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REACTIONS OF MAGNESIUM IN DIFFERENT ATMOSPHERES

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Abstract
In this investigation the oxidation behavior of magnesium particles 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 magnesium during combustion and revealed that measurements carried out under carbon dioxide show a different oxidation behavior than those under air. Therefore calculations of TGA curves usinga Jander 3D model in Mathematica and kinetic adjustment of the TGA curve by Fortran code of an autocatalytic model were used to find kinetic parameters. The kinetic parameters of the reaction of magnesium under air could be calculated by Jander 3D model and by FindMinimum of Mathematica. Furthermore the activation energy of the oxidation of magnesium could be calculated. High temperature X-ray diffraction analysis on the powders reveals the formation of magnesium carbides in the oxidation reaction under carbon dioxide.

Introduction

Metal particles have been used for years in energetic materials, pyrotechnics and propellants. The natural tendency of metal particles to superficially passivateis 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[2-5]. 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 [6-8].

The goal of this investigation is the characterization of the oxidation behavior of magnesium powder in different atmospheres, to offer a better understanding of the kinetics of the combustion reaction of magnesium.

For the study of particle oxidation often Jander 3D models are used as for Ti,TiNor ZrC[9, 10,12,13] or the shrinking core model [11]. The kinetics of the oxidation reaction of Mg in air has been already analyzed by *Dippold*, using a first order reaction for Mg particles of 44 µm [12]. In this analysis, a consistent model could only fit the measurement curvesdone for heating rates of 2 °C min^{-1}, than for 5 and 10°C min^{-1} due to it is better resolution. In this work from *Dippold*, analysis of reactionmechanism was done on basis of Arrhenius equation with pre-exponential A and activation energy E_A in combination with least squares fit methods in Mathematica.Detailed description of calculationcan be foundin [13].

$$k = A \cdot e^{-\frac{E_A}{R \cdot T}} \quad (1)$$

Opposite to this simple reaction pathwhen Mg oxidizing in air, the investigations of *Mollering* and*Flint*[14] revealed that combustion of magnesium under carbon dioxide lead to formationof magnesium carbides within certain temperature ranges. The reactionof

magnesiumwith carbon dioxideshould occur through various secondaryand partialreactions. The following reactionsshowthe oxidation behaviorof magnesiumwithcarbon dioxide.

$2\ Mg + CO_2 \rightarrow 2\ MgO + C$ (2)

$Mg + CO_2 \rightarrow MgO + CO$ (3)

$C + CO_2 \leftrightarrow 2\ CO$ (4)

$5\ Mg + CO_2 \rightarrow 4\ MgO + MgC_2$ (5)

$Mg + 2\ C \rightarrow MgC_2$ (6)

$2\ Mg + 3\ C \rightarrow Mg_2C_3$ (7)

$2\ MgC_2 \rightarrow Mg_2C_3 + C$ (8)

In this case, Equation (2) and (3) show the general reaction of the magnesium with carbon dioxide. The investigations of *Mollering* and*Flint*showed as well that about 50 % of puremagnesium and carbon dioxide transformsinto magnesium oxide (Eq.(2)).Approximately 25 %of the starting materialswill transform into carbon monoxide andmagnesium oxide(Eq.(3)), whilethe remaining 25 %transforms into magnesiumcarbides(Eqs.(5) to (8)). Otherpartial reactions arise as a secondaryreactionbetween thecarbonformed with the remaining magnesium, orby direct reactionof magnesiumwith carbon dioxide to form magnesiumcarbides. At 900 °C and above, the reaction between the remaining carbon and carbon dioxide is formed (Eq. (4)). From the beginning of the oxidation process, MgC_2 forms preferably to decompose at approximately 500 °C into $Mg_2C_3$and carbon (Eq.(8)). The decomposition of Mg_2C_3 occurs at temperatures above 700 °C [14].

According to this information, this investigation aim also to confirm this magnesium carbide formation when working under CO_2 atmospheres, using different CO_2 contents.

