Thermochimica Acta 517 (2011) 98–104

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Non-isothermal and isothermal kinetics of high temperature oxidation of micrometer-sized titanium particles in air

Olga Schulz[a,*], Norbert Eisenreich[a], Stefan Kelzenberg[a], Heike Schuppler[a], Jochen Neutz[a], Evgenii Kondratenko[b]

[a] Fraunhofer Institut für Chemische Technologie (ICT), Joseph-von-Fraunhofer-Str. 7, D-76327 Pfinztal, Germany
[b] Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert Einstein Str. 29a, D-18059 Rostock, Germany

ARTICLE INFO

Article history:
Received 12 August 2010
Received in revised form 24 January 2011
Accepted 27 January 2011
Available online 27 February 2011

Keywords:
Temperature-resolved X-ray diffraction
Oxidation of micrometer-sized titanium particles
Dense rutile layer
Kinetic parameters

ABSTRACT

The oxidation behaviour of micrometer-sized titanium particles was investigated in the temperature range from 323 to 1473 K in air using high-temperature X-ray diffraction and thermogravimetric (TG) analysis with multiple heating rates (2, 5, and 10 K/min). The investigated titanium particles were directly transformed to rutile without the formation of other polymorphic crystalline phases. Moreover, only traces of titanium nitride were observed below 700 K. Assuming mono-modal particles, a Jander model for three-dimensional diffusion was applied to derive the kinetic parameters of the oxidation of titanium particles (5 and 20 μm) from fitting the TG measurements using a least squares fit procedure. The model described reasonably well the oxidation process when all the TG experiments (multiple heating rates and two different particle sizes) were simultaneously used for the fitting. For titanium particles the oxidation occurs by a three-dimensional diffusion through a dense rutile layer and differs from the one-dimensional diffusion in a stratified structure of bulky materials. The derived diffusion coefficients ranged from 10^{-14} to 10^{-7} cm^2/s in the temperature interval 700–1400 K.

1. Introduction

The evolving importance of micro- and nanocrystalline materials is extended in many fields ranging from catalysis, over ceramic powder synthesis to addition in explosives and propellants [1–6]. The use of titanium and titanium alloys increases continuously during the last fifty years due to its specific properties like good corrosion resistance, very high thermal stress resistance, low thermal conductivity and superior strength-weight ratio. For example, titanium is commercially applied in aerospace, military, chemical and automotive industries [1–6]. In medicine, titanium displayed a gained importance as ideal material due to the exceptional biocompatibility, which is used in bone surgery and dentistry [7]. Its application may be further extended when using titanium micrometer- and nanometer-sized particles for example as coating material.

A literature review revealed that there are some studies about the oxidation of pure titanium and oxidation kinetics [3,8]. The kinetics was studied at different temperatures [9–11] and the results show that the titanium oxidation might follow different kinetic laws (logarithmic or cubic at low temperatures, parabolic at 873 K and 973 K and linear or even paralinear between1023 K and about 1273 K) [11]. However, there is still a relatively weak fundamental understanding of the oxidation process of titanium, especially, of micrometer-sized particles. The size of the particles can strongly influence the responsiveness as well as the oxidation behaviour. For example, Eisenreich et al. [1] demonstrated that ultra fine (50–100 nm to 1 μm) aluminum particles were oxidized at lower temperatures than coarser particles or bulk metal due to an increased ratio of surface to volume and the related high relevance of a 10 nm layer reacting controlled with chemical kinetics instead of diffusion. Therefore, the aim of the present study was to investigate the kinetics of oxidation of micrometer-sized titanium particles and to compare it with literature data obtained from more bulky specimens. To this end, in situ high-temperature (up to 1473 K) X-ray diffraction characterisation was combined with thermogravimetric (TG) analysis using multiple heating rates. The latter experiments were kinetically evaluated. The obtained kinetic data may be helpful for planning technological processes/applications of particles of this size range.

2. Experimental

Two batches of titanium particles with average diameters of around 5 and 20 μm were produced by explosion of titanium wire and supplied by SIBTHERMOCHIM (Russia). The diameters of the particles were determined by laser diffraction using a Mastersizer S, Malvern Instruments GmbH (Germany). This method can be classified as light diffraction analysis which uses laser as light

---

[*] Corresponding author.
E-mail address: olga.schulz@ict.fraunhofer.de (O. Schulz).

