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Thermal behavior of oxidation of TiN and TiC nanoparticles

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Abstract Titanium nitride and carbide oxidation have been studied using TG and DSC. Titanium nitride shows a oxidation behavior were both techniques detect a unique phenomenon. Titanium carbide shows a variable behavior depending on the heating rate and sample size. Low masses and heating rates provide similar results to titanium nitride. However, using moderate sample sizes and scanning rates a two-stage oxidation is observed. The first step is extremely fast and exothermic, consuming the oxygen trapped inside the nanoparticle bed. The second is controlled by the diffusion of the oxygen and CO_2 through the sample. Thermal safety conclusions are extracted from this observation. Energies of activation calculated using traditional kinetic models are lower than those found in the literature, being an indication of the influence of the specific surface of the material.

Keywords Titanium nitride · Titanium carbide · Nanoparticles · Kinetic analysis · Oxidation · Thermal safety

Introduction

Humans have coexisted with nanoparticles—both generated in natural processes (erosion, volcanic eruptions), or artificial (combustion)—from immemorial time. In general, they were composed by common metal oxides, ceramics and organic products. However, nowadays there is an immense inventory of new products generated in recent years, which had not been freed to the atmosphere until the last 15 or 20 years. As an example, in 1990 carbon nanotubes did not exist in the laboratories or in the industry, neither quantum dots, nor tungsten nanofibres. An increasing interest of studying nanomaterials using Thermal Analysis is easily detected along last years. Two examples are the study of stability of composites containing nanoparticles [1] and oxidation of highly reactive materials such as aluminum nanopowder [2].

In general, it is still too soon for knowing present or future effects of those materials on people and environment, in spite of which the number of applications using them is dramatically increasing. The nano number of products grows to a vertiginous rate. If in November of 2006 about 300 nanoproducts were available in the market [3], that number practically duplicated only 8 months later as cited by the Woodrow Wilson International Center.

There is a lack of knowledge of physical, chemical, and biological properties of the new materials, and weak or inexistent regulations of the market of both nanoproducts and processes involving them. As a consequence, it is urgently required creating the knowledge bases for the development of new technologies that allow a sustainable development of nanotechnology and guarantee clean productive processes, safer and healthier workplaces and innocuous and inoffensive products for the safety and the health of people and environment.

Some projects have faced this problem. At European level, perhaps the most relevant has been NanoSafe I and II (Safe production and use of nanomaterials—chances and risks), which developed a wide spectrum of studies on detection, traceability and characterization techniques

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for engineered nanoparticles, both air and liquid media, advanced technologies to limit both exposition to nanoparticles and leaks to environment, and risk management strategies. Other projects, such as iNTeg-Risk, include risks derived from nanotechnology within their scope.

At Spanish level, this task was carried out by NanoSost, a huge Singular and Strategic Project leaded by our group. Its objectives cover methods for the generation of standard materials, assessing chemical and biological risks, detecting nanoparticles at the workplace, preventing exposure to nanoparticles, and developing new protective materials and risk management systems. One of the singular aspects of NanoSost is including chemical risk, covering thermal stability of nanoparticulated materials, chemical reactivity, and behavior of materials containing nanoparticles.

This article in inside the subproject dedicated to the study of chemical reactivity and shows the potential risks related to the use in oxidation conditions of nanoparticulated titanium nitride (TiN) and titanium carbide (TiC) using non-isothermal techniques Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TG).

Experimental

The samples of nanoparticulated TiN and TiC, both of 30 nm of diameter, are supplied by Flubetech, S. L. Analysis are carried out with a simultaneous TGA/DSC-1, a DSC-30 and a DSC-821 all of them from Mettler Toledo. Standard alumina pans are used for TG, and standard aluminum pans with perforated lids are used for recording DSC curves. All records were performed in air atmosphere of 100 mL/min for TGA/DSC-1, 50 mL/min for DSC-30, and 50 mL/min for DSC-821.

Additionally, samples of titanium carbonitride—$TiC_{0.7}N_{0.3}$—with a particle size below 150 nm and a purity of 97% and provided by Sigma-Aldrich are used for comparison in the set of experiments performed with the DSC-30 with a flow of air of 50 mL/min.

