OXIDATION KINETIC STUDIES OF TIC-PARTICLES USING X-RAY DIFFRACTION

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Abstract

The use of metal particles on the micro and nano scale in blast enhanced explosives has been investigated quite extensively in recent years. There is a growing interest in the characterization of such systems and in analyzing the effects of using new metal particles with varying sizes. In order to use metal particles in explosives with an increased blast rate, it is paramount to know at what speed the metal particles oxidize and what energy is released during the underlying reaction.

The present work deals with the reaction kinetics of slow oxidation of metal particles as a partial aspect. Therefore the oxidation reaction kinetics of titanium carbide (TiC) using X-ray diffraction (XRD) and thermogravimetric measurements in the temperature range of 25-1500 °C in air is determined. The oxidation processes are analyzed by XRD to determine the extent of oxidation and the oxide structure. In combination with non-isothermal measurements using simultaneous thermal analysis (STA) with varying heating rates, the intermediate and end products of the reaction can be identified, and also the course of the reaction can be determined by performing In-situ XRD measurements.

Afterwards the kinetic parameters are determined by thermodynamic calculations applied to the obtained TGA curves assuming a multi-stage Avrami-Eroveef reaction and performing a regression using the software “Mathematica”.

Introduction

In the field of energetic systems, metal particles are frequently added to explosives and propellants in order to achieve a considerable increase in reaction energy with the high heat of formation of the metal oxides produced. If added to explosives, metal particles prolong the effective impulse to the environment over time.

Due to the high heat of formation and the good handling properties aluminum particles are often used to increase performance [1]. A disadvantage of aluminum particles is the protective passivation layer that forms during storage. The reaction with atmospheric oxygen leads to the formation of a thin oxide layer on the particle surface. This leads to a low conversion rate and thus to a lower energy release [2] [3] [4].

A possible alternative to the pure metal particles are the metal carbides which are resistant to oxidation under standard conditions. In literature, some studies can be found describing the oxidation of TiC-particles [5] [6] [7]. Subject of this work are the investigations on TiC-particles regarding the slow oxidation behaviour up to 1500 °C under air by means of X-ray diffraction (XRD) and simultaneous thermogravimetric measurements (STA) and to determine reaction path and the kinetic parameters.

To determine the kinetic parameters, known models are adapted to the measurement curves and the respective accuracy between measurement curve and fit is controlled. An overview on the most important models is given in [8].

Experimental part

Thermodynamic considerations

TiC reacts with oxygen to form titanium dioxide (TiO_2). In general, the complete oxidation reaction proceeds formally according to equation (1) and in case of incomplete oxidation according to equation (2):

(1)

$$\mathbf{TiC + 2\ O_2 \rightarrow TiO_2 + CO_2}$$

(2)

$$2\ \mathrm{TiC} + 3\ \mathrm{O_2} \rightarrow 2\ \mathrm{TiO_2} + 2\ \mathrm{CO}$$

A variety of possible reaction schemes with different enthalpies of reaction are possible during the oxidation of TiC (Table 1).

Table 1: Overview of the calculated mass increases and reaction enthalpies of the theoretically possible partial reactions in the oxidation of TiC at room temperature

reaction equation	theoretical mass increase [%]	enthalpies of reaction [kJ/mol]
$TiC + 2 O_2 \rightarrow TiO_2 + CO_2$	33,4	-1066,14
$TiC + O_2 \rightarrow TiO_2 + C$	33,4	-671,74
$2 TiC + O_2 \rightarrow 2 TiO + 2 C$	6,7	-665,36
$4TiC + 3 O_2 \rightarrow 2 Ti_2O_3 + 4 C$	20,0	-2144,92
$6 TiC + 5 O_2 \rightarrow 2 Ti_3O_5 + 6 C$	24,5	-3550,34
$4 TiO + O_2 \rightarrow 2 Ti_2O_3$	12,5	-814,19
$3 TiO + O_2 \rightarrow Ti_3O_5$	16,7	-777,13
$6 Ti_2O_3 + O_2 \rightarrow 4 Ti_3O_5 + 2C$	3,7	-665,92
$2 Ti_3O_5 + O_2 \rightarrow 6 TiO_2$	7,2	-480,12

The equilibrium constants of the possible reactions are shown in Figure 1. All reactions show an exothermic course with equilibrium on the product side.