0040-6031/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2011.01.038

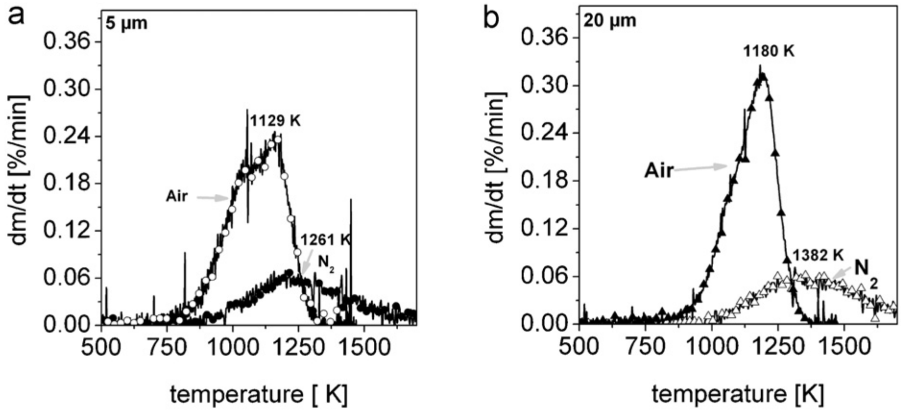

Fig. 1. Comparison between DTG curves of titanium particles with a size of 5 µm (a) and 20 µm (b) heated with 10 K/min in air and nitrogen.

source. According to this method the size of the diffraction angle is inversely proportional to the particle size. The Brunauer, Emmett, Teller (BET) method was applied for determining specific surface areas (S_{BET}) of titanium particles probing Krypton adsorption at 77.35 K on a Micrometrics ASAP 2000 instrument. The obtained S_{BET} values of the 5 and 20 µm particles amounted to 0.3 and 0.2 m^2/g, respectively. The size and shape of the particles were also analyzed by field emission scanning electron microscopy (FE-SEM) using a SUPRA 55 VP, Carl Zeiss SMT AG, Germany. The crystalline phases formed during oxidation were determined by in situ high-temperature X-ray diffraction analysis using a Bruker AXS D8 diffractometer with a high temperature cell. All oxidation experiments were performed at temperatures below the melting point of titanium (T_{melt} = 1941 K). Diffraction patterns of the particles were taken at a 2θ range between 20° and 80°. During the temperature-controlled experiments, samples were heated up in steps of 25 K from 323 K to 1473 K. At each step, the temperature was held for 2 h and diffraction patterns were taken with a scan rate of 0.05°/s. The heating rate from one temperature level to the next one was 1 K/s. The diffraction patterns were evaluated using the TOPAS software of Bruker AXS [12,13] which give relative intensities or concentrations versus temperature; however, the data scatter substantially, at least at low peak intensities. The progress of the reaction was also investigated using a difference method described elsewhere [14]. This difference method monitors the changes in a series of diffraction patterns as a function of time or temperature using the whole pattern or a part of it containing characteristic peaks and provides smooth curves also for weak peaks. The resulting curves are compared to thermoanalytical curves. The non-isothermal thermogravimetric analysis (TG) was carried out with heating rates for titanium of 2 K/min, 5 K/min and 10 K/min up to 1473 K (Netzsch STA 449C Jupiter). Isothermal thermogravimetric analyses were performed for 50 h at 923 K, 973 K, 1073 K and 1173 K for 20 µm titanium particles and 773 K, 823 K, 873 K, 923 K and 973 K for 5 µm particles. The evaluation of the oxidation kinetics of titanium particles based on the experimental data of thermal analysis utilized the Jander model for three-dimensional diffusion applying the Routine "FindMinimum" of Mathematica® 7 by Wolfram Research, Inc. to the chi-square function, which enables a non-linear least squares fit [15].

3. Results and discussion

3.1. Non-isothermal oxidation behaviour and X-ray diffraction analysis

Thermogravimetric (TG) analysis of oxidation of titanium particles in air was carried out in the temperature range of 323–1473 K. Irrespective of the size of the particles, a significant weight increase was observed in these experiments indicating that the particles reacted either with oxygen or nitrogen. From a thermodynamic point of view, the reaction with air leads primarily to the formation of titanium oxide as the main reaction product. The in situ XRD analysis and TG study with pure nitrogen supports this conclusion. Nevertheless, the formation of titanium nitride cannot be completely excluded.

Fig. 1 shows differentiated thermogravimetric curves (DTG) obtained upon the interaction of titanium particles with air and pure nitrogen. Since no oxygen was used in the latter experiment, we investigated independently the formation of titanium nitride. It is clearly seen from this figure that the gaseous environment has an influence on reaction-induced changes of the weight increase. In general, the reaction of titanium particles with air starts at lower temperatures. Compared to the DTG curves with nitrogen, those with air are characterized by (i) a significantly higher weight increase, and (ii) maxima shifted to approximately 150–200 K lower temperatures. Both curves overlap above 1000 K indicating a competition between the formation of titanium oxide and nitride. However, titanium nitride is easily oxidized in air as demonstrated in a previous X-ray diffraction study [16]. Based on the above discussion, it is suggested that the contribution of titanium nitride formation to the TG curves during oxidation of titanium particles in air is not significant. Therefore, we discuss now the effect of the particles size on their oxidation in air.

Fig. 2 compares the TG curves obtained during oxidation of 5 and 20 µm sized particles. The total weight increase amounted to 64.8

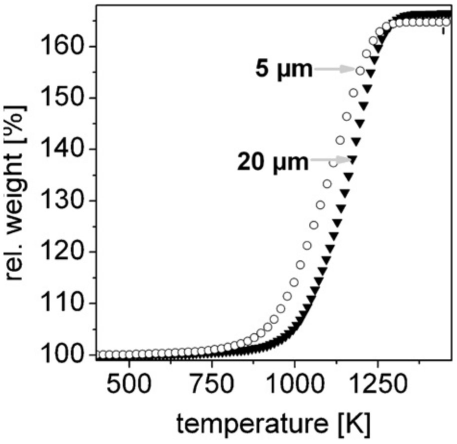

Fig. 2. Non-isothermal TGA curves of titanium particles heated with 10 K/min.