Results and discussion

Titanium nitride (TiN) and titanium carbide (TiC) are extremely hard, up to 9.5 Mhos, are refractories, have melting points around 3,000 °C and are used for coating metallic pieces to improve the superficial properties, specially protecting and hardening. Powder of TiC has black aspect while TiN is golden. For this reason, TiN is also used for decorative purposes due to its color. It gives a non-toxic coating useful in medical applications. Both TiN and TiC can be oxidized at high temperature or using pure oxygen.

In order to assess the thermal risk, the most traditional models are based on the theory of thermal explosion of Semenov [4], which has been applied using Thermal Analysis data [5], and the method of Frank Kamenetskii [6]. Both theories require the total heat of reaction and some kinetic data. The simple model of Semenov only requires the energy of activation.

Titanium nitride

Works on the TiN oxidation are of essentially focused on thin films and plates [7–11], but also to powder at high temperature [12–15], and porous nanocristaline media [16, 17]. Tracking of the process with X-ray photoelectron spectroscopy were carried out by Saha et al. [18]. Some authors try to fit a kinetic model to this oxidation [19–22]. Tomkins [23, 24] studied this process changing both temperature and oxygen concentration. None of these works uses nanoparticulated TiN.

Analysis of oxidation of TiN is done using coupled TG and DSC with a series of sample sizes from 2.3 to 3.2 mg and heating rates from 1 to 20 °C/min. All the results are normalized to sample size to allow comparison. Reaction 1 shows the stoichiometry of the process.

$$TiN + O_2 \rightarrow TiO_2 + 1/2N_2 \qquad (1)$$

DSC results are displayed in Fig. 1. They show a typical behavior, with a shift to higher temperatures when the heating rate is increased. Integrals of all curves are shown in Table 1. A constant value of the integral suggests that only one transformation is detected.

The TG results, Fig. 2, show a consistent increase of mass in a single ramp, confirming that a single step of the transformation is observed.

Taking the change of mass between 300 and 500 °C, it turns out to be a 27.6% (see Table 1). This value is lower than the stoichiometric (29.1%), being in good agreement

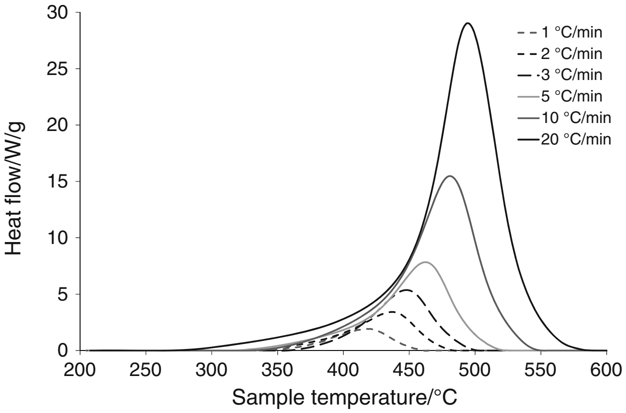

Fig. 1 DSC experiments of TiN going from 1 to 20 °C/min in heating rate

Table 1 Mass evolution between 300 and 500 °C, and integral of the DSC peak

Heating rate/°C/min	Mass variation	Integral/J/g
1	27.1	6,147
2	27.0	6,261
3	27.7	6,123
5	27.6	6,274
10	27.9	6,259
20	28.4	6,042
Average	27.6	6,184
Standard deviation	0.5	95

