4 wt% interval depending on reaction conditions.
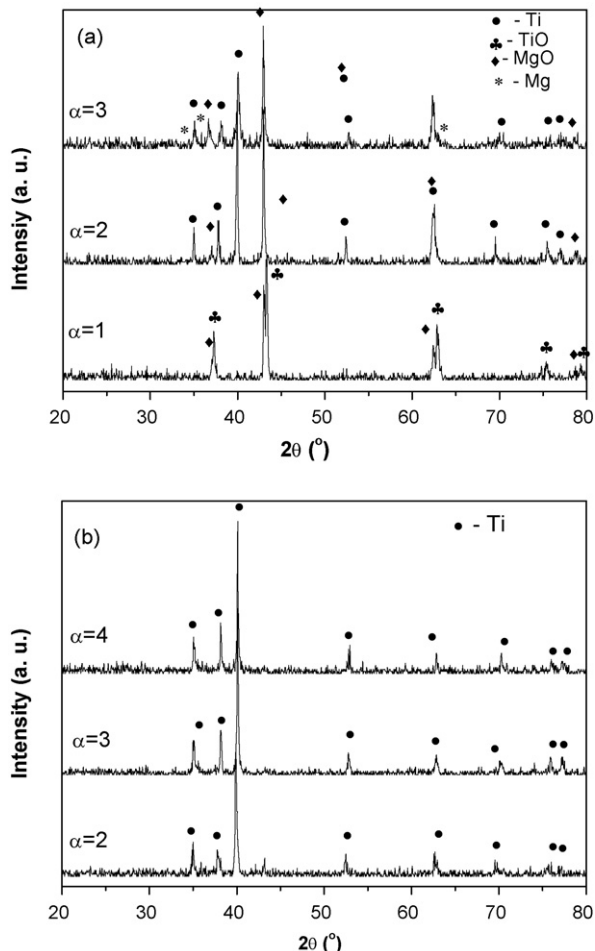
Fig. 8a–c shows Ti particles morphology prepared from the reaction mixtures containing 2.0, 3.0 and 4.0 mol Mg. Under the given conditions, from 10 and 100 μm aggregated titanium particles were formed. These aggregates have a porous microstructure and consist of fine Ti particles. The surface microstructure of the Ti aggregates is shown in Fig. 8a*–c*. Smooth surface Ti aggregates consisting of micrometer size pores were obtained at α = 2.0 and 3.0 (Fig. 8a* and b*), whereas only fine and round shape particles can be seen at α = 4 (Fig. 8c*).

4. Discussion

The combustion method described above shows a promise in the synthesis of micrometer-sized titanium powder. The synthesis is based on the combustion process of $TiO_2 + \alpha Mg$ exothermic mixture. The method clearly demonstrates, that an excess of Mg (0.75 mol) is required to produce titanium powder with relatively low content of oxygen. It is believed, that the presence of oxygen in Ti powder is due to the spatial inhomogeneity of the reaction mixture caused by the size difference between Mg and TiO_2 particles. A comparison between the size of Mg (50–125 μm) and TiO_2 particles (<0.5 μm) shows a difference of several order. This is why an incomplete reduction of TiO_2 occurs during the combustion process, leaving behind a sufficient amount of oxygen in the final products. Incompleteness of the reduction reaction can be partially eliminated by increasing the sample diameter. According to the temperature–time profiles shown in Fig. 9, an increase in sample diameter positively effects on the maximum temperature and the duration of the combustion process, thus activating the reduction process of TiO_2. Unfortunately, in the case of large diameter we are not able to increase the sample diameter above 8.0 cm. However, extrapolation of the analysis data shown in Fig. 10, clearly demonstrates what is expected to obtained, if continue to increase the sample diameter. As seen, Ti powder with an oxygen content of
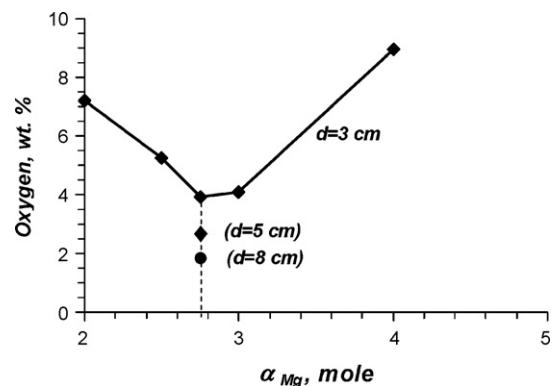