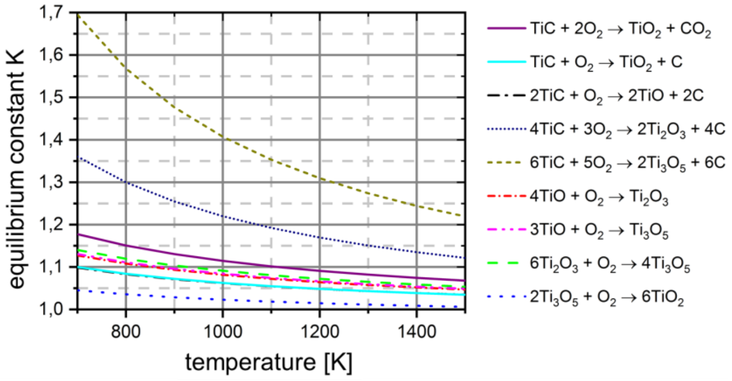


Figure 1: calculated equilibrium constants of the theoretically possible partial reactions in the oxidation of TiC at room temperature

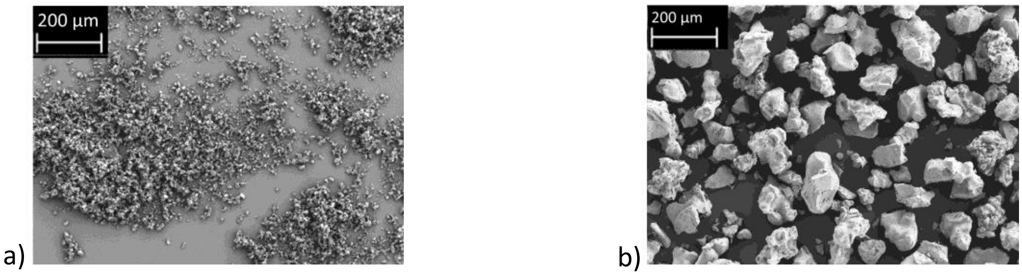
Particle characterization

The oxidation behaviour is investigated on particles with a mean particle size of 5.78 µm and 79,37 µm. The particles are investigated with regard to their particle size distribution (laser diffraction) and specific surface area (BET method). The results are summarized in Table 2.

Table 2: particle size distribution and specific surface of the used TiC-particles

label	Particle size d_{50} (d_{width}) [µm]	Spec. surface area[m²/g]
TiC4	5,78 (11,41)	2,61
TiC150	79,37 (106,90)	1,59

The SEM images (Figure 2) clearly show the size difference of the used particles.



a) b)

Figure 2: SEM images of the used TiC-particles a) TiC4 b) TiC150

XRD Measurement

The XRD measurements of the initial samples (see Figure 3) exclusively show the fcc-structure of TiC and no protective oxide layer. The lattice parameters determined by Rietveld refinement are 0,433 nm.

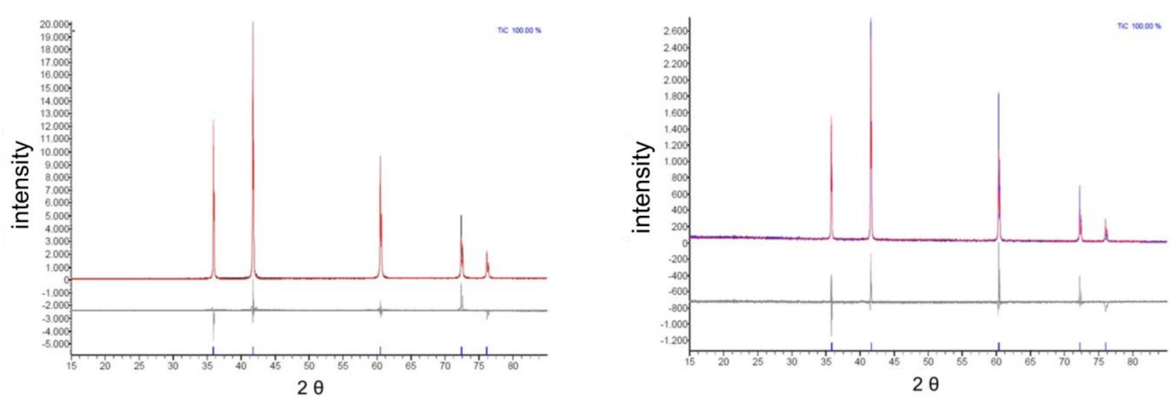


Figure 3: XRD measurements of the initial samples a) TiC4 b) TiC150

Isothermal oxidation experiments were carried out at temperatures of 600 to 1150 °C over a period of up to 1140 hours. XRD measurements on all samples show oxidation from TiC to rutile. By-products or intermediates cannot be detected. The time-dependent curve of the diffraction intensities is then carried out using the Difference-method or Rietveld-refinement. The results of the different evaluation methods show comparable results with regard to existing crystal structures but clear differences in the I-t curve.

