Thermogravimetric Analysis of Molybdenum Oxide (MoO_3) Decomposition

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Abstract

Molybdenum and molybdenum oxide are used as components in pyrotechnic mixtures as fuel or oxidizer, especially in fast reacting thermites. Samples from molybdenum were investigated by thermal analysis and evaluated for the derivation of kinetic parameters for the oxidation and reduction in the case of molybdenum oxide.

Introduction

The oxidation of metals has obtained widespread because of the generation of high amounts of energy. Therefore, energetic materials, including high explosives, solid rocket propellants and pyrotechnics use metal particles in addition to other compounds. These particles provide a strong and fast heating on combustion or detonation especially if nano-particles are involved to react effectively [1].

Thermites include a metal mainly aluminium and an oxide. Often used oxides are Fe_2O_3 and CuO. In addition, MoO_3 is intensively investigated for application in thermites [2-5]. The mainly used oxides split off partially its oxygen at elevated temperatures with the highest one of Fe_2O_3, then lower CuO and MoO_3. One approach to understand the mechanism thermite reactions bases on this oxygen split-off which explains the high thermal stability [6].

The thermal behaviour of molybdenum is not in detail analysed in the literature, therefore this paper wants to present the results of ongoing investigations.

Samples

The sample of molybdenum powder (CAS 7439-98-7) is distributed by Sigma-Aldrich (3050 Spruce Street, Saint Louis, MO 63103, www.sigmaaldrich.com). The purity of the powder is specified with 99.99 % based on trace metal analysis. The average particle size is given as $\leq 150 \mu m$.

Figure 1 shows SEM images of characteristic particles of the molybdenum particles (Zeiss-SEM Supra 55 VP, Carl Zeiss SMT AG, Germany). These images contradict the specifications of the particle supplier. It shows that the particles agglomerate and the distribution is composed of bigger crystalline particles and many smaller ones. This fact might make the application of oxidation and decomposition models difficult.

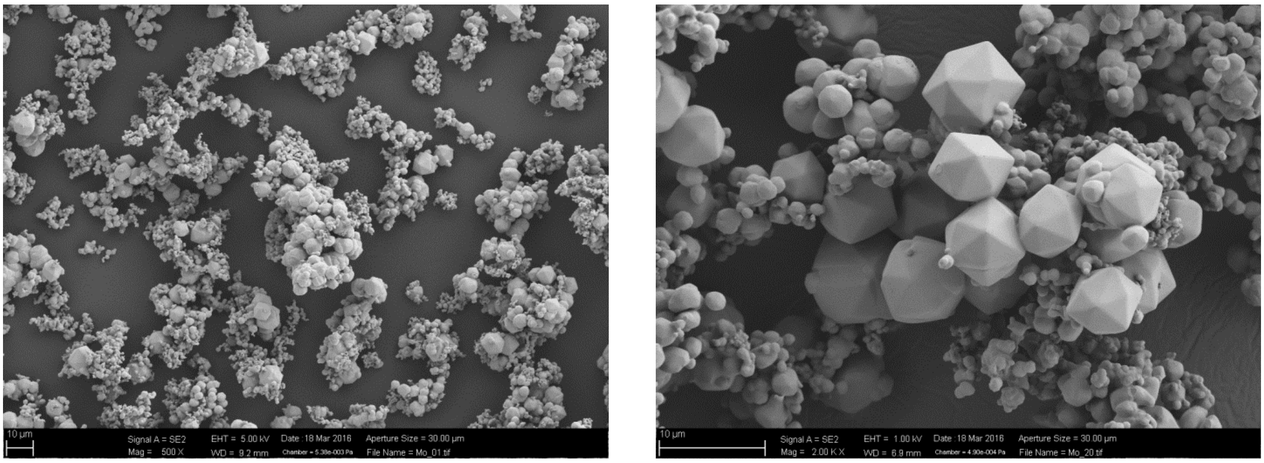

Figure 1: SEM images of the sample.

The thermodynamic data of molybdenum and the molybdenum oxides are given in table 1.

Formula	Melting point [°C]	Boiling point [°C]	Density [g/cm^3]	Heat of formation [kJ/mol]	Heat capacity [J/mol/K]	Decomposition [°C]
Mo	2623(1)	4639(1)	10.2(1)	0(2)	29.73(2)	-
MoO_2	1100 (decomposition) (1)		6.47(1)	-587.9(2)	61.87(2)	1100
MoO_3	801(1)	1155(1)	4.7(1)	-745(2)	92.42(2)	780-1200

Table 1: Thermodynamic data of molybdenum and the molybdenum oxides.

