

OXIDATION OF (Ti,W)C CERAMIC POWDERS

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Abstract

The oxidation of (Ti,W)C ceramics have been studied as a part of the program to investigate of properties of powder materials. Thermogravimetry, derivative thermogravimetry (TG-DTG), and differential thermal analysis DSC have been used in the non-isothermal study of powder oxidation (Ti,W)C in dry air atmosphere. The powder of crystalline carbide cermets with a ratio of W:Ti equals 0.3 was used in this study. The diagrams were recorded on a sample mass 3.42 mg on the Setaram apparatus in temperatures ranging from 25 to 1000°C. Seven different heating rates were used. The analytical techniques SEM, WDX, EDX and XRD were used in the research. The kinetics of the oxidation process was followed by the integral method by applying the Coats–Redfern's approximation. The kinetic models of particular stages of (Ti,W)C oxidation were evaluated from the dynamic mass losses data. The values of apparent activation energy E and the pre-exponential factor A of each stage of the oxidation were calculated.

Keywords: cermets, kinetics of oxidation, oxidation of titanium-tungsten carbide

Introduction

Cermets are made using the powders metallurgy method. Their dominance over conventional sintered carbides consists on a resistance to oxidation in higher temperatures, and wear resistance in high temperatures during machine cutting. Titanium-tungsten carbides are components of the newest generation of cermets [1]. There is a lack of information concerning the mechanism and kinetics of (Ti,W)C oxidation in literature. In dry air atmosphere pure tungsten carbide WC oxidizes to stable oxide WO_3 [2]. That process begins even in ambient temperatures. Its rate is low until the temperature is 473 K and it is getting much higher parallel with the temperature's growth [3]. Titanium carbide in dry atmospheric air oxidizes to oxycarbide and titanium suboxide in temperatures lower than 693 K. Activation energy of that process is contained in range of 125–150 kJ mol⁻¹. Anatase forms over that temperature. The rate of that reaction is limited by oxygen's diffusion through oxycarbides and titanium suboxide layer and it is

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typical that activation energy in range of 42–71 kJ mol⁻¹. As the volume of layer rises the crystallizing anatase cracks and facilitates both oxygen diffusion inside and the forming of Ti₂O₃. Oxidation rate is described by parabolic law in the range of lower temperatures and over 693 K oxidation is described by line law [4–8].

The aim of our work was to obtain of information about the mechanism and kinetics of carbides oxidation (Ti,W)C in dry air atmosphere.

Experimental

The crystalline titanium-tungsten carbide Baldonit Company production used in the present investigation in powder form had the ratio W:Ti equal 0.3. The contents of contaminations did not exceed 0.011 mass%. The grain sizes were measured by the Fisher method and had a mean diameter of about 4.2 μm with the bed porosity equal 0.405. A phase and structural composition was analyzed using an X-ray diffraction method (Philips X'Pert diffractometer). TG-DSC thermoanalytical measurements occurred in a dry air atmosphere which contained 20 vol.% of oxygen, under the pressure equivalent of the atmospheric used Setaram apparatus. These investigations were realized at the following heating rates: 3, 5, 10, 15 and 20 K min⁻¹ in temperatures ranging from 293 and 1273 K for the mass sample equal 3.42 mg. The results of experiments were verified by repeating the experiments under the same conditions and additionally for samples 5, 10 and 15 mg.

We used following analytical techniques: scanning microscoping (microscope JEOL JSM 6100) and X-ray microanalysis (Spectrometer WDS Oxford ISIS 300).

Results and discussion

Experimental results of the thermal analysis of (Ti,W)C are shown in Fig. 1. From the dependencies of heat flows (HF) on temperature one can see that the analysed oxidation process is complex. It is not a one stage process. The particular curves are similar but with the heating rate is increased the maximum of heat flows is higher, special for the second extreme.