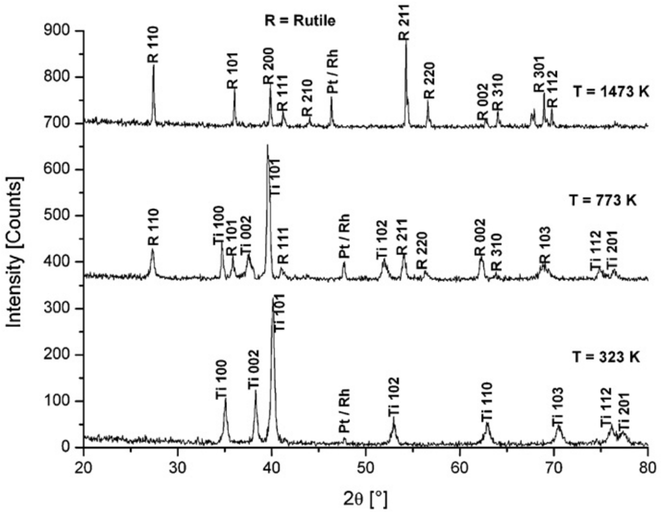

Fig. 3. Selected temperature-resolved diffraction patterns of Ti particles with a size of 5 μm at 323 K, 773 K and 1473 K (rutile = R).

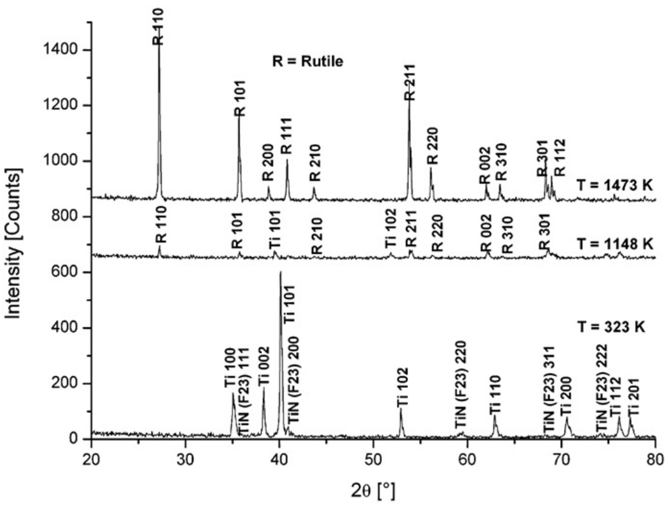

Fig. 4. Selected temperature-resolved diffraction patterns of Ti particles with a size of 20 μm at 323 K, 1148 K and 1473 K (rutile = R).

and 66.6%, respectively. These values are very close to the theoretical value (67%) for complete conversion of titanium to titanium dioxide. Therefore, we suggest that the latter process dominate over titanium conversion to the corresponding nitride. Using these results, the content of oxygen or nitrogen or both in the passivation layer of fresh titanium particles was estimated, which was about 0.4% for titanium particles with a mean diameter of 20 μm and 2.2% for those with a mean diameter of 5 μm.

Despite the fact that the total weight increase is very similar for 5 and 20 μm sized particles, their TG profiles are different. This means that the oxidation of differently sized particles occurs with different conversion rates. For quantifying the titanium oxide formation, we used a temperature (T_{50}) for achieving 50% conversion of metallic titanium particles to the oxide. These parameters determined from Fig. 2 amounted to approximately 1090 and 1153 K for the oxidation of the 5 and 20 μm particles, respectively. It should be mentioned that the difference in the T_{50} values was also valid for the case when the TG profiles were normalized with respect to the specific surface areas of the corresponding particles (the results are omitted for brevity). Therefore, it can be concluded that the smaller particles are oxidized than the bigger ones at lower temperatures. This may be attributed to the effect of the particle size on the ratio of surface to volume.