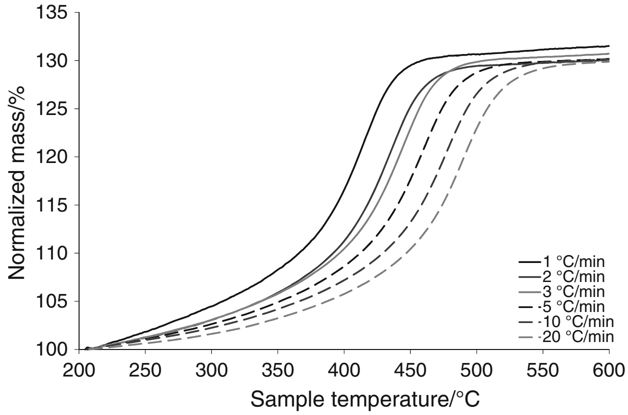

Fig. 2 TG experiments of TiN going from 1 to 20 °C/min in heating rate

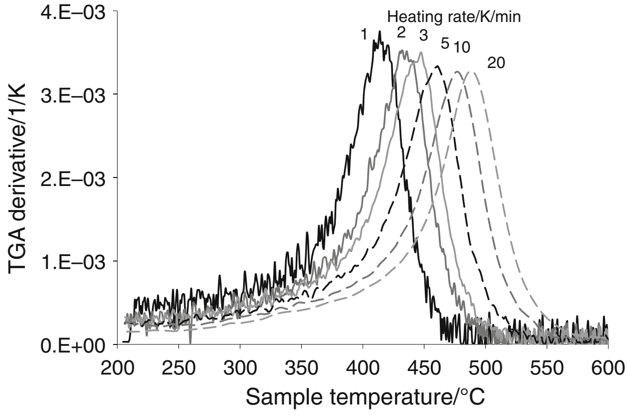

Fig. 3 Derivative of TG curves: DTG

with the analysis provided by Flubetech, S. L. for these samples.

The derivatives of the TG curves, Fig. 3, show a single peak behavior similar to the one shown by the DSC registers, Fig. 1, and it is another indication that this oxidation is due to a single phenomenon and assuming that it is possible to use the kinetic methods described in the "Introduction" section.

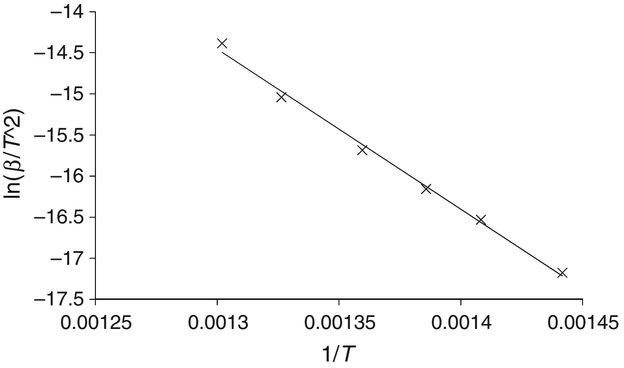

Fig. 4 Kissinger plot for TiN

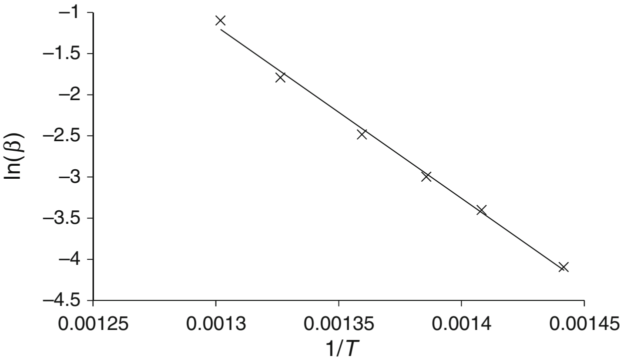

Fig. 5 Ozawa plot for TiN

The Kissinger's method [25] produces an energy of activation of 162 ± 6 kJ/mol, and all the points follow a linear tendency (see Fig. 4). The Ozawa's method [26] also has a satisfactory linear tendency (see Fig. 5) and leads 165 ± 6 kJ/mol of activation energy. The Ozawa method used in the manuscript refers to the determination of the activation energy from the DSC peak temperature using the Doyle approximation for the integral of the Arrhenius, while the Kissinger method that uses the simplified Coats and Redfern approximation. The small difference between the activation energies obtained from both methods are due to the different percentage of error of the two approximation methods used for the integration of the Arrhenius equation.