Fig. 6. XRD patterns of combustion products before (a) and after acid leaching (b).

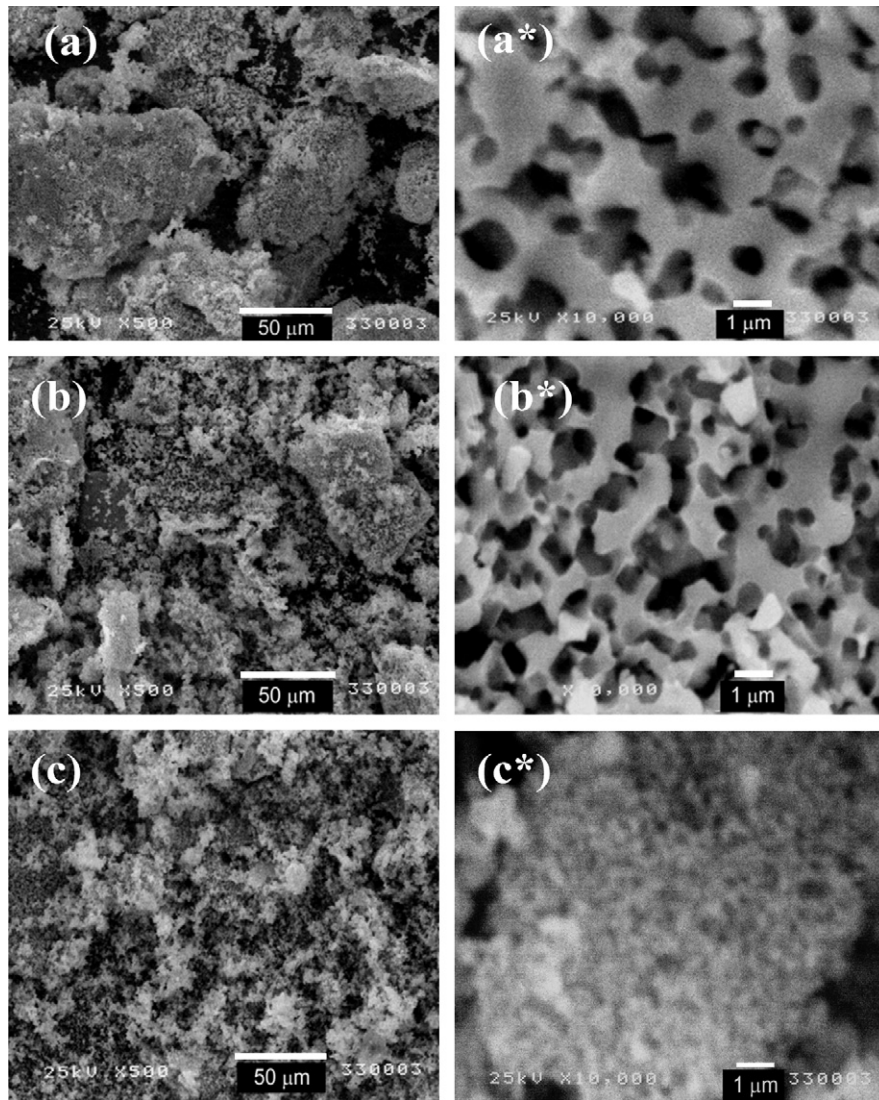**Fig. 7.** Oxygen content upon Mg mole number.