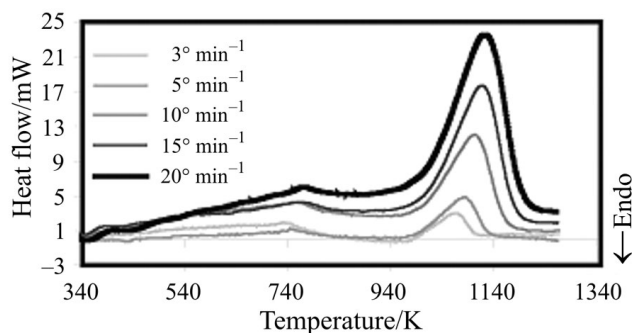


Fig. 1 Heat flow as a function of temperature and a heating rate of the (Ti,W)C powder

The kinetic analysis of the thermal oxidation of carbide was performed via the TG curve. The quantitative evaluation of TG curves are known to be of TG curves is difficult if two or more transformation processes overlap. In some series of experiments an initial, minor decrease of sample mass was observed. An increase in the heating rate of the sample caused a shifting of curves to higher temperatures. The stage of relative increase of sample mass on temperature is illustrated on Fig. 2. It can be seen that the reaction is irreversible and the rate of increase of sample mass is different in the first and the second stage of the oxidation process. Therefore the entire process of increase of mass was divided on two stages. This result was in accordance with the dependencies of heat flows on temperature (Fig. 1). The increases of sample mass in particular stages were a basis of kinetic description of the oxidation process. The conversion degree (α) was calculated from dependence:

$$\alpha = \frac{\Delta m_t}{\Delta m_k} \quad (1)$$

where Δm_t is the increase of sample mass [mg] in time t [min], Δm_k is the total increase of sample mass [mg] in all stages.

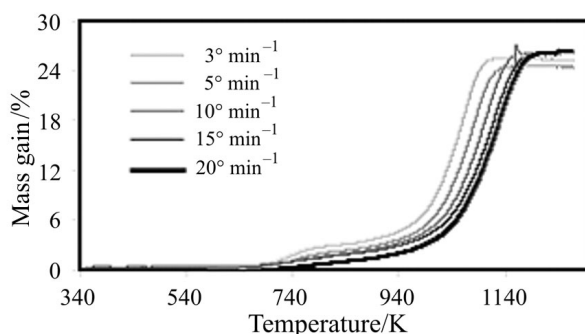


Fig. 2 Mass gain as a function of temperature and a heating rate of the (Ti,W)C powder

The rate of the heterogenous solid state process (r) can be expressed by

$$r = \frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

where $k(T)$ is the reaction rate constant at absolute temperature T [K], $f(\alpha)$ is a conversion function dependent on the mechanism of the reaction.

The dependence of the reaction rate constant on temperature can be described by Arrhenius equation

$$k(T) = A \exp \left\{ -\frac{E}{RT} \right\} \quad (3)$$

where A is the preexponential factor [min^{-1}], E is the apparent activation energy [kJ mol^{-1}] R is the gas constant.

Equation (2), after taking dependence (3) into account, has the form:

$$\frac{d\alpha}{dt} = A \exp\left\{-\frac{E}{RT}\right\} f(\alpha) \quad (4)$$

Investigations under non-isothermal conditions occur at programmed sample temperature changes. Most often the line change of temperature in time is employed

$$\begin{aligned} T &= T_0 + \beta t \\ dT &= \beta dt \end{aligned} \quad (5)$$

where T_0 is the initial sample temperature, β is the heating rate [K min^{-1}].

For these conditions the Eq. (4) has the form

$$\frac{d\alpha}{dT} = A \frac{1}{\beta} \exp\left\{-\frac{E}{RT}\right\} f(\alpha) \quad (6)$$

After an integration of Eq. (6) we receive

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left\{-\frac{E}{RT}\right\} dT \quad (7)$$

One can see that both the derivative $d\alpha/dT$ and the function $g(\alpha)$ are dependent on the temperature. The integral in the right side of Eq. (7) does not have an analytical solution. Equations (6) and (7) represent the dependencies' basis for the description of the experimental results of kinetic investigations at line changes of sample temperature in time.

In describing the results of non-isothermal measurements, the Coats–Redfern's approximation equation is generally the most advantageous.

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (8)$$

In this method of calculation it is assumed that the term $(1-2RT/E)$ is approximately constant and equal $(1-2RT_m/E)$, where T_m is the inflexion point temperature of the $\alpha(T)$ curve. A and E parameters are calculated for the function $f(\alpha)$ which offer the best description of the experimental results. In literature many different models of solid-state reactions are described [9, 10].