In situ high temperature X-ray analysis according to [17] was applied to identify crystalline phases during oxidation of titanium particles in the temperature range from 323 to 1473 K (Figs. 3 and 4). Several previous studies dealt with phase transitions in oxygen–titanium-systems such as TiO, Ti_2O_3, TiO_2 and Ti_6O or oxygen–titanium alloy systems using X-ray diffraction analysis [18–21]. It is known that the solubility of oxygen from air in solid titanium is very high and there exists a controversial discussion of the titanium–oxygen state [18–22]. For example, Vergara and coworker [23] studied temperature effects on titanium oxidation state of titanium bulk and thin film. They found that the oxygen content varied in dependence on the thickness of the sample. Hence, the presence of Ti_2O_3 and TiO_2 as reaction product was detected between 500 K and 600 K and at room temperature only TiO_2 for bulk oxidation. Thin film oxidation occurs via the formation of TiO. As oxygen rich modification of titanium oxide only TiO_2 exists which occurs in three modifications: anatase, brookite and rutile [24–26]. The thermodynamic stable modification in solid state is rutile, which was detected in our experiments. Figs. 3 and 4 demonstrate the representative diffractograms of 5 and 20 μm titanium particles, respectively. The vertical scale of X-ray diffraction patterns was adapted to the individual intensity of the particles during the oxidation. Irrespective of the reaction temperature, the rutile modification of TiO_2 was the only crystalline phase detected in the 5 μm particles. For the 20 μm particles, only very weak peaks of titanium nitride with a face-centred cubic (F23) lattice [27] were additionally identified between 323 K and 673 K. Therefore, our below discussion is focused on the formation of rutile from metallic titanium.

For a better illustration of the temperature-induced transformation of Ti to TiO_2, we compare in Fig. 5a and b the intensities of the reflexes of Ti (Ti 101) and TiO_2 (R 101) normalized according to the difference method described in [14]. In agreement with the above TG analysis, significant differences in the oxidation activity of 5 and 20 μm sized titanium particles were identified by the X-ray study. The 5 μm particles were oxidized to rutile starting at 640 K, while no intensive rutile signals were observed upon oxidation of the 20 μm particles below 800 K. In the case of 20 μm particles, the amount of rutile phase and the crystallite size increased strongly above 1120 K. Moreover, the intensity of titanium signal decreased strongly to a low value at 625 K as can be seen on Fig. 5b. This might be due to the shielding of the outer rutile layer of the particles [28]. Another reason might be the formation of amorphous titanium oxide; a slight weight gain in TG curve was observed in this temperature range.

The crystallite sizes of titanium oxide were calculated from the peak width profile analysis using fundamental parameter analysis of the software TOPAS of Bruker AXS [12,13]. The changes in the crystallite sizes of rutile phase from the titanium particles are presented in Fig. 6. Rutile crystallites of 23 nm were formed from titanium particles with a size of 5 μm starting at 848 K. They grew to 339 nm with a temperature increase up to 1373 K. In the case of titanium particles with a size of 20 μm, the rutile crystallites of 27 nm were firstly observed at 898 K. Their size finally increased to 200 nm at 1398 K. The error in assessing the crystallite sizes is represented by a value of 1–2%. During the experiments no cracking of the rutile layer was observed. Hence the formation of a multilayer oxide was prevented. In summary, the rutile crystallites formed from the 5 μm particles are 41% bigger than those formed from titanium particles with a size of 20 μm. This is probably due to the higher specific surface of the smaller particles, which favors a faster growth of the crystallites.

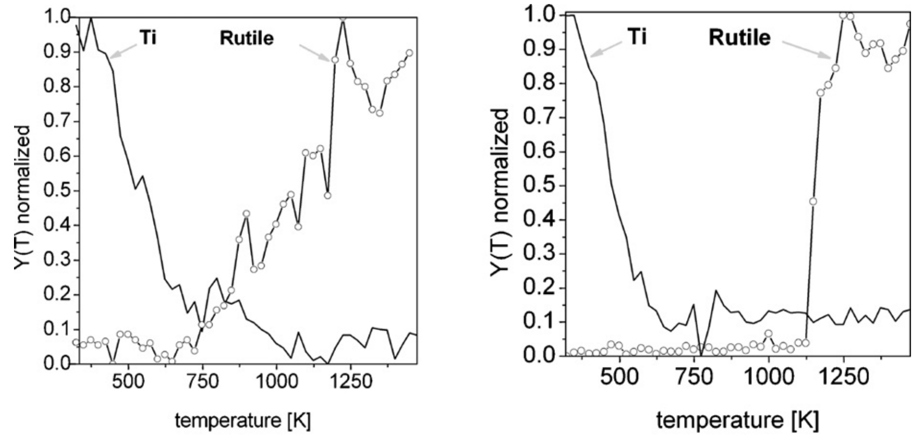

Fig. 5. Normalized intensity curves of titanium particles with size of 5 μm (a) and 20 μm (b).

3.2. Description of kinetics of the titanium particles

It is widely accepted that non-isothermal TG experiments have the potential for providing important kinetic and mechanistic insights into oxidation of metal particles [1,6]. This is due to the fact that the TG response contains the full data set from zero conversion at the initial temperature to full conversion at the end temperature. In order to ensure the required accuracy of the kinetic parameters determined from kinetic evaluation of these responses, TG experiments should be performed at several heating rates. In the present study, we applied the Jander model for three-dimensional diffusion [29] for quantitative description of oxidation of titanium particles of 5 and 20 μm at three heating rates of 2, 5, and 10 K/min. This model is the three-dimensional analogon of the (one-dimensional) Jander equation and describes diffusion being the rate-controlling step of the reaction in a product layer (assumed to be TiO_2) of a spherical particle, whereas the chemical reaction is assumed to occur instantaneously. The diffusion might be the inwards oxygen diffusion. In our study, titanium was oxidized to rutile.