(1) CRC Handbook of Chemistry and Physics, 90th Edition Lide 2010
https://www.webelements.com/compounds/molybdenum/molybdenum_dioxide.html

(2) M. Biennewies, E. Milke, Thermochemical Data of Elements and Compounds, 2nd ed., Wiley-VCH, Weinheim 1999

Experimental

For determination of the chemical reaction kinetic parameters, a thermogravimetric (TGA) and a differential scanning calorimetric (DSC) measurement of the particles were performed. The particles were used to study the oxidation process of molybdenum and the reduction process of the resulting molybdenum oxide. The analysis was carried out with heating rates β of 2, 5 and 10 K/min in synthetic air atmosphere using a Netzsch STA 449C Jupiter thermo-microbalance (Netzsch-Gerätebau GmbH, Selb, Germany). The sample size was nearly constant 11 mg for all heating rates.

Results

DSC measurements

The DSC-curve of the full temperature interval is shown in Figure 2 with its strong initial oxidation phase the sublimation and decomposition of MoO_3 at 1080 K. The melting point is found at 1068 K. The heats of reactions were determined by peak integration to 2.23±0.03 J/g for the oxidation process and -0.464 J/g for reduction of molybdenum oxide.

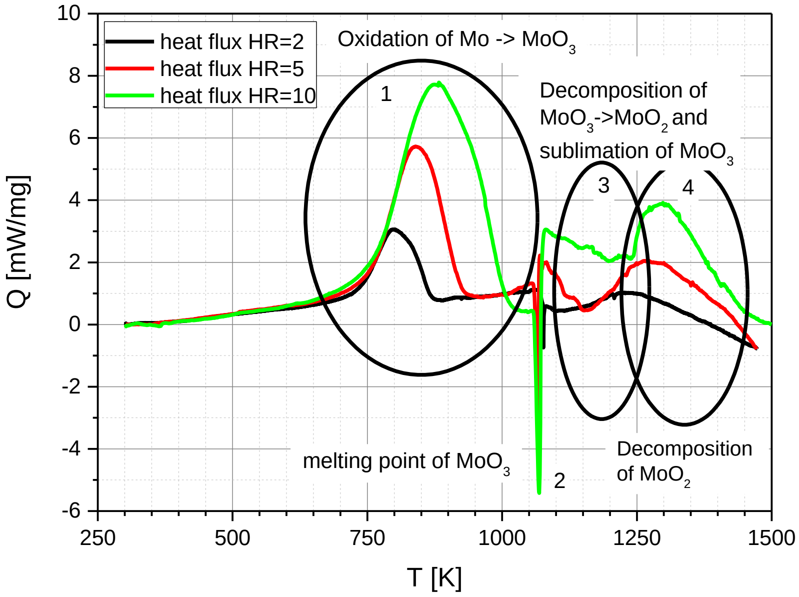

Figure 2: Differential scanning calorimetric measurements of molybdenum in synthetic air atmosphere for heating rates of 2, 5 and 10 K/min.

TGA measurements

The TG-measurements are given in Figure 3.

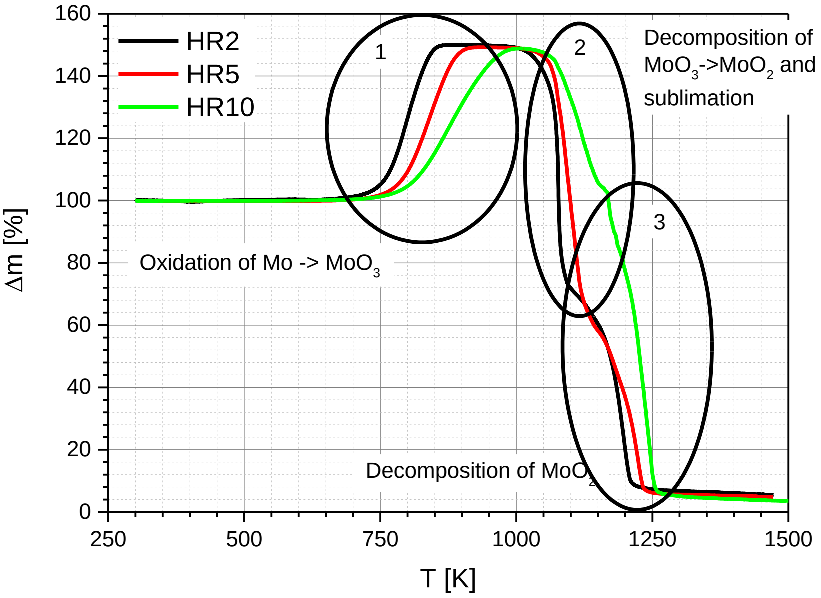

Figure 3: Thermogravimetric measurements of molybdenum in synthetic air atmosphere for heating rates of 2, 5 and 10 K/min.