Finally, the results of the isoconversional method of Kissinger–Akahira–Sunose (KAS) [27–29] is shown in Fig. 6. The results for conversions below 0.15 have not been used to calculate its activation energy because the disturbance due to the subjectivity in the base line selection. The final result of activation energy is shown in Fig. 7 which is consistent with the previous models.

In the case of TiN, other methods non-requiring the assumption of a kinetic model, such as non-parametric

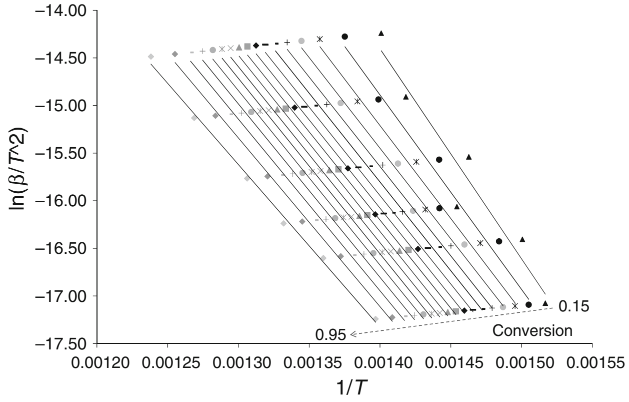

Fig. 6 KAS method applied for TiN samples for conversions from 0.15 to 0.95

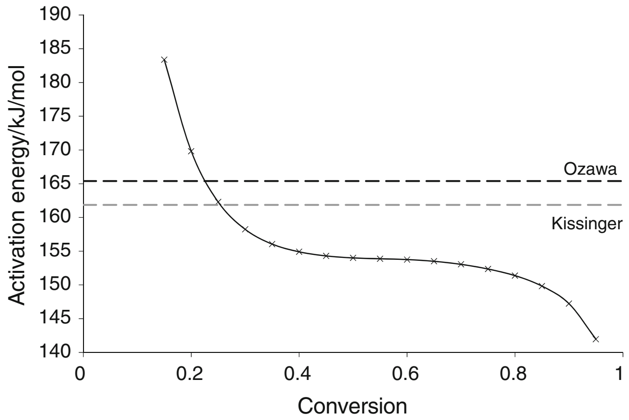

Fig. 7 Activation energy in front of the conversion for the TiN

kinetics (NPK) [30, 31], does not give accurate results due to the crossing of the curves at low conversions.

Usual literature values of the energy of activation goes from 184.1 kJ/mol [32, 33] to 220.1 kJ/mol [14], and the highest one is 237.4 kJ/mol. [34] All of them are higher that the results of this article, confirming the influence of particle size and specific surface. Unfortunately, materials used in literature correspond to thin coatings of TiN on metals or sintered materials and the absolute kinetic comparison is not possible.

The function of conversion is obtained by dividing the DSC curve by the Arrhenius equation. Because the pre-exponential factor is not known, it is avoided in the equation and the value of the maximum for a series of experiments is used as a normalization factor. If the result of the Kissinger's method is used, this normalized function of conversion is shown in Fig. 8. In this case, the curve of 20 K/min presents an irregularity and the values corresponding to lower conversions are considered non-significant.

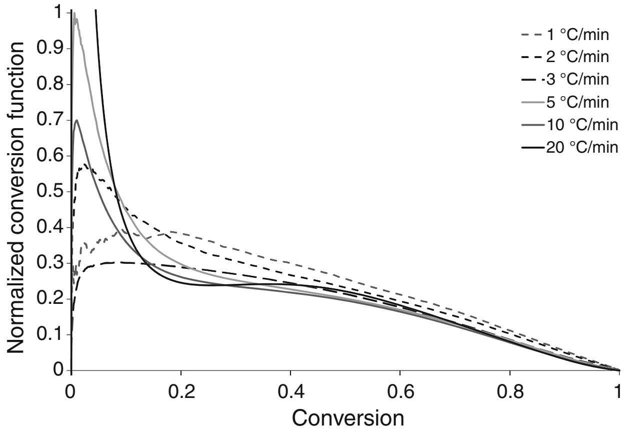

Fig. 8 Conversion function for the TiN experiment calculated using the activation energy of the Kissinger method