On the basis of the analysis of the experimental results, it was decided that a proper oxidation process of samples occurs in two steps. Every stage of the sequential process was treated as an independent reaction.

The first stage of (Ti,W)C oxidation, resulting from the experiments, occurred in a temperature range between about 630–900 K. An investigation of solid products at this stage of the reaction, by X-ray diffraction and X-ray microanalysis methods, revealed the presence of an interstitial solution of oxygen in the (Ti,W)C. No presence of titanium and wolfram oxides was found [11].

The conversion degrees were calculated for particular steps of the process, and the next Arrhenius parameters E and A were calculated, from Eq. (8), for different forms of $g(\alpha)$ functions in heterogenous reactions. The results of calculations, for the best models described in the first stage of the process, are listed in Table 1. A measure of the quality of the model fitting can be the correlation coefficient $-r$. One can see that A and E parameters are different for various kinetic models and various heating rates. On the basis of kinetic parameters which are shown in Table 1, the dependence between Arrhenius parameters for this stage was calculated

$$\ln A = 0.1664E - 2.5812$$

Table 1 Kinetics parameters. Stage I

Heating rate/ K min ⁻¹	Model	E / kJ mol ⁻¹	A / min ⁻¹	r	$\Delta\alpha^*$	T_m / K	ΔT^* / K
$\beta=3$	F1	106.41	2.8096E+06	-0.9941	0.02-0.99	732	631-806
	A2	47.78	9.5510E+01	-0.9922			
	A3	27.90	2.9528E+00	-0.9894			
$\beta=5$	F1	82.95	9.2787E+04	-0.9910	0.02-0.99	742	630-854
	A2	37.88	2.0748E+01	-0.9871			
	A3	21.19	1.3886E+00	-0.9805			
$\beta=10$	F1	104.10	1.9507E+06	-0.980	0.02-0.99	750	681-845
	A2	45.72	1.3522E+02	-0.974			
	A3	26.27	5.4540E+00	-0.964			
$\beta=15$	F1	82.01	8.4539E+04	-0.9695	0.02-0.99	766	686-894
	A2	35.99	9.0230E+01	-0.9570			
	A3	19.66	2.7304E+00	-0.9362			
$\beta=20$	F1	122.78	2.8743E+07	-0.9783	0.02-0.99	768	692-853
	A2	52.75	7.5951E+02	-0.9724			
	A3	30.91	2.1225E+01	-0.9641			

* $\Delta\alpha$, ΔT – range taken to calculations

The dependence of conversion degree on temperature for a random nucleation F1 model is shown in Fig. 3. The dependence of $\ln((\alpha)/T)$ function vs. $1/T$ for the same model is presented in Fig. 4. The proper description is obtained if runs of $k(T)$ functions are the same for the different series of kinetic experiments. In Figs 5–7 the runs of these functions for different models are shown. From these figures one can see that the best model is F1. In Figs 6 and 7 the $k(T)$ curves are different for various heating rates. From these dependencies one can see that, in the test exacting the same runs of the $k(T)$ curves for different heating rates of samples is a useful tool for choosing the proper kinetic model.

The second stage of (Ti,W)C oxidation process was encircled in temperatures ranging between about 860 and 1200 K. The results of oxidation products investigations, after the second step, revealed the presence of two solid phases: TiO₂ (rutile) and WO₃.

