### **REACTIONS OF METAL CARBIDES IN DIFFERENT ATMOSPHERES**

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### Abstract

In this investigation the oxidation behavior of zirconium carbide and titanium carbide is studied. Non-isothermal measurements using simultaneous thermal analysis (STA) with varying atmospheres, heating rates and particle sizes have been carried out. These allowed the characterization of the oxidation reaction of zirconium- and titanium carbides during combustion. Furthermore, the investigation revealed that measurements carried out under carbon dioxide show a different oxidation behavior than those carried out under air, pure oxygen or atmospheres with different carbon dioxide content. Therefore thermodynamic calculations using a shrinking core model (SC-model) in Mathematica were applied to the TGA-curves, to find the kinetic parameters of the reactions.

### Introduction

Metal particles have been used for years in energetic materials, pyrotechnics and propellants. The natural tendency of metal particles to superficially passivate is normally detrimental, since less passivation leads to more energy release. However, in some specific cases it may lead to a significant increase in the blast and thermal properties of such materials [1]. This optimum increase in performance could only be reached if the relevant parameters for the oxidation kinetics are well known [2-3]. Specific metal carbides like zirconium carbide and titanium carbide showing a low pre oxidation degree [4], what have raised the number of studies aiming to improve their application on this field. For this reason, the study of the oxidation kinetic of these particles is nowadays a topic of great interest.Oxidation kinetic determination is of interest in many applications, especially in the characterization of both bulk metals and thin films and in safety analysis of dust explosions [5, 6].

Carbides have been widely used for metal hardening in fabrication of working tools. For this reason, a number of studies on the oxidation behaviour of this material have been carried out in the past [7-14].Recently, several investigations are found regarding ZrC, to analyze the oxidation mechanism and kinetic behaviour.

The goal of this investigation is the characterization of the oxidation behaviour of zirconiumand titanium carbide powder in different atmospheres, to offer a better understanding of the kinetics of the combustion reaction of zirconium- and titanium carbide.

The complete oxidation in air of zirconium carbide is shown in Eq. (1) and in Eq. (2) for the titanium carbide inambient atmosphere.

$ZrC + 2O_2 \square ZrO_2 + CO_2$	(1)
$TiC + 2 O_2 \Box TiO_2 + CO_2$	(2)

The theoretical mass increase of 19,4 % from zircon carbide to zircon oxide and 33,4 % from titan carbide to titan oxide can be calculated by the molar masses [15].

During non-isothermal analysis, these reactions have been found to take place through at least two steps with the formation of an intermediate  $ZrC_xO_y$  [7-11]. These reactions can be described as follows [7-13]. An initial weight increase followed by a weight reduction.

$$ZrC + 2 O_2 \rightarrow ZrO_2C + O_2 \rightarrow ZrO_2 + CO_2$$
(3)

$$ZrC + O_2 \rightarrow ZrC_xO_y \rightarrow ZrO_2 + CO_2$$
(4)

For particle oxidation often Jander 3D models (J3D-model) are used as for Ti or TiN [16, 17] also used for metal carbide oxidation [9-11] or the shrinking core model (SC-model) [18]. Assuming sufficient separation of the two steps the kinetic evaluation was performed by simply adding a Jander 3D model for the oxidation step and 1st order reaction for the  $CO_2$  evolvement. The agreement of model and experimental data was good only for the higher heating rate (better separation of the reactions).

This paper also aims to improve he model by using a two-step model in combination with a shrinking core model for the initial oxidation of the particles.

### Experimental

Thermo gravimetric analysis has been used for the determination of theoxidation kinetics and its corresponding parameters. STA-Simultaneous thermal analysis (Netzsch STA 449C Jupiter) was used with heating rates of 2, 5 and 10 °C min<sup>-1</sup>in a temperature range of 25 – 1500°C. Air, pure carbon dioxide, pure oxygen and corgon 18 (18 % carbon dioxide, He) atmospheres have been tested. The thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out simultaneously.