The following relation between the reaction rate and the degree of conversion (x) of titanium particles is valid when the weight increase is normalized from 0 to 1:

$$D(t-t_0) = [1-(1-x)^{1/3}]^2 \tag{1}$$

where t_0 is the starting time of the reaction with virtually zero conversion, and it was used as a parameter of the least squares fit procedure of isothermal TG data. It was also assumed that the reaction rate D follows the Arrhenius equation ($D(T) = Z\exp[-E/(RT)]$). The applied reaction model adapts a linear heating and relates it to the normalised selected weight increase from 0 to 1, which is assumed to be proportional to the volume increase. Z has the unit of 1/s in the data evaluation. Diffusion coefficient units of cm^2/s are obtained when correlating x to the volume a (in cm^3) of one particle (with assumed mono-modal distribution of the particles diameter). This means that the diffusion coefficient has to be multiplied by $a^{2/3}$.

The normalized weight increase for experimental TG curves under linear heating is given as follows:

$$x[Z,E,b,T] = b\left(1-\left(1-\sqrt{\frac{Z}{\beta}\int_0^T e^{-E/R\tau}d\tau}\right)^3\right) \tag{2}$$

Z is the pre-exponential factor and E is the activation energy, b is a scaling factor between 0 and 1, β is heating rate. The conversion of the units of the diffusion coefficient occurs in the same way as in the isothermal case.

3.3. Non-isothermal kinetics of the titanium particles

A non-linear least squares fit [15] was applied to evaluate the experimental data in the temperature range between 700 K and 1400 K. The evaluation at a single heating rate gave a very good agreement between the experimental and calculated TG curves, as shown in Fig. 7. This is also valid for simultaneous fitting of

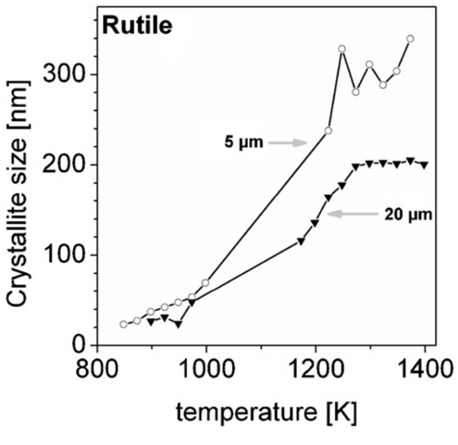

Fig. 6. The change in the crystallite size of rutile from titanium particles at different temperatures.

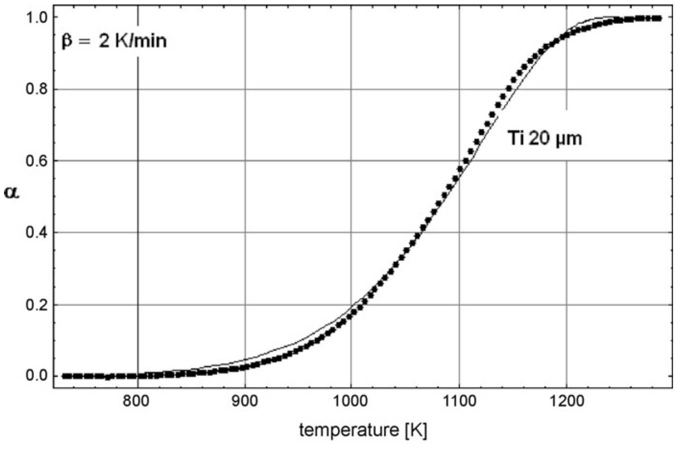

Fig. 7. Selected non-isothermal TG curve and fitted curve of titanium particles with size of 20 μm heated with 2 K/min.

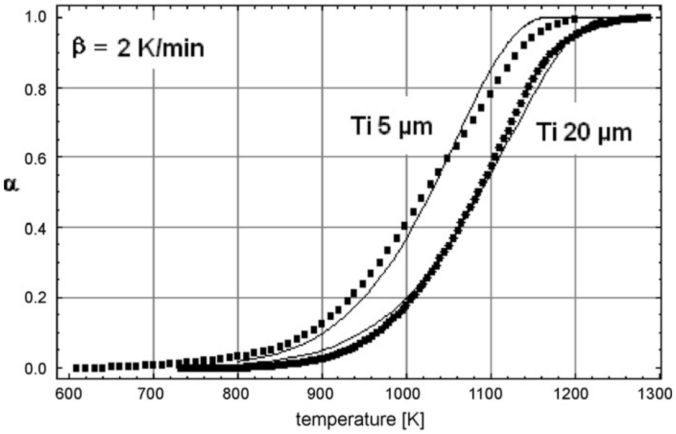

Fig. 8. Non-isothermal TG curves (symbols) and fitted curves (lines) of titanium particles with size of 5 µm and 20 µm heated with 10 K/min.

Table 1
Arrhenius parameters of titanium particles with size of 5 µm and 20 µm obtained from the fitting of non-isothermal measurements of a single heating rate and simultaneous fitting of multiple heating rates (see Fig. 12).