Fig. 8. SEM images of Ti powder: a–c, Ti particles prepared with 2.0, 3.0 and 4.0 mol of Mg respectively; a*–c*, surface morphology of Ti prepared with 2.0, 3.0 and 4.0 mol of Mg respectively.
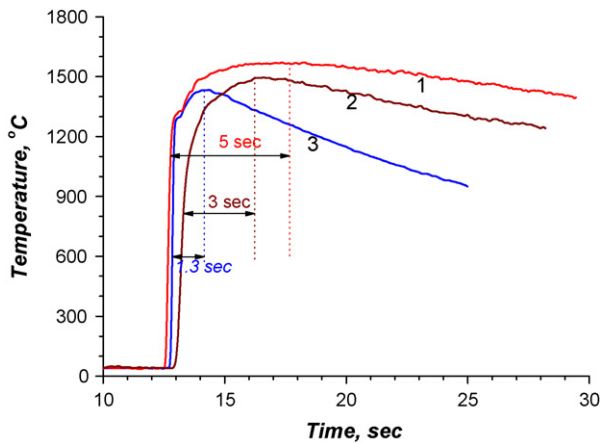

Fig. 9. Temperature–time profiles of Ti + 2.75Mg system versus sample diameter: 1, 5.0 cm; 2, 3.0 cm; 3, 1.0 cm.
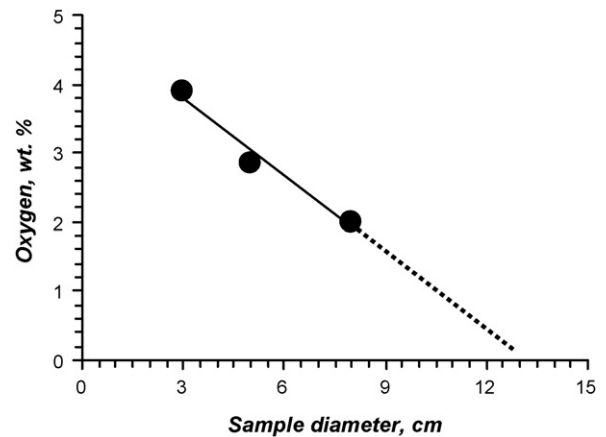

Fig. 10. Oxygen content upon the sample diameter (dot line shows the extrapolation).

less than 0.5% by weight can be obtained from the reaction samples having diameter above 12 cm.

Considering that the industrial Kroll process is power-consuming and contains a high content of alkali metal chloride (LiCl, KCl, NaCl, etc.), we may find the combustion process suitable for the Ti powder production on a large scale. The industrial application of this process seems technically attractive and cost effective. However, for any viable commercial application of pure Ti, the oxygen content should be kept at a level of thousand mass parts per million and the further investigation into decreasing oxygen content to an acceptable level is required.

5. Conclusion

(1) A combustion process to produce titanium powder in two steps using TiO_2 and Mg powders was proposed. In the first step, TiO_2 was fixed with variable amount of Mg, hand compacted into the metallic cup, and combusted under the argon pressure. The entire process was finished within several seconds and the titanium particles were formed at 1200–1750 °C. In the second step, leaching of the reaction product with nitric acid was performed and phase pure and micrometer size Ti powder was obtained. The powder morphology was experimentally studied upon the Mg concentration (α): at $2.0 \leq \alpha \leq 3.0$ titanium 1–5 μm in size were obtained, whereas homogenous fine powder less than 1 μm in size was prepared with 3.5–4.0 mol of Mg. Under the optimized reaction conditions Ti powder with an oxygen content of 2.0% by weight was obtained.

(2) Combustion process can produce the titanium powder in shorter steps compared with the other existing methods. The industrial application of this process seems technically attractive and cost effective, but for this application, further investigation into decreasing oxygen concentration to an acceptable level is required.

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