Experimental

Thermo gravimetric analyses have been used for the determination of theoxidation kineticsand itscorresponding parameters. STA-Simultaneous thermal analysis (Netzsch STA 449C Jupiter) was used with heating rates of 2, 5 and 10 °C min^{-1}in a temperature range of 25 – 1000°C. Air, pure carbon dioxide and corgon 18 (18 % carbon dioxide, He) atmospheres have been tested.The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out simultaneously.

Two different sized commercial magnesium powders (-325 mesh, -100+200 mesh) produced by Alfa Aesar were analyzed. Particleswere examined by scanning electron microscopy (SEMSUPRA 55 VP, Carl Zeiss SMT AG, Germany).

The sizes of the different magnesium particles were determined 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).

Finally, oxidation experiments were conducted in situ by using high temperature X-ray diffraction(HT-XRD) equipment which recorded diffraction patterns by a scintillation counter in temperaturesteps of 10 °C with a recording time of 120 min per pattern (XRD Bruker AXS D8 Serie 2) under carbon dioxide atmosphere.

Results and Discussion

1. Particle characterization

The smaller particles of magnesium (-325 mesh) show a diameter of d(0.5) = 38.120 µm and a specific surface of 5.123 $m^2 g^{-1}$ (Fig.1). The larger particles of magnesium (-100+200 mesh)have a diameter of d(0.5) = 121.900 µm (Fig. 2). The specific surfaceof the larger magnesium particles is smaller with 3.356 $m^2 g^{-1}$.SEM analysis reveals no difference in the shape of the particles between the smaller and bigger sized magnesium particles.

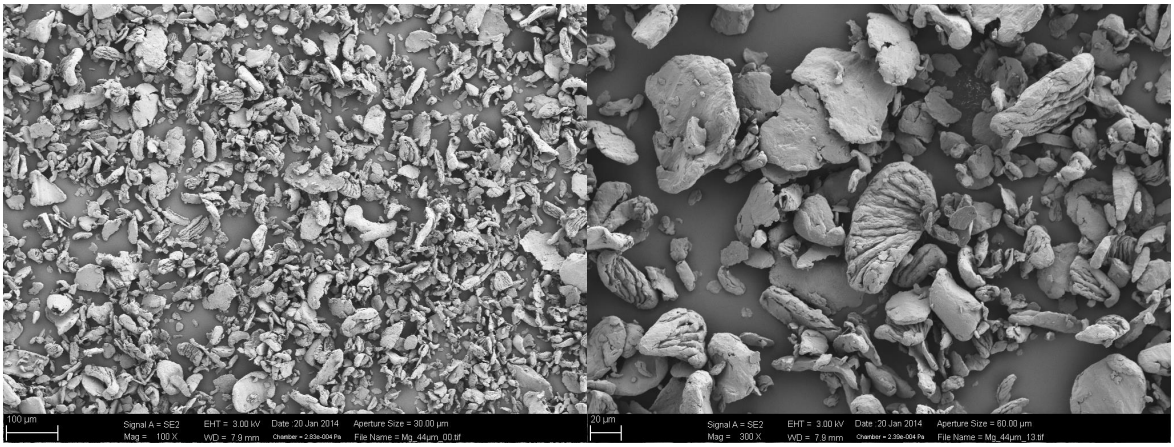

Figure 1: SEM micrographs of magnesium powder (-325 mesh, Alfa Aesar).

