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NON-ISOTHERMAL KINETIC OF OXIDATION OF TUNGSTEN CARBIDE

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Tungsten carbide, WC, has shown dissimilar thermal behavior when it is heated on changeable heating rate and flow of oxidant atmosphere. The oxidation of WC to WO_3 tends to be in a single and slow kinetic step on slow heating rate and/or low flux of air. Kinetic parameters, on non-isothermal condition, could be evaluated to the oxidation of WC to heating rate below 15°C min^{-1} or low flow of air (10 mL min^{-1}). The reaction is governed by nucleation and growth at 5 to 10°C min^{-1} then the tendency is to be autocatalytic, JMA and SB, respectively.

Keywords: *kinetic model, non-isothermal kinetics, oxidation, tungsten carbide*

Introduction

Tungsten carbide has many desirable properties as high hardness, high melting temperature, high fracture toughness, high thermal conductivity and low thermal expansion [1–3]. Thus, WC has many applications in key high technologies from mechanical and chemical industries, and one of them has been as a substitute for noble metals like Pt, Pd and Ir in catalysis [1, 2]. With the same propose, WC has been frequently used as permanent chemistry modifier for eletrothermal atomic absorption spectrometry (ETAAS) supported on the integrated platform of a transversely heated graphite atomizer (THGA) and can (a) increase the useful life of the graphite tube, (b) became easier the atomization via kinetic or catalytic effects, (c) stabilize thermally the analyte and (d) minimize the back absorption [3–6]. The thermal analysis can be an important tool to evaluate and optimize heating programs of the atomizer, elucidate reactions mechanisms in the liquid phases, and others. Oxidation of WC, powders and sintered sample, has been studied in the temperature range 500–1200°C, and products as W, WO_2 and WO_3 has been suggested depending on oxygen pressure [7]. Kinetic parameters regarding oxidation process of Ti–W carbide using Coats–Redferns method has been obtained [8]. Two steps of oxidation were observed independent of the heating rate.

In this study the thermal behavior of the tungsten carbide under in several flows oxidizing atmosphere and heating rate has been verified and the kinetic parameters obtained.

Kinetic considerations

By using TG non-isothermal procedures, the thermal transformation of a material can be mathematically described by the kinetic triplet (E, log$A$ and $f(\alpha)$). Thus, a solid-state Arrhenius-type reaction can be expressed by the general equation [9–12].

$$\frac{d\alpha}{dt}=\frac{A}{\beta}\exp\left(\frac{-E}{RT}\right)f(\alpha) \qquad (1)$$

where the fractional degradation (α) is temperature (T) dependent during an increasing constant heating rate (β). Accordingly, the isoconversional F–W–O method, that is the angular and linear coefficient of a plot of logβ *vs.* $1/T$ at different and constant α, gives the $E(\alpha)$ and A values, respectively [9–12].

In order to calculate the best fit kinetic model that represents WC oxidation, the $y(\alpha)$ and $z(\alpha)$ functions have been defined [13–15]. Koga has utilized the generalized time introduced by Ozawa in order to calculate the $y(\alpha)$ and $z(\alpha)$ functions from non-isothermal and isothermal thermogravimetric data for a solid-state reaction, since the E and log$A$ are known.

$$y(\alpha)=\frac{d\alpha}{d\theta}=Af(\alpha) \qquad (2)$$

$$y(\alpha)\theta=f(\alpha)g(\alpha)=z(\alpha) \qquad (3)$$

The maximum of the normalized $z(\alpha)$ and $y(\alpha)$ functions *vs.* the α plot is indicative of the kinetic model function and kinetic exponents that theoreti-cally better represent the studied process. Thus, it is possible to define the kinetic triplet (E, A and $f(\alpha)$) that better represent the mechanism for WC oxidation.

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Experimental

Samples (10±1 mg) of tungsten carbide (WC) from Aldrich (99% and <10 micron) were submitted to the thermal oxidation in synthetic air atmosphere (80% nitrogen and 20% oxygen). Samples and reference (α-alumina powder) were heated in an open α-alumina pan in a SDT2960 from TA-Instruments from 40 to 1000°C, under air atmosphere (10 to 150 mL min^{-1}) at several different heating rates (5, 10, 15, 17.5 and 20°C min^{-1}).