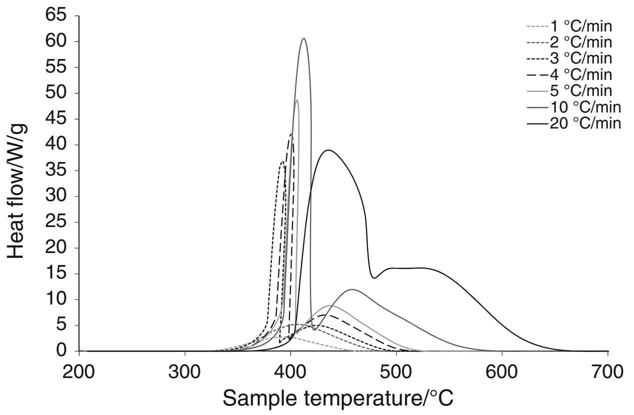

Fig. 9 DSC experiments of TiC going from 1 to 20 °C/min in heating rate

Titanium carbide

Several authors studied the kinetics of the oxidation of TiC both with temperature scanning techniques [35–39] and at different concentrations of oxygen and total pressure [40].

A similar procedure as is applied above for TiN is used to TiC. Samples have been tested using the TGA/DSC-1 with a range of heating rates from 1 to 20 °C/min and sample sizes from 8 to 12 mg. Reaction 2 shows the expected oxidation.

$$TiC + 2O_2 \rightarrow TiO_2 + CO_2 \qquad (2)$$

Figure 9 shows the results of DSC.

At normal scanning, from 5 to 10 K/min, rates two peaks are observed. As expected, decreasing the heating rate overlapping of the two peaks is reduced. However, when the scanning rate is reduced from 3 to 2 °C/min, the first peak collapses, and only one peak is recorded. The total integral of the curves is practically independent from the heating rate, indicating that the observed phenomenon

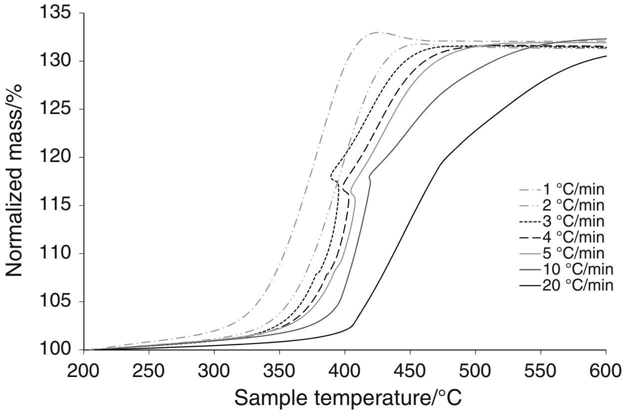

Fig. 10 TG experiments of TiC going from 1 to 20 °C/min in heating rate

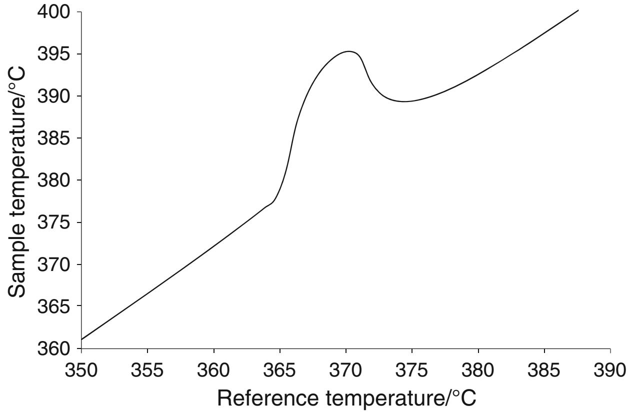

Fig. 11 Difference between the sample temperature (T_s) and the reference temperature (T_r) at a heating rate of 3 °C

is always the same. The first peak contains approximately the 40% of total integral and corresponds to a very fast transformation. The shape of the second peak at 20 °C/min suggests a diffusion controlled process.