Heating rate [K/min]	Activation energy [kJ/mol]	Pre-exponential factor [cm^2/s]
2	201	10.8E-2
5	173.8	4.8E-3
10	182	1.4E-2
2-, 5-, 10[a]	189	6.1E-3

[a] Simultaneous fitting of all heating rates.

two TG curves recorded during oxidation of both titanium particles (5 and 20 µm) at the same heating rate (Fig. 8). The derived kinetic parameters are listed in Table 1. The values of the activation energy are 173.8 kJ/mol and 201 kJ/mol. The pre-exponential factor amounted to 4.8×10^{-3} cm^2/s and 10.8×10^{-2} cm^2/s. When the fitting procedure was performed for the simultaneous analysis of all three TG curves and both particle sizes, only one data set of kinetic parameters was generated. The fitting was not so perfect compared to that of a single heating rate TG experiment (Fig. 9). One reason might be the particle size distributions which are not mono-modal as assumed by the reaction model. However, the estimated pre-exponential factor (6.1×10^{-3} cm^2/s) and activation energy (189 kJ/mol) were very similar to those determined from the single curve evaluation. Therefore, we suggest that the Jander model for three-dimensional diffusion can be applied for describing the kinetics of oxidation of titanium particles of 5 µm and 20 µm. In other words, the reaction occurs in diffusion-controlled regime and the oxidation mechanism of these particles does not significantly depend on reaction temperature (323–1473 K) because it is the same at all temperatures.

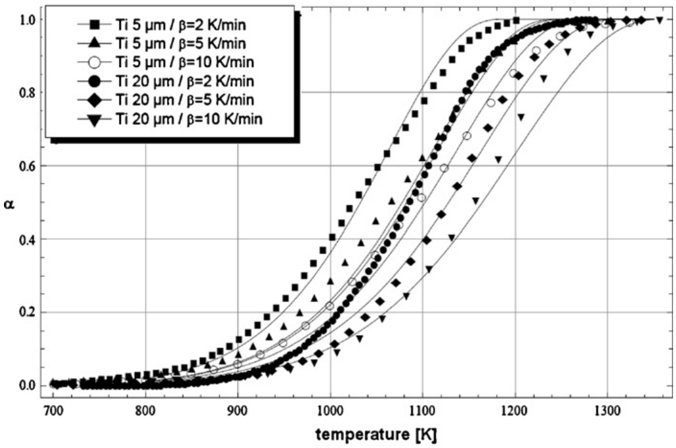

Fig. 9. Non-isothermal TG curves (symbols) and fitted curves (lines) of titanium particles with size of 5 µm and 20 µm heated at different heating rates.

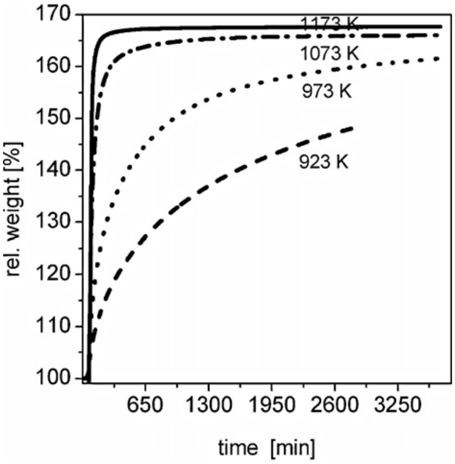

Fig. 10. Isothermal TG curves of titanium particles with a size of 20 µm heated at different temperatures.

3.4. Isothermal kinetics of the titanium particles

Isothermal, thermogravimetric experiments are also used for studying diffusion processes. In the case of larger metal particles, the chemical reaction is much faster than the diffusion process. Isothermal curves consist in the initial time phase of a non-isothermal curve when the sample is heated to the desired temperature. This part has to be analyzed by a non-isothermal approach or omitted for the data evaluation. However, for reaction models other than first order, this initial conversion has to be taken into account as starting value for the reaction. In the applied least squares fit procedure here this is accounted for by an initial time to be used as a fitting parameter as described above.Fig. 10 shows the experimental relative mass change of isothermal thermogravimetric curves. As expected, the higher the reaction temperature, the stronger and the steeper the mass changes. This means that the oxidation of titanium particles is strongly accelerated by temperature. The Jander model for three-dimensional diffusion was also applied to kinetically evaluate these experiments. Fig. 11

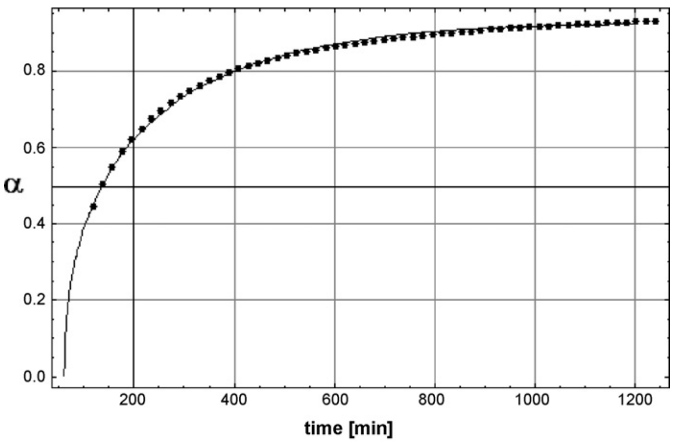

Fig. 11. Isothermal TG curve (symbols) and fitted curve (line) of titanium particles with a size of 20 µm heated 50 h at 923 K.