Results and discussion

In a first experiment, the heating rate was fixed at 20°C min^{-1} and it can be verified through TG-DTG curves, Fig. 1, changes regarding to the WC oxidation from one to two or more steps when the flow of air was increased from 10 to 150 mL min^{-1}. Thus, when the air flow is fixed in 100 mL min^{-1} and the heating rate is increased from 5 to 15°C min^{-1}, it can be verified in TG curves, Fig. 2, only one step to the WC oxidizing to WO_3 and more than two ones when the heating rate is upper than 17.5°C min^{-1}. In this way, the heating rate and flow of air tend to change the mechanism to the oxidation of the WC. Some suggested reaction to the oxidation of WC can be seen in Table 1. Having been fixed the flow of air in 100 mL min^{-1}, the probable reaction to oxidation of WC forming WO_3 at lower heating rate (5°C min^{-1}) is the reaction (4) or (6), when it is achieved the maximum oxidation (18.34%), Tables 1 and 2. It corresponds to the formation of pure WO_3 and in an apparent one step. This behavior is followed to the heating rate 10 and 15°C min^{-1}, but there is a decreasing of the expected residue in 0.33 and 1.74%, respectively. It may be due to the occluded WC in the nucleous of WO_3 originated, or presence of intermediaries like W, W_2C or WO_2. Previous paper [7] has suggested that, in accordance to the thermodynamic calculations, reaction running with oxidation of carbon and formation of W or W_2C as preferential product. In that case, it would have a loss of mass of 3.06 and 6.13% to W_2C and W, respectively. This route could be possible if it is considered a consecutive oxidation of W_2C or W to WO_3.

It has been evaluated the aspect of the TG-DTG curves when it is fixed the heating rate with variable flow of air, Fig. 1, the presence of several intermediates may be considered. Thus, increasing the flow of air, the tendency to present upper one step is evident. Apparently, when the flow of air is 10 mL min^{-1}, only one step is observed, but increasing the one to 50 mL min^{-1} or superior, the arising of steps with fast kinetic is evidenced. Some possible intermediates as W, W_2C, WO_2 or W_xO_y could be now considered before oxidation to WO_3.

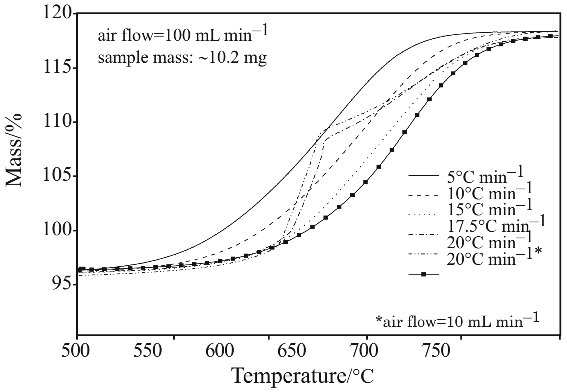

Fig. 2 TG curves of the oxidation of WC at flow of air and different heating rates

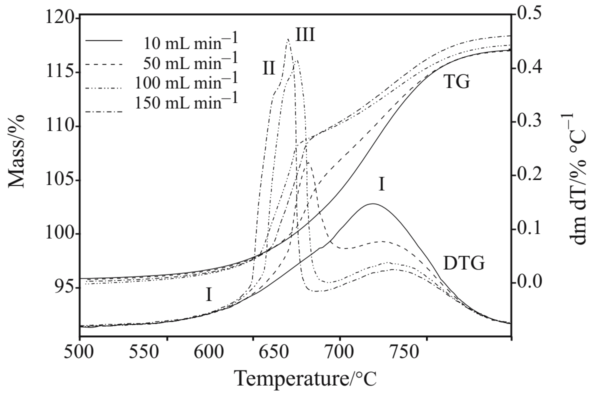

Fig. 1 TG-DTG curves of the oxidation of WC at 20°C min^{-1} and different flow of air

Table 1 Some fundamental WC oxidation reaction [7]

No.	Reactions	Oxidized products/%
1	$WC+O_2\rightarrow WO_2+C$	+16.34
2	$WC+3/2O_2\rightarrow WO_2+CO$	+10.21
3	$WC+3/2O_2\rightarrow WO_3+C$	+24.51
4	$WC+2O_2\rightarrow WO_3+CO$	+18.34
5	$WC+2O_2\rightarrow WO_2+CO_2$	+10.21
6	$WC+5/2O_2\rightarrow WO_3+CO_2$	+18.34

Table 2 Oxidation of the WC depending on heating rate and air flow

Heating rate/ °C min^{-1}	Air flow/ mL min^{-1}	$WC\rightarrow WO_3$/ % expected	Ox. product/ % obtained
5	100	+18.34	+18.34
10	100		+18.28
15	100		+18.02
17.5	100		+17.87
20	10		+17.83
20	50		+17.88
20	100		+18.80
20	150		+19.17

Therefore, the oxidation in one or multiple steps depends on even heating rate though flux of air.