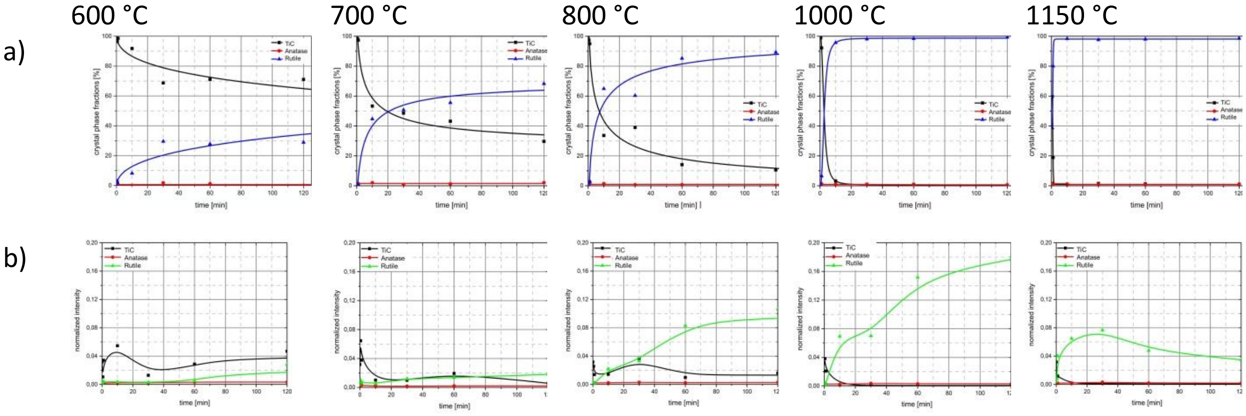


Figure 4: Analysis of XRD-measurements of isothermal experiments a) Rietveld refinement a) Difference method

For a possible modelling of the oxidation behaviour of the TiC particles, the isothermal XRD measurements are kinetically evaluated. The intensity-temperature-curves of TiC and TiO_2 are adapted by means of an irreversible reaction of first order and thus the velocity constant k is determined. The pre-exponential factor A and the activation energy E_A result from the slope and the y-axis section of the graphical application k versus 1/T to log A=4,3 1/s and E_A=117,3 kJ/mol.

The temperature dependent fit curves of TiC and TiO_2 are shown in Figure 5.

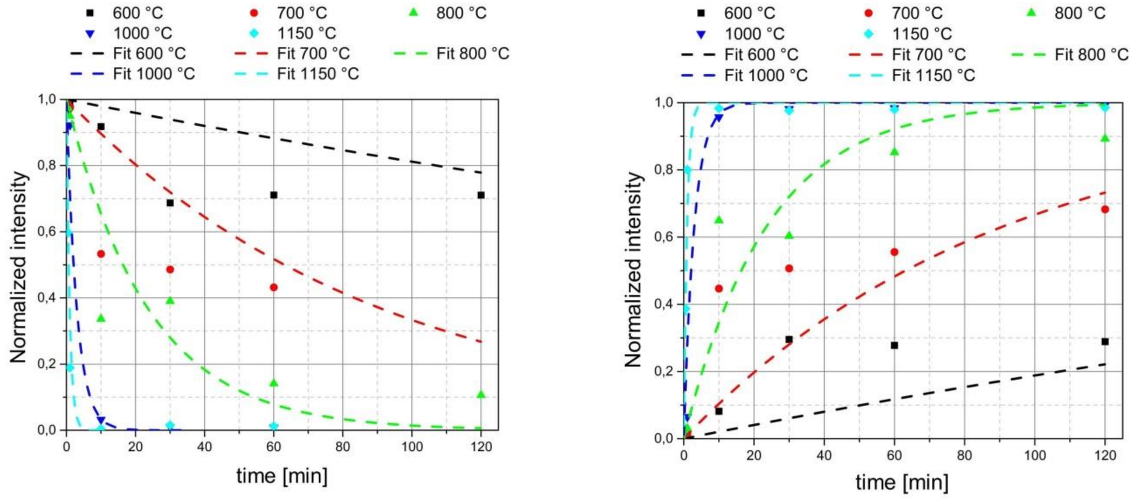


Figure 5: : Temperature-dependent fit over time with the crystal structural components of TiC and rutile determined by the Rietveld refinement

In-situ XRD measurements between room temperature and 1000 °C with a step width of 25 K are performed under air on the smaller TiC4 particles. Figure 6 shows the intensity temperature curves of the three detected crystal structures (TiC, anatase and rutile) resulting from the individual measurements. Figure 7 shows crystal structure fractions determined using the Rietveld refinement.