Titanium carbide powder by Sigma Aldrich (titanium (IV) carbide <4 micron) and two different sized commercial zirconium carbide powdersby Alfa Aesar(-325 mesh) and H.C. Starck(ZrC Grade B d6.7) were analyzed. Particleswere examined by scanning electron microscopy (SEMSUPRA 55 VP, Carl Zeiss SMT AG, Germany). The diameter of the particles wasdetermined by laser diffraction (Mastersizer 2000, Malvern Instruments Ltd, UK) and the specific surface was calculated by BET Quantachrome Instruments. The heat of combustionwas measured by bomb calorimetry (Kalorimetersystem C2000 basic, IKA-Werke GmbH & CO. KG).

### **Results and Discussion**

The smaller particles of zirconium carbide (ZrC Grade B d6.7) have a diameter of  $d(0.5) = 3.8 \ \mu\text{m}$  and a specific surface of 2.4 m<sup>2</sup>g<sup>-1</sup> (Fig. 1). The larger particles of zirconium carbide (-325 mesh) have a diameter of  $d(0.5) = 7.9 \ \mu\text{m}$  (Fig. 2). The specific surface of the larger zirconium carbide particles is smaller with 1.2 m<sup>2</sup>g<sup>-1</sup>. The titanium carbide powder (titanium (IV) carbide <4 micron) have a diameter of 5.78 \ \mum and a specific surface of 2.613 m<sup>2</sup>g<sup>-1</sup> (Fig. 3).



Figure 1: SEM micrographs of zirconium carbide powder (ZrC Grade B d6.7) by H. C. Starck.



Figure 2: SEM micrographs of zirconium carbide powder (-325 mesh) by Alfa Aesar.



# Figure 3: SEM micrographs of titanium carbide powder (titanium (IV) carbide <4 micron) by Sigma Aldrich.

The following figures show the TGA curves obtained during zircon carbide oxidation in carbon dioxide. It can be observed that for larger particle sizes the curve is shifted to higher temperatures. The shape of the curve is also different. The dependence on the particle size of the TG curve (Fig. 4) reveals that the initial reaction is diffusion controlled. According to the larger specific surface the smaller particles react faster.



Figure 4: TGA-curves of different zirconium carbide particle sizes under carbon dioxide atmosphere.

TGA-curves obtained under various atmospheresare presented in Figure 5. The reactions in air and pure oxygen present nearly the same shape at the beginning but close to the end the reaction in pure oxygen accelerates and ends abruptly at the relative mass of  $ZrO_2$  (119.4 %). The reaction in pure  $CO_2$  is delayed but reaches the relative mass of the hypothetical  $ZrCO_2$  (131 %) before decaying in two steps to the mass of  $ZrO_2$  (119.4 %). This might point to the oxidation of carbonformedduring reaction [11-13]. The reaction in corgon let to a curve shifted to even higher temperatures.





For TiC samples nearly all experimental results are currently available. Already the reaction in air exhibits to be more complex and might not be straightforward to be kinetically evaluated [15]. Therefore only one figure presenting the TG curves obtained in  $CO_2$  and corgon are shown (Fig. 6).





#### Two step reaction models

Themathematical description of reaction kinetics(Eq (4)) is given by Eqs (5) and (6) with heating rate A and conversion rate  $\alpha$ . The reaction mode of Eq. (5) is assumed to be diffusion controlled and can therefore be described analytically by the J3D-model or the SC-model. Solutions of f( $\alpha_1$ ) for J3D and SC model are presented in Eq. (7) and Eq.(8). This equations were used to solve Eq.(6) by assuming a first order decomposition for the follow-on decomposition reaction of the zirconium oxycarbide.

$$\frac{d\alpha_1}{dT} = \frac{k_1(T)}{A} f(\alpha_1)$$
(5)

$$\frac{d\alpha_2}{dT} = \frac{k_1(T)}{A} f(\alpha_1) - k_2(T)\alpha_2$$
(6)

$$f(\alpha_1) = \frac{3(1-\alpha_1)^{\frac{2}{3}}}{2(1-(1-\alpha_1)^{\frac{1}{3}})} \quad \text{for J3D-model}$$
(7)

$$f(\alpha_1) = \frac{(1 - \alpha_1)^{\frac{1}{3}}}{2(1 - (1 - \alpha_1)^{\frac{1}{3}})} \quad \text{for SC-model}$$
(8)