Modelling

For reaction kinetics of the oxidation process a one-step model was assumed with trial of some different mechanisms.

$$A \rightarrow B$$

1st order reaction, an Avrami-Erofeev (AE) model and a shrinking core model were applied. To determine the Arrhenius-Parameters, pre-exponential factor Z and activation energy E, a one-step reaction was fitted to the experimental thermogravimetric data of the oxidation of the molybdenum particles. A direct least-squares fit was applied (see [7]) to the sigmoid curve normalized to 1 and 0, using the inverse function α(T) in the Equation with the Exponential Integral E_i:

$$S(E,T) = \frac{E}{R} E_i\left(-\frac{E}{RT}\right) + T e^{-\frac{E}{RT}}$$

$$\frac{d\alpha(T)}{dT} = -\frac{k(T)}{\beta}\alpha(T);\ \ \alpha(T) = e^{-\frac{Z}{\beta}S(E,T)} \text{ for 1st order} \tag{1}$$

$$\alpha(T) = e^{-\frac{Z}{\beta}S(E,T)^n} \quad \text{for Avrami-Erofeev} \tag{2}$$

The shrinking core model and its representation of thermal analysis curves is described in [8], due to its character of 3^{rd} order polynomial, it will be represented by α_{sc}[T].

Three thermogravimetric measurements were performed and two of these curves of the mass gain were analysed by a non-linear least-squares fit simultaneously. The curves with a heating rate of 10 K/min do not fit into the simultaneous fits with sufficient agreement. The results are shown in Figure 4 and Figure 5 as well as in Table 2 and discussed below.

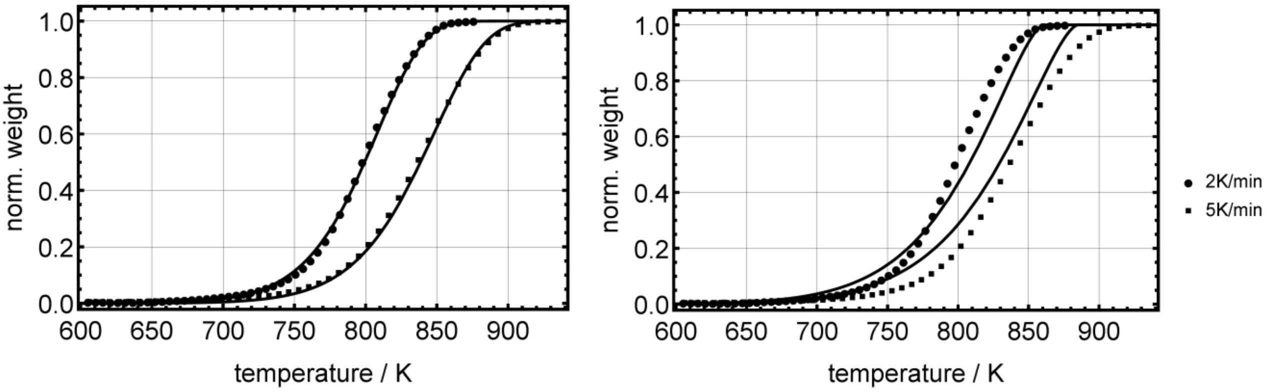

Figure 4: Thermogravimetric measurements of molybdenum in synthetic air atmosphere for heating rates of 2 and 5 and its least squares fit with AE-model (left) and SC-model (right).

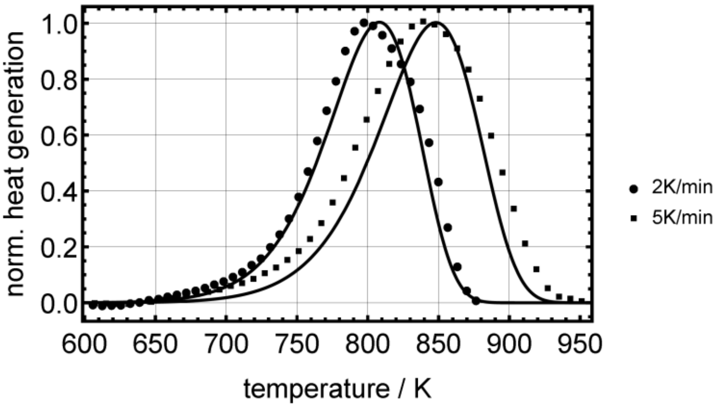

Figure 5: DSC-measurements of molybdenum in synthetic air atmosphere for heating rates of 2 and 5 and its least squares fit with AE-model).