As the thermal behavior to the oxidation of WC, under both low heating rate and flux of air, apparently show similar mechanism, the TG-DTG curves; at heating rates 5, 10, 15°C min^{-1} could be kinetically evaluated.

Kinetic parameters determination

The kinetic parameters, E and log$A$, for the WC thermal oxidation, from heating rate 5 to 15°C min^{-1}, Fig. 2, were calculated applying software (TGAKin V4.0A) developed by Blaine [16] from experimental TG-DTG curves, Fig. 2, using the F–W–O isoconversional method. Figure 3 portrays the E values *vs.* fractional WC thermal oxidation for a specific degree of reaction conversion. The values shows a significant increasing of E from ≈120 to next 220°C min^{-1} indicating a complex mechanism to the oxidation of WC, besides only one step to that reaction observed on TG curves, or the product WO_3 growing on the not reacted WC is handicapping its oxidation.

The next step in the kinetic study, having chosen the E_a=120 kJ mol^{-1} as initial value, is to evaluate the best kinetic model function $f(\alpha)$ to theoretically reproduce the WC thermal oxidation [17–20].

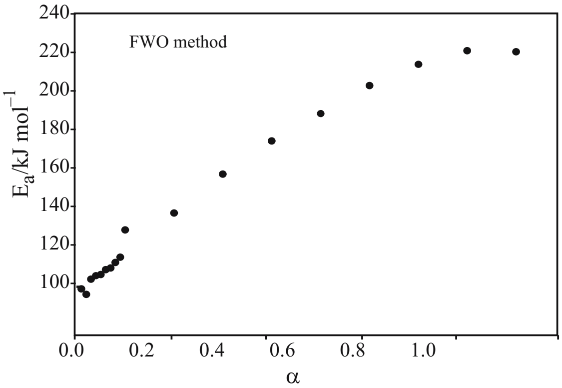

Fig. 3 The values of E_a at various α calculated using the Flynn–Wall–Ozawa method for the thermal oxidation of WC

Thus, the α maximum for the $z(\alpha)$ and $y(\alpha)$ from Eqs. (2) to (3), Fig. 4 and Table 3, were calculated from experimental non-isothermal data to obtain the WC oxidation. According to the Málek´s method, if $0<\alpha_y<\alpha_z$ and the α_z maximum value is near 0.60–0.66, it is possible to suggest the JMA and/or SB model to represent the WC thermal degradation mechanism [13].

In order to evaluate the applicability of the suggested kinetic model function, a simulated DTG curve for the WC thermal oxidation was calculated considering a JMA with n>1 and the SB`s kinetic models, Table 4. The exponent n in the JMA model was determined according to the maximum of the $y(\alpha)$ function, (α^*_y), as represented by the following Eqs [13, 14, 21]:

$$n=\frac{1}{1+\ln(1-\alpha_y)} \tag{4}$$

Otherwise, the kinetic exponents, m and n, of the SB model, Table 3, can be calculated in two steps. First, the p value is determined by the succeeding Eqs [17, 21] considering the obtained α^*_y:

$$p=\frac{\alpha^*_y}{(1-\alpha^*_y)} \tag{5}$$

A plot of ln$y(\alpha)$ *vs.* ln(α^p (1–α)) for the 0.3>α>0.8 interval follows a linear relationship where the slope is the n value. Finally, the m value can be calculated from the correlation $m=pn$.

And thus, the $f(\alpha)$ for the normalized simulated DTG curve considering the JMA or SB kinetic model function can be represented by the equations:

$$\frac{d\alpha}{dT}=\frac{A}{\beta}\exp\left(\frac{-E}{RT}\right)n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n} \tag{6}$$

or

$$\frac{d\alpha}{dT}=\frac{A}{\beta}\exp\left(\frac{-E}{RT}\right)\alpha^{m}(1-\alpha)^{n} \tag{7}$$

An overlay graph is plotted with normalized, simulated and experimental DTG curves of the WC thermal degradation according to the JMA (Eq. (6)) and SB (Eq. (7)) kinetic model, Fig. 5.