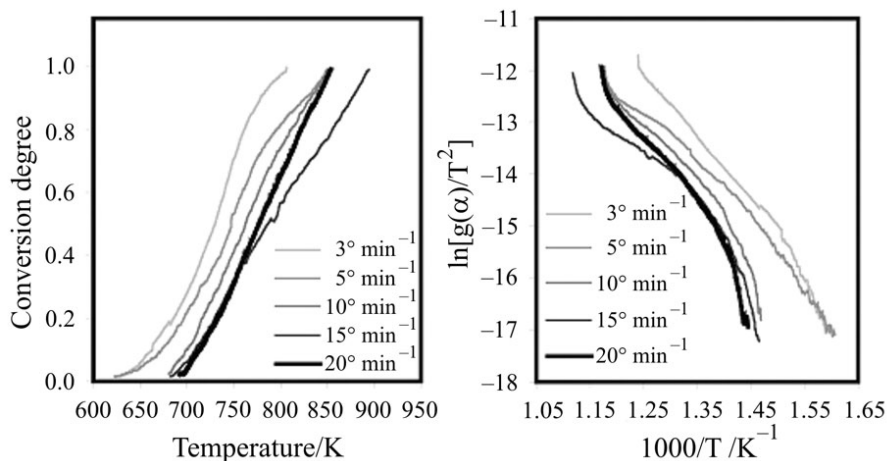


Fig. 3 Dependencies of conversion degree on temperature and $\ln(g(\alpha)/T^2)$ on $1/T$. Stage I. Nucleation model F1

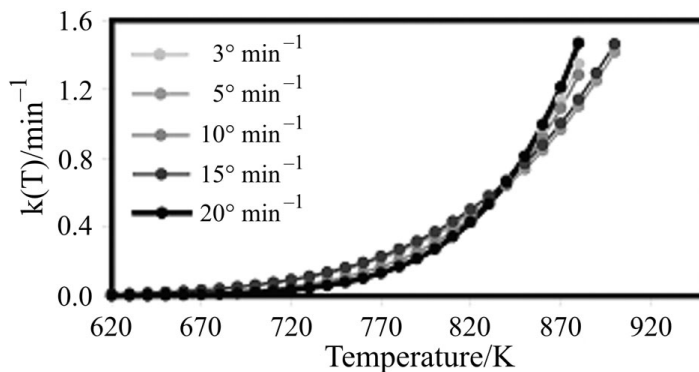


Fig. 4 Dependencies of $k(T)$ on temperature. Stage I. Nucleation model F1

The results of kinetic parameters calculations for this oxidation stage are presented in Table 2. The dependence between kinetic parameters for this stage can be described by the equation

$$\ln A = 0.1086E - 2.379$$

Kinetic analysis of this step has shown that the best models are R1 and R2. The dependencies of $k(T)$ functions on temperature, for these models and different heating rates, are presented in Fig. 7. From these graphs it is seen that the R2 model gives the same runs of $k(T)$ curves for different heating rates.

Table 2 Kinetics parameters. Stage II

Heating rate/ K min ⁻¹	Model	<i>E</i> / kJ mol ⁻¹	<i>A</i> / min ⁻¹	<i>r</i>	$\Delta\alpha^*$	<i>T_m</i> / K	ΔT^* / K
β=3	R1	119.34	2.053E+04	-0.99706	0.02–0.99	1041	865–1109
	R2	163.21	4.3645E+06	-0.99871			
β=5	R1	127.16	6.293E+04	-0.9952	0.02–0.99	1046	896–1144
	R2	147.18	9.0098E+05	-0.9978			
β=10	R1	118.16	3.2757E+04	-0.99796	0.02–0.98	1051	898–1157
	R2	133.26	2.4404E+05	-0.99646			
β=15	R1	120.72	6.6845E+04	-0.99768	0.02–0.99	1054	934–1195
	R2	137.44	3.9257E+05	-0.99721			
β=20	R1	114.313	2.9197E+04	-0.99572	0.02–0.99	1056	911–1203
	R2	133.86	2.6649E+05	-0.99784			