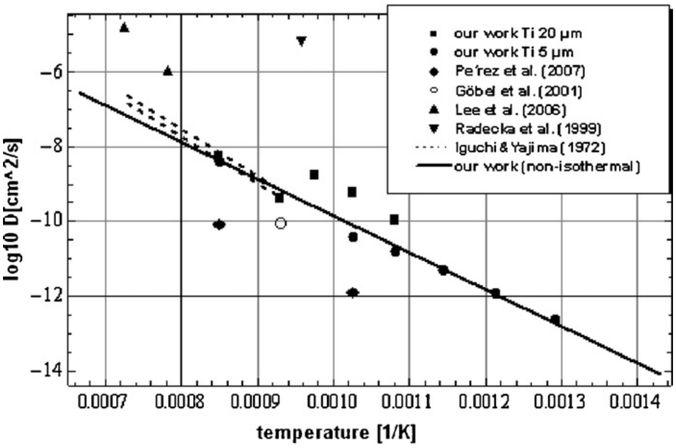

Fig. 12. Comparison of diffusion coefficients from the present work with the literature data (non-isothermal data are marked by solid line).

compares the experimental and the simulated isothermal thermogravimetric curves at 923 K. It can be seen that the model describes correctly the experimental data. This is also valid for other reaction temperatures. The determined diffusion coefficients at different temperatures are summarized in an Arrhenius plot in Fig. 12. From this plot, the activation energy was determined. It did not significantly depend on the particle size and amounted to 180.1 kJ/mol and 182.4 kJ/mol for the particles with size of 5 μm and 20 μm, and the values of the pre-exponential factor are 4.9×10^{-3} cm^2/s and 4.7×10^{-3} cm^2/s, respectively. These values are also very close to that determined from the non-isothermal experiments (Table 1). Such a good agreement between the two different kinetic approaches supports strongly the applicability of the Jander model for describing the kinetics of oxidation of μm-sized titanium particles in air. For isothermal curves the *Shrinking-Core* [30] model was also successfully tested beneath the Jander model finding an agreement with a deviation of maximal 1–2% of both calculated curves.

The literature data [31–35] are broadly dispersed around the data determined from the present isothermal and non-isothermal experiments (Fig. 12) which cover the temperature range between 700 K and 1400 K. The diffusion coefficients of Perez [32] and of Göbel et al. [34] were obtained based on an assumed inward oxygen diffusion and dissolution in the titanium matrix. The diffusion coefficients of Perez [32] run parallel to our experimental data in the temperature range between 973 K and 1173 K covering about two decimal orders of magnitude. The diffusion coefficient of Göbel et al. [34], $1.8 \pm 0.3 \times 10^{-10}$ cm^2/s, is closer to our data at 1027 K. The observed differences may arise due to the stratified structure [32] of the scale and formation of compact layer from a gradual consolidation of the scale during the oxidation of pure titanium [32]. In the case of titanium particles a dense scale forms in the entire temperature interval. Although the diffusion coefficients of Iguchi and Yajima [33] are very close to our data, they are based on the diffusion coefficients of point defects in reduced rutile (TiO_2) in the temperature range between 1073 K and 1373 K. Lee and coworker [35] measured self-diffusion coefficients, which differ considerably from the data here in isothermal conductivity experiments on TiO_2 single-crystal and published data on chemical diffusion coefficients of titanium and oxygen in the temperature range between 1173 K and 1373 K. Data at higher temperature were obtained from investigations of Hoshino et al. and Rosa [36,37], and the extrapolation seems also to fit into the diffusion data range found here. From the diffusion coefficients obtained by the non-linear least squares fit of a three-dimensional model of the particle oxidation in this paper, which assumed instantaneous reaction of oxygen with titanium, it is difficult to distinguish between oxygen or titanium diffusion through the rutile layer. However, the comparison with the diffusion coefficients described in the literature [31–37] might favor inward oxygen diffusion in the particles similar to diffusion in bulky materials or rather bulky oxidized materials, although it cannot be finally decided without doubt. Despite deviations, the rough consistency of diffusion coefficient results with literature data of various origin confirmed the particle oxidation to occur by formation of a dense oxide layer which progresses from the outer surface to the centre, controlled by diffusion.

4. Conclusion

The special focus of this study was the investigation of the oxidation behaviour of micrometer-sized titanium particles using methods of thermal analysis (TG) and temperature-controlled X-ray diffraction and the description of its kinetics. For all samples, the rutile phase was the only identified reaction product as a dense layer conserving more or less the spherical structure.