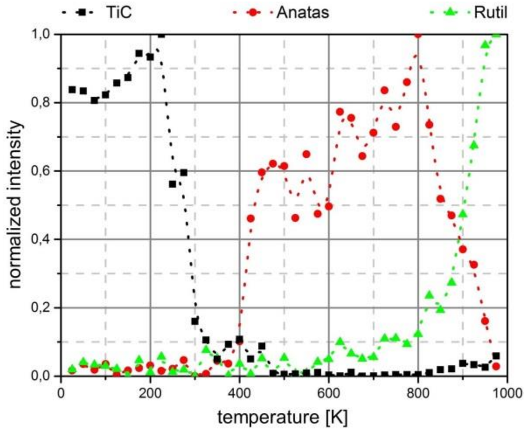


Figure 6: intensity temperature curves of the three detected crystal structures (TiC, anatase and rutile) resulting from the in-Situ XRD-measurements

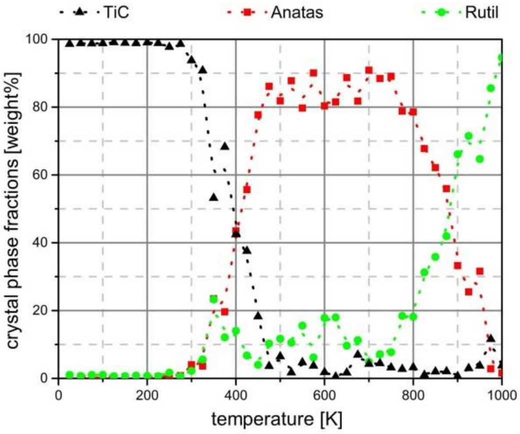


Figure 7: Crystal structure fractions determined using the Rietveld refinement during in-situ XRD measurements of TiC4-particles under air up to 1000 °C

The TiC intensity decreases at temperature above 225 °C and anatase with a tetragonal crystal structure forms above 350 °C. At 580 °C rutile with tetragonal crystal structure is detected. At 800 °C the intensity of the rutile exceeds that of anatase. Brookite and intermediate products are not detectable.

The increase of TiC intensity up to 225 °C is mainly due to the preferred orientation of the crystal structure towards the (200)-peak.

TG Measurement

The theoretical maximum mass increase of the TiC-particles with complete oxidation according to equation (1) is 33.4 mass %.

TG measurements were performed in oxygen with heating rates of 5, 10 and 20 K/min up to 1500°C. The mass increase of both particle sizes relative to initial mass is shown in Figure 8 and Figure 9**.**

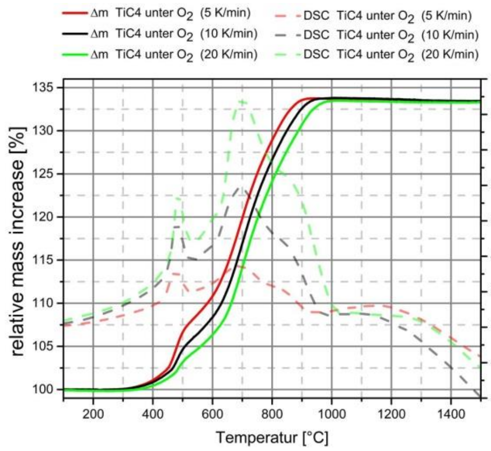


Figure 8: TGA-measurement of TiC4-particles under oxygen up to 1500 °C

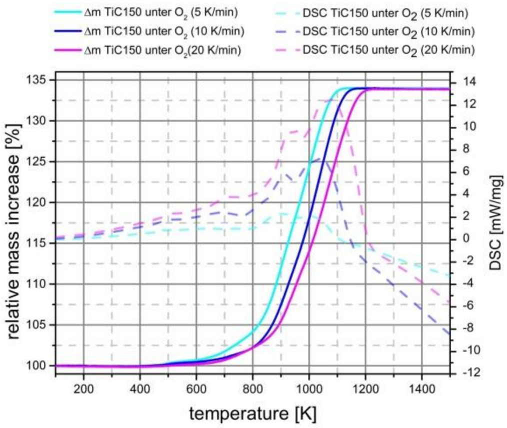


Figure 9: TGA-measurement of TiC150-particles under oxygen up to 1500 °C

According to the DSC-signal the reaction steps are determined and are summarized in Table 3.