Just to give an idea of the relevance of these results, from the thermal safety point of view, the generation of the first peak does not depend from the surrounding atmosphere, but only from the trapped oxygen as it is confirmed by the constant integral of the DSC peak of the phenomenon. As a consequence, a hot spot in a storage of TiC could initiate the reaction, freeing quite instantaneously an energy of about 4,600 J g^{-1}. If a specific heat of 0.85 J K^{-1} g^{-1}—corresponding to TiO_2—is assumed, the adiabatic temperature increase would be over 5,000 °C. The thermal explosion is then unavoidable.

The analysis of the TG curves (Fig. 10) confirms the two steps transformation. The first fast transition involves a 40% of the total mass change. The high amount of energy evolved by the very fast oxidation produces an accumulation of heat (see Fig. 11) in the low conductive alumina pans, creating the perturbations observed in the curves of Fig. 10.

Table 2 shows the mass increments and the integrals of the DSC curves, the experiment performed at 20 °C/min is excluded from the calculations because it has not finished reacting at the end of the experiment. These results are consistent between experiments. Note that the standard deviation is below the 1% of the total. The stoichiometric conversion is calculated to be a 33%. The recorded value of 31.8% is consistent with the analysis provided by Flubetech, S. L.

Table 2 Mass evolution between 200 and 600 °C and integrals of the DSC curves

Heating rate/°C/min	Mass variation	Integral/J/g
1	32.1	11,670
2	31.3	11,500
3	31.4	11,640
4	31.5	11,570
5	31.9	11,630
10	32.4	11,690
(20)	(30.9)	(11,620)
Average	31.8	11,617
Standard deviation	0.4	70

The two-peak phenomenon was also observed by Voitovich et al. [41–43], who proposed two reactions for the oxidation process. Authors assume that the first one corresponds to a fast reaction and that the second one to a slower transformation. However, constancy of integrals as we observed does not support this hypothesis, suggesting two mechanisms for the same reaction. Shimada and Kozeki [44] proposed a four-stage kinetic model for this oxidation, with an alternation of slow and fast stages. The activation energies for the slow stages were 125 and 150 kJ/mol.

Ribeiro et al. described a similar effect for the oxidation of tungsten carbide [45]. They proposed a first stage consisting on the oxidation by the oxygen trapped inside the porous of the sample, and a second one controlled by the diffusion of oxygen and carbon dioxide through the material. Authors also indicate that diffusion could be obstructed by the produced layer of tungsten oxide.

If the initial fast consumption of trapped oxygen were responsible for the first peak, and diffusion controls the second step, using thin layers of sample the two-peak phenomenon should disappear. To check this hypothesis, samples of TiC were prepared using sample sizes below 1 mg in standard aluminum pans with pierced lids, and recorded in a DSC-30 cell. Results of this set of samples are shown in Fig. 12. All of them show no multiple peaks during the oxidation, reinforcing the proposed hypothesis of diffusional control. The absence of multiple peaks