$\Delta\alpha^*$, ΔT^* – range taken to calculations

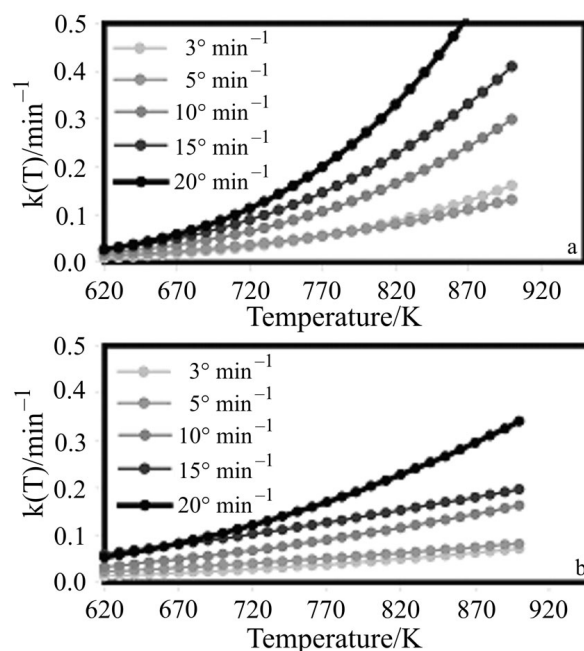


Fig. 5 Dependencies of *k(T)* on temperature. Stage I: a – Nucleation model A2, b – Nucleation model A3

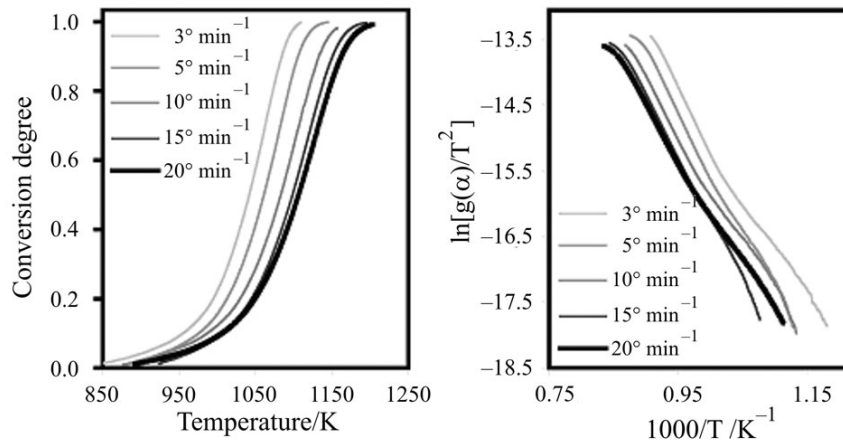


Fig. 6 Dependencies of conversion degree on temperature and $\ln(g(\alpha)/T^2)$ on $1/T$. Stage II. Reaction model R2

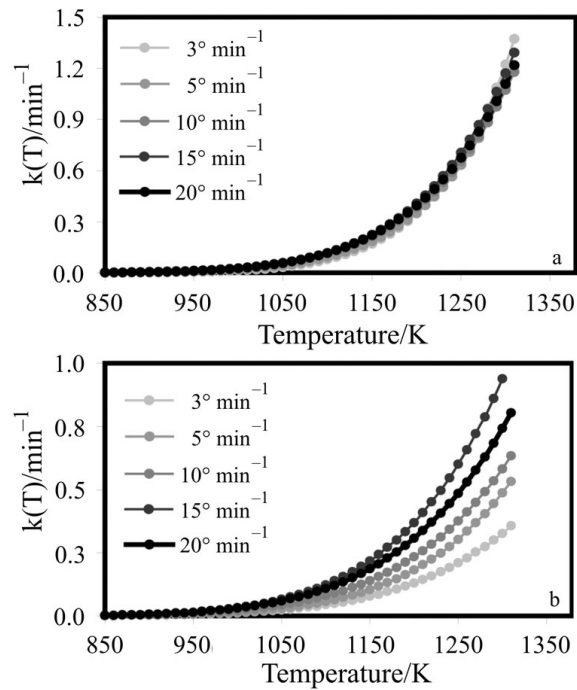


Fig. 7 Dependencies of $k(T)$ on temperature. Stage I: a – Reaction model R2, b – Reaction model R1

Conclusions

The proper oxidation process runs in two stages. The product of the first stage was the interstitial solution of oxygen in the (Ti,W)C. The products of the second stage were TiO₂ and WO₃. The kinetics of the oxidation process can be described the F1 model (Stage I) and the R2 model (Stage II).

The choice kinetic models gives good accuracy. They are useful in a wide range of conversion degrees and temperature changes.

The dependencies between kinetic parameters were:

for I $\ln A = 0.1664 E - 2.5812$

for II $\ln A = 0.1086 E - 2.379$.

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