The decomposition/sublimation step was analysed with a two-step 1^{st} order reactions and two steps of AE-reactions see below (3) and (4):

$$A \rightarrow B \rightarrow C$$

The consecutive reactions are sufficiently separated that an additive combination of the two subsequent reactions can be used. In this case the TG curve is constructed by:

$$y(T) = a\,\alpha_1(T) + (1-a)\alpha_2(T); \qquad a \leq 1 \tag{3}$$

With α_1 and α_2 from equation (1), respectively (2).

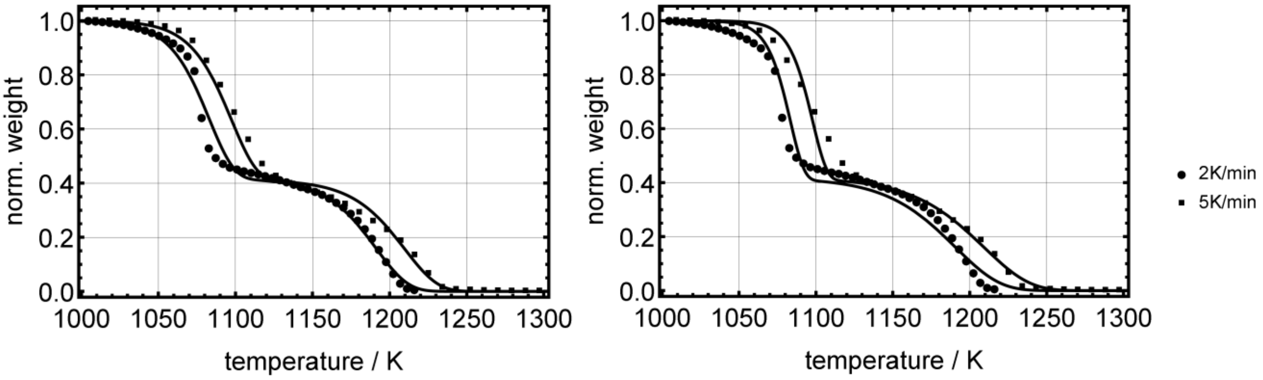

Figure 6: Thermogravimetric measurements of molybdenum in synthetic air atmosphere for heating rates of 2 and 5 and its least squares fit with a combined 1st order model (left) and a combined AE-model (right).

The decomposition of molybdenum oxide is described by

$$2MoO_3 \rightarrow Mo_2O_5 + O \tag{4}$$

$$Mo_2O_5 \rightarrow 2MoO_2 + O \tag{5}$$

In parallel sublimation of MoO_3 occurs at temperatures higher than 800 °C.

The results of the least squares fit procedures are listed in Table 2. The best fits are indicated by the lower standard deviations which suggest the AE-mechanisms for all reaction, the oxidation as well as for the combined decompositions and sublimations.

reaction	**$\log_{10} Z_1$**	**E_1 [kJ/mol]**	**$\log_{10} Z_2$**	**E_2 [kJ/mol]**	**n_1**	**n_2**	**Standard deviation**
1st order: Mo-oxidation	6.52	148.5					0.024
AE: Mo-oxidation	4.46	117.3			1.36		0.0087
SC: Mo-oxidation	10.08	226.5					0.054
1st order: Mo-oxide decomposition	26.6	608.4	22.34	573.3	0.583	0.588	0.028
AE: Mo-oxide decomposition	18.2	434.57	27.3	684.7	1.76	0.73	0.021

Table 2: Results of the various least squares fit procedures

Conclusion

Some experiments to investigate the behaviour of Mo on oxidation in air and the subsequent decomposition and sublimation were performed. The results are, however, not very consistent. Although the standard deviations favour AE-mechanisms, the agreement of curves of thermal analysis and models is not convincing. Might be, the particles of not unique size distribution (Figure 1) are the reason, might be, the reactions depend on heating rate. Especially, the rate of 10 K/min could be too high to get reliable results. The decomposition and the sublimation of the molybdenumoxides overlap which makes a discussion very difficult, too. In the gas phase a complicated mixture of molybdenumoxides are detected [9-23]. With consolidated results the literature will be discussed in more detail.

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