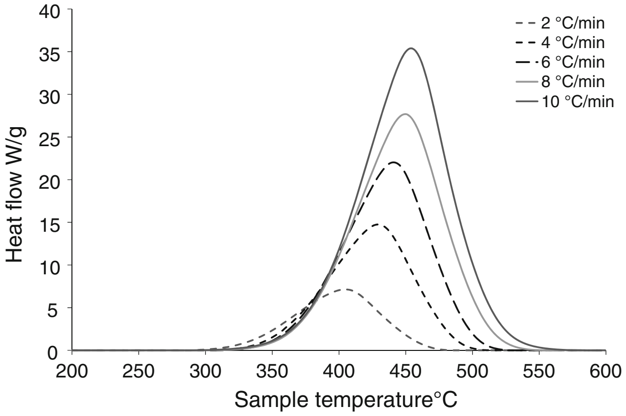

Fig. 12 DSC experiments with samples of TiC around 1 mg

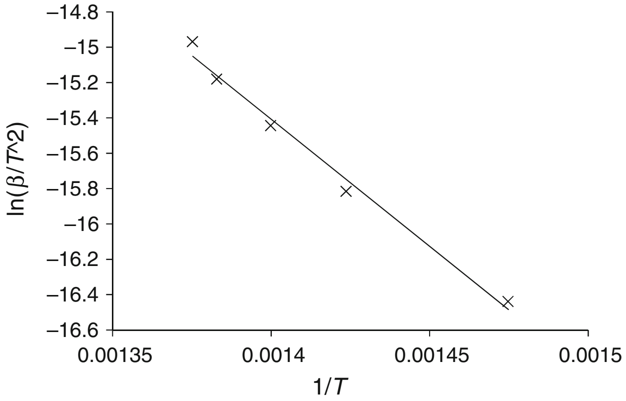

Fig. 13 Kissinger plot for TiN

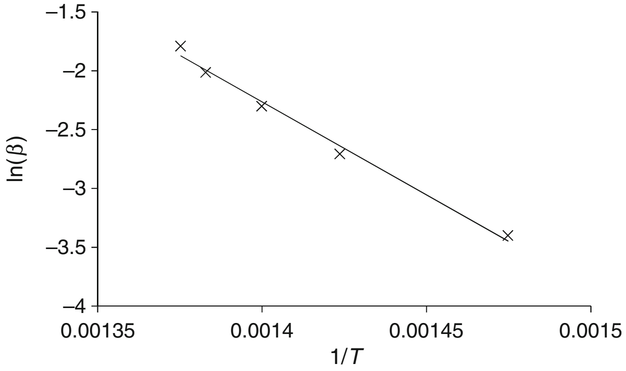

Fig. 14 Ozawa plot for TiN

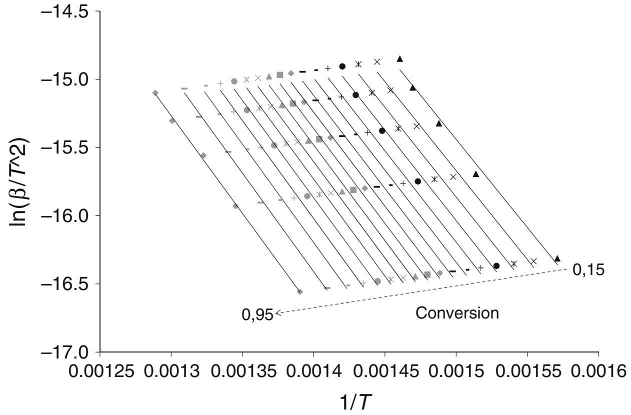

Fig. 15 Isoconversional KAS method applied for TiC samples for conversions from 0.15 to 0.95

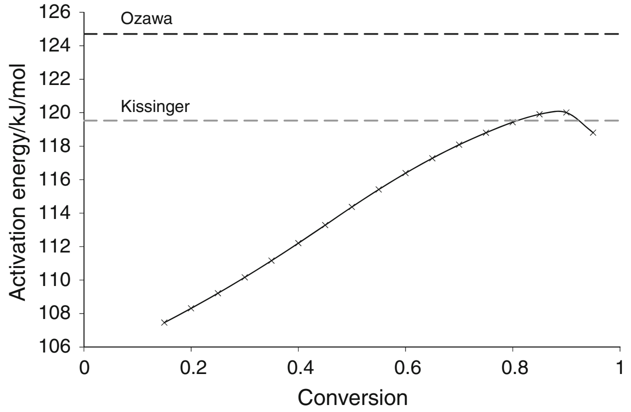

Fig. 16 Evolution of the activation energy with the conversion

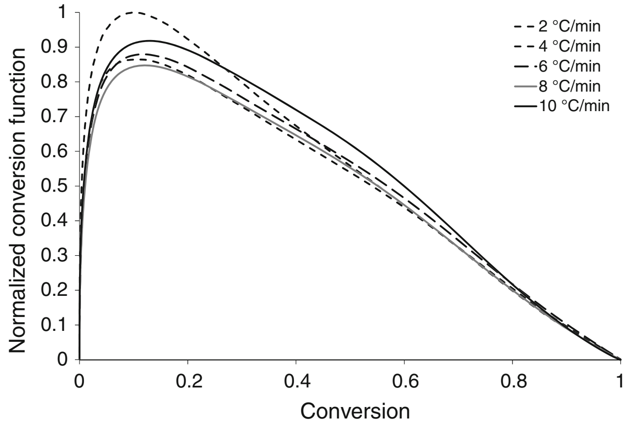

Fig. 17 Conversion function for the TiC experiment calculated using the activation energy of the Kissinger method