Table 3: Overview of the reaction steps determined with the aid of the first derivative at heating rate 5 K/min

		Reaction temperature
TiC4	Step 1	482 °C
	Step 2	708 °C
	Step 3	837 °C
TiC150	Step 1	492°C
	Step 2	740 °C
	Step 3	916 °C
	Step 4	1036 °C

In Figure 8 it can be seen, that the mass increases of the TiC4 particles shifts parallel to higher temperatures with higher heating rates. In the case of the TiC150 particles (Figure 9), the first two stages are independent of the heating rate, stages three and four show the same displacement as the small particles.

As the data for the four reaction steps can be separated, normalization and fit are done for every step independently before the fit is done for the complete reaction.

The fit was performed for all heating rates in four sequentially steps with the three parameters activation energy E_A, frequency factor A and reaction order n. The best match between the measurement curve and the theoretical plots was obtained with a multi-stage Avrami-Erofeev reaction (Figure 10 and Figure 11). The correlations were 0.9998 (TiC4) and 0.9977 (TiC150). The determined fit parameters are summarized in Table 4.

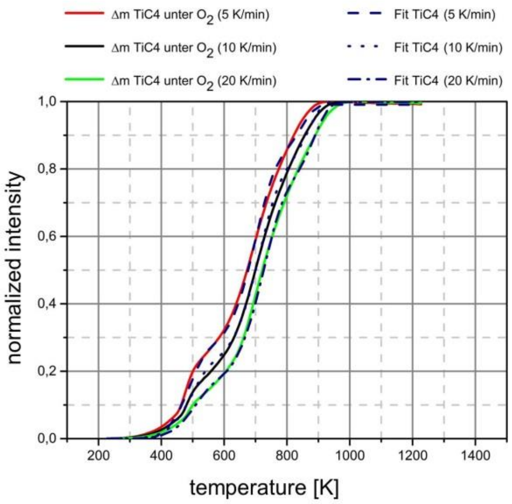


Figure 10: non-isothermal TGA measurements on the TiC4 particles under oxygen and the determined fit curves

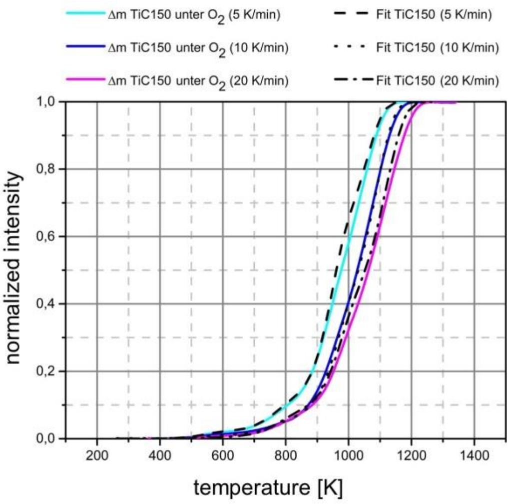


Figure 11: non-isothermal TGA measurements on the TiC150 particles under oxygen and the determined fit curves

Table 4: determined fit parameters for the oxidation of the TiC4- and TiC150-particles under oxygen (Avrami-Erofeev model)

	Log A [1/s]	**E_A [kJ/mol]**	**reaction order n**
TiC4			
step 1	8,94	149,94	0,59
step 2	2,61	79,83	0,70
step 3	8,98	227,30	0.38
TiC150			
step 1	3,95	148,67	0,61
step 2	22,30	228,92	0,06
step 3	12,42	327,86	0,66
step 4	7,13	244,16	0,90

Results and Discussion

The oxidation reaction of TiC-particles was investigated by TG- und XRD-measurements. It was shown that the oxidation of TiC is very complex and takes place in several steps.

In the case of the XRD-measurement no intermediate products other than anatase and rutile can the detected. Therefore the isothermal oxidation from TiC to rutile could be fitted by a first order reaction. Different heatings rates were used in TG measurements. For both particles sizes, four reactions steps were identified and could be fitted with a multi-step Avrami-Erofeev model function with the help of one kinetic triplet.

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