The J3D-model and the SC-model Eq (5) can be solved analytically. Therefore also Eq (6) can be solved to result in an integral that for using the SC-model was already described in literature[8, 9]. The solution is more difficult because it involves a cubic equation  $g(\alpha)$  similar to Ginstling-Brounshtein equation with two complex roots:

$$g(\alpha_1) = \int \frac{d\alpha_1}{f(\alpha_1)} = \frac{1 - 3\alpha_1^{\frac{2}{3}} + 2\alpha_1}{6}$$
(9)

The assumption of these roots is discussed in other papers [17, 18] and the solution is:

$$\alpha_{2} = e^{-S_{2}(T)} \int_{0}^{t} \frac{k_{1}(\tau)e^{-S_{2}(\tau)}(1-\alpha_{SC})^{\frac{1}{3}}}{2(1-(1-\alpha_{SC})^{\frac{1}{3}})} d\tau \text{ with } S(T) = \frac{Z}{A} \int e^{-E_{A}/RT} dT$$
(10)

S(T) was calculated via the asymptotic series [8, 9], the TG-curve by  $\alpha_1 m_a + (1-m_a)\alpha_2$  with  $m_a = (mass_{ZrO2} - mass_{ZrC})/(mass_{ZrCO2} - mass_{ZrC})$ . The models also enable the analysis of DSC curves which correspond to the derivatives of  $\alpha_1$  and  $\alpha_2$ . They are however not presented in this paper.

Figure 7 shows the adjustment by using Shrinking Core model of the TGA-curve of zirconium carbide oxidation under pure carbon dioxide. In relation to this the kinetic parameters are  $Log_{10}Z = 25.23$  and  $E_A = 513.14$  kJ mol<sup>-1</sup> for  $k_1(T)$  and  $Log_{10}Z = 7.55$  and  $E_A = 206.91$ kJ mol<sup>-1</sup> for  $k_2(T)$  with a standard deviation of 6 %.



## Figure 7: Kinetic adjustment of the TGA-curve by using Shrinking Core model; TGA-curve of zirconium carbide under pure carbon dioxide with heating rate of 10 °C min<sup>-1</sup>.

The adjustment by using Shrinking Core model of the TGA-curve of zirconium carbide oxidation under corgon reveals figure 8. The kinetic data for the reaction in corgon are different as already obvious under pure carbon dioxide (Fig. 7). The kinetic parameters of the zirconium carbide oxidation under corgon  $areLog_{10}Z = 3.75$ ,  $E_A = 148.97$ kJ mol<sup>-1</sup> for  $k_1(T)$  and  $Log_{10}Z=5.1$ ,  $E_A=182.08$  kJ mol<sup>-1</sup> for  $k_2(T)$  with a standard deviation of 14 %. The agreement of experimental data and calculated curves is rather bad, especially for the reaction in corgon. Therefore the mechanisms might be different from the SC-model and a first order decomposition.



Figure 8: Kinetic adjustment of the TGA-curve by using Shrinking Core model; TGA-curve of zirconium carbide under corgon with heating rate of 10 °C min<sup>-1</sup>.

### **Conclusion and Outlook**

The oxidation behavior of zirconium carbide and titanium carbide was investigated in different atmospheres by thermo gravimetric analysis. Influence of particle size on oxidation of zirconium carbide was investigated additionally.

Influence of particle size distribution of zirconium carbide showed a slower reaction behavior by larger particles as expected. Gaseous atmospheres used during experiments showed a higher reaction rate for higher concentrations of both oxidizing agents – oxygen and carbon dioxide. Same effect for oxidation in carbon dioxide atmosphere could be observed for titanium carbide particles.

Modeling of oxidation kinetics was done for zirconium carbide by assuming a two-step reaction being diffusion controlled in first step and first order decomposition in second step. Fit quality was not fully satisfying for the assumed reaction model.

Further investigations on possible reaction models should be done to determine the reaction mechanism taking place during oxidation.

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