The Jander model of three-dimensional diffusion successfully described the kinetics of the oxidation of differently sized (5 and 20 μm) titanium particles over a temperature interval of 700–1400 K. This is valid for both isothermal and non-isothermal conditions using inter alia multiple heating rates. The derived kinetic parameters from least squares fitting of both experiment types are within those previously reported in literature for more bulky materials using other experimental procedures. A Shrinking-Core model was tested only for fitting isothermal gravimetric analysis. A good agreement between the experiment and the model was achieved, too.

References

[1] N. Eisenreich, H. Fietzek, M. Juez-Lorenzo, V. Kolarik, A. Koleczko, V. Weiser, Propell. Explos. Pyrot. 29 (2004) 137–145.
[2] A.A. Gromov, Y.I. Strokova, T.A. Khabas, A.G. Melnikov, H.-J. Ritzhaupt-Kleissl, J. Eur. Ceram. Soc. 28 (2008) 1731–1735.
[3] P. Kofstad, K. Haufe, Oxydation von Titan, Werkstoffe und Korrosion, 11, 1956, pp. 642–649.
[4] R.D. Schuiling, B.W. Vink, Geochim. Cosmochim. Acta 31 (1967) 2399–2411.
[5] S. Becker, M. Schütze, A. Rahmel, Oxid. Met. 39 (1993) 93.
[6] M.A. Trunov, M. Schoenitz, X. Zhu, E.L. Dreizin, Combust. Flame 140 (2005) 310–318.
[7] W.R. Lacefield, Adv. Dent. Res. 13 (1999) 21–26.
[8] O. Kubaschewski, Oxidation of Metals and Alloys, second ed., London Butterworths, 1962.
[9] K. Hauffe, K. Seyferth, Reaktionen in und an festen Stoffen, Springer Verlag, Berlin, 1966.
[10] J. Stringer, J. Less-Common Met. 6 (1964) 207–213.
[11] J. Stringer, Acta Metall. 8 (1966) 758–766.
[12] TOPAS, 4 User Manual, Bruker AXS GmbH, Karlsruhe, 2008.
[13] TOPAS, 4 Tutorial, Bruker AXS GmbH, Karlsruhe, 2008.
[14] N. Eisenreich, W. Engel, J. Appl. Cryst. 16 (1983) 259.
[15] N. Eisenreich, J. Therm. Anal. 19 (1980) 289–296.
[16] O. Schulz, N. Eisenreich, H. Fietzek, M. Juez-Lorenzo, E. Kondratenko, Part. Part. Syst. Charact., 2011, doi:10.1002/ppsc.201000020.
[17] V. Kolarik, M. Juez-Lorenzo, W. Engel, N. Eisenreich, Fresenius J. Anal. Chem. 346 (1993) 252–254.
[18] P.G. Wahlbeck, P.W. Gilles, J. Am. Ceram. Soc. 49 (1966) 180–183.
[19] J.L. Murray, Bull. Alloy Phase Diag. 8 (1987) 148–156.
[20] S. Andersson, B. Collen, U. Kuylenstierna, A. Magneli, Acta Chem. Scand. 11 (1957) 1641–1652.
[21] B. Holmberg, Acta Chem. Scand. 16 (1962) 1245–1250.
[22] S. Yamaguchi, M. Koiwa, M. Hirabayashi, J. Phys. Soc. Jpn. 21 (1966) 2096.
[23] L.I. Vergara, M.C.G. Passeggi Jr., Appl. Surf. Sci. 187 (2002) 199–206.
[24] D.-W. Kim, N. Enomoto, Z. Nakagawa, J. Am. Ceram. Soc. 79 (1996) 1095–1099.
[25] K. Sugiyama, Y. Takeuchi, Z. Kristallogr. 194 (1991) 305–313.
[26] A.F. Holleman, I. Wiberg, Lehrbuch der anorganischen Chemie, 33 ed., verbesserte und stark erweiterte Auflage, 1985.
[27] K. Becker, F. Ebert, Z. Phys 31 (1925) 268.
[28] V. Kolarik, M. Juez-Lorenzo, N. Eisenreich, W. Engel, J. Therm. Anal. 38 (1992) 649–655.

[29] W.R. Ott, B.K. Speronello, Thermochim. Acta 31 (1979) 237–242.
[30] O. Levenspiel, Chemical Reaction Engineering, ISBN: 0-471-53016-6, 1972.
[31] M. Radecka, P. Sobas, M. Rekas, Solid State Ionics 119 (1999) 55–60.
[32] P. Perez, Corros. Sci. 49 (2007) 1172–1185.
[33] E. Iguchi, K. Yajima, J. Phys. Soc. Jpn. 32 (1972) 1415–1421.
[34] M. Göbel, V.A.C. Haanappel, M.F. Stroosnijder, Oxid. Met. 55 (2001) 137–151.
[35] D.-K. Lee, H.-I. Yoo, Solid State Ionics 177 (2006) 1–9.
[36] K. Hoshino, N.L. Peterson, C.L. Wiley, Diffusion and points defects in TiO_{2-x}, J. Phys. Chem. Solids 46 (1985) 1397–1411.
[37] C.J. Rosa, Metall. Trans. 1 (1970) 2517–2522.