allows the application of the common kinetic methods to analyze the results.

The Kissinger's method gives an activation energy of 120 ± 8 kJ/mol with a satisfactory lineal tendency (see Fig. 13). The Ozawa's method has an acceptable linear tendency (see Fig. 14), leading to an energy of activation of 125 ± 8 kJ/mol (see Fig. 15).

With these data, it is possible to apply the KAS method that leads to an average energy of activation of 113.8 kJ/mol, which is consistent with the other two methods (see Fig. 16).

The calculation of the conversion function using the energy of activation produced by the method of Kissinger leads to Fig. 17. It can be noticed that all the experiments follow the same pattern.

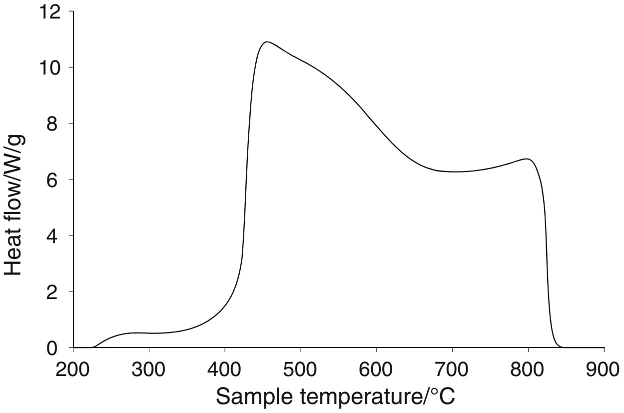

Fig. 18 $TiC_{0.7}N_{0.3}$ at 20 °C/min and a sample size of 28.8 mg

Several records can be used to demonstrate the influence of oxygen diffusion. One of the most clear (see Fig. 18) was obtained using a thick layer of sample of titanium carbonitride—$TiC_{0.7}N_{0.3}$—and low gas flow (50 mL/min). The DSC curve has a flat shape indicating a diffusional controlled reaction. Zhilyaev et al. [46] also studied the oxidation of this type of compounds, reporting some anomalies of the process of oxidation.

Conclusions

The oxidation of nanoparticulate titanium nitride and titanium carbide is used as an example of the difficulties of thermoanalytical studies of nanomaterials.

Nanoparticles of titanium nitride have a high heat of oxidation, but moderate rates of reaction. This behavior allows the use of traditional methods to determine its thermal safety, and its kinetics. The heat of reaction is 6.2 ± 0.1 kJ g^{-1}, and the energy of activation is in the order of 160 kJ mol^{-1}.

Nanoparticulate titanium carbide oxidation is very exothermic and fast. Results of TG and DSC are essentially affected by the amount of trapped gases in the porous medium, and their diffusion along the process. Moderate heating rates and sample sizes give unexpected results. In order to obtain kinetic information, it can be recommended adjusting the sample size to allow fast diffusion of gases. The heat of reaction is 11.6 ± 0.1 kJ g^{-1}, and the energy of activation is in the order of 120 kJ mol^{-1}.

From the point of view of the thermal safety of titanium carbide storage, results from DSC have a high relevance. The initial peak of oxidation detected with moderate sample size could lead to powerful thermal explosions if not suitable storage conditions were used. As an example, displacement of trapped oxygen by an inert gas could be strongly recommended.

A final recommendation for studying gas–nanoparticulate materials with Thermal Analysis techniques is carrying out a scanning of sample sizes and heating rates. Recording the different observations give valuable information both for obtaining kinetic data and safety information.

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