Table 3 Kinetic model

Heating rate/ °C min^{-1}	Air flow/ mL min^{-1}	E_a/ kJ mol^{-1}	log$A$/ min^{-1}	Function		SB model		JMA model
				α^*_y	α^*_z	n	m	n
4.96	100	120	5.86	0.17	0.64	0.92	0.19	1.2
10.04	100	120	6.02	0.18	0.61	0.91	0.20	1.3
14.88	100	120	6.28	0.24	0.59	1.08	0.34	–
20.00*	10*	120	7.00	0.42	0.56	1.35	0.97	–

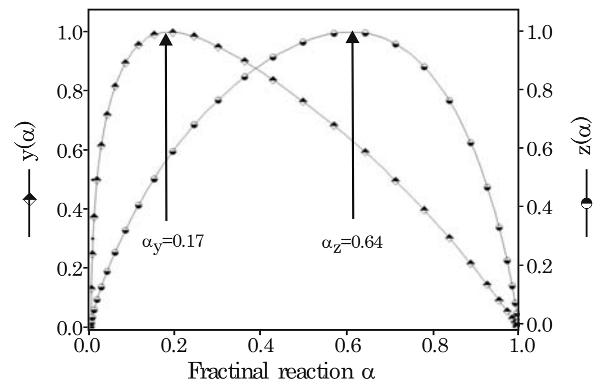

Fig. 4 Normalized $y(\alpha)$ and $z(\alpha)$ functions *vs*. fractional reaction for the thermal oxidation of WC

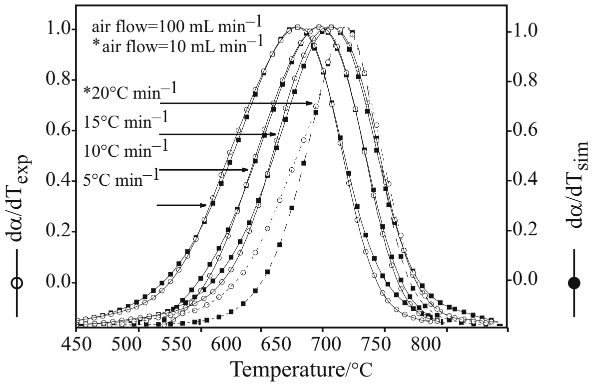

Fig. 5 Normalized experimental and simulated DTG curves using the SB and/or JMA model

Table 4 Description, symbol and main characteristics of the evaluated mathematical kinetic model functions $f(\alpha)$

Mechanism (symbol)	$f(\alpha)$	Main characteristics
Johnson–Mehl–Avrami (JMA)	$n(1-\alpha)[-\ln(1-\alpha)]^{1-\frac{1}{n}}$	Nucleation and growth (n=1.5, 2, 3, 4)
Reaction order (RO)	$(1-\alpha)^n$	*n* order
Šesták and Berggren (SB)	$\alpha^m(1-\alpha)^n$	Autocatalytic

Knowing better model to represent the thermal oxidation of the WC, the suitable log*A* can be calculated according to the defined kinetic exponents using the equation below [22]:

$$A=\frac{\beta E}{RT_p^2Q_p}\exp\left[\frac{E}{RT_p}\right] \tag{8}$$

where T_p is the temperature of the DTG peak and Q_p is determined by the following equation:

$$Q_p=n\alpha_y^m(1-\alpha_y)^{n-1}-m\alpha_y^n(1-\alpha_y)^n \tag{9}$$

The found value, log*A*, Table 3, is in agreement with values considering a first order reaction [9].

The kinetic parameters found to the oxidation of the WC on extreme low heating rate or low flow of air indicates a mechanism governed by nucleation and growth of nuclei at or near crystal surfaces (reaction I). This process becomes more heterogeneous and tends to autocatalytic model when the heating rate is increasing. Thus, a catalytic reaction starts to govern the process and several intermediates may be originated (reactions II and III), Fig. 1. This kind of behavior was also observed to the non-isothermal oxidation of TiC but kinetic parameters were not evaluated [23].

Conclusions

The oxidation of WC is dependent on the heating rate and the flow of air. Thus, experiments in low heating rate or low flow of air, the oxidation tend to be in apparent one step. In that condition, the kinetic parameters could be obtained. At low heating rate the reaction tends to be governed by nucleation and growth of nuclei and after this, the oxidation process is deviated to autocatalytic (SB) model.

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