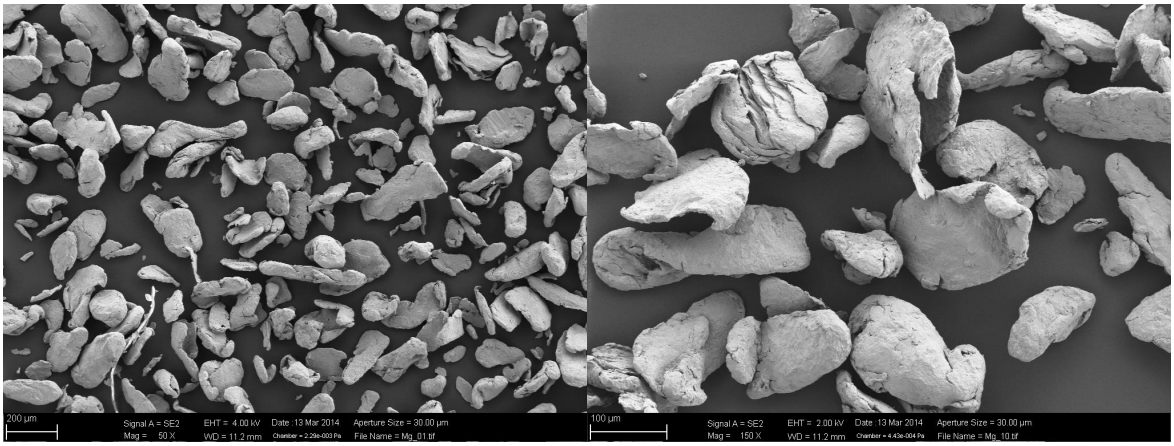

Figure 2: SEM micrographs of magnesium powder (-100+200 mesh, Alfa Aesar).

2.TGA

The complete oxidation reaction of Magnesium in air is shown in Equation (9).

$$Mg + \frac{1}{2} O_2 \rightarrow MgO \quad (9)$$

The calculated mass increase during the transformation of magnesium into magnesium oxide is 65,8 %. Experimental measurements had shown the same value of mass increase.

The following pictures reveal the obtained TGA curves of magnesium when it is oxidized under air (Fig.3), carbon dioxide(Fig. 4) and corgon 18 (Fig. 5) atmospheres. Figure 3 and 4 reveala common behavior between oxidation under air and CO_2. For higher heating rates the curve is shifted towards higher temperatures. A difference between Figure 3 and 4 is how the mass increase is suddenly stopped. When using CO_2, the end of mass intake is more abrupt (Fig. 3). This abrupt ending of the mass increase observed when carbon dioxide is used; at approximately 1000 K for the smaller heating rate and 1080 K for the higher heating rate, could be the indication of a different oxidation mechanism between air and CO_2

atmospheres. This could confirm what *Mollering*and *Flint* suggested, a different path of reaction [14].

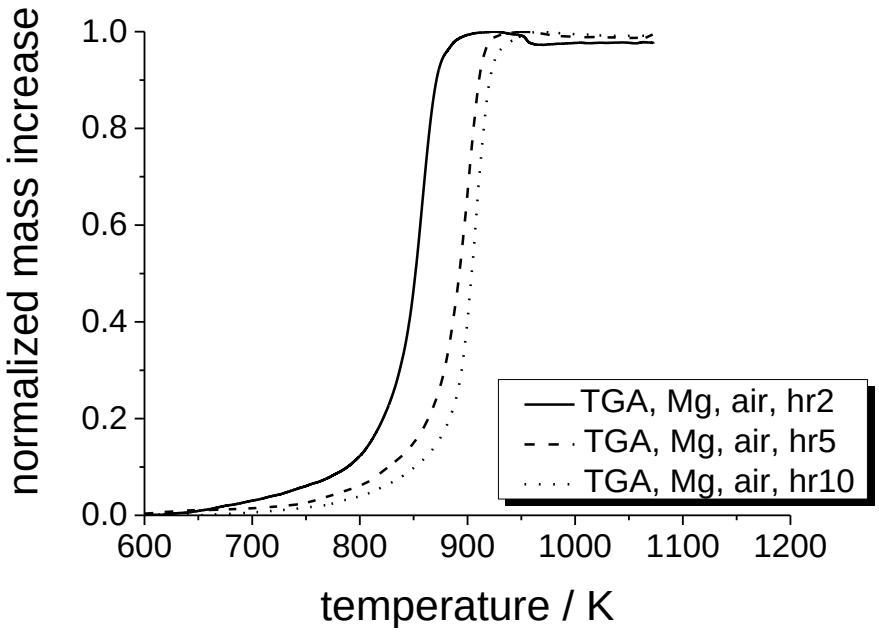

Figure 3: TGAmeasurements of magnesium (-325 mesh) under air with heating rates of 2, 5 and 10 °C·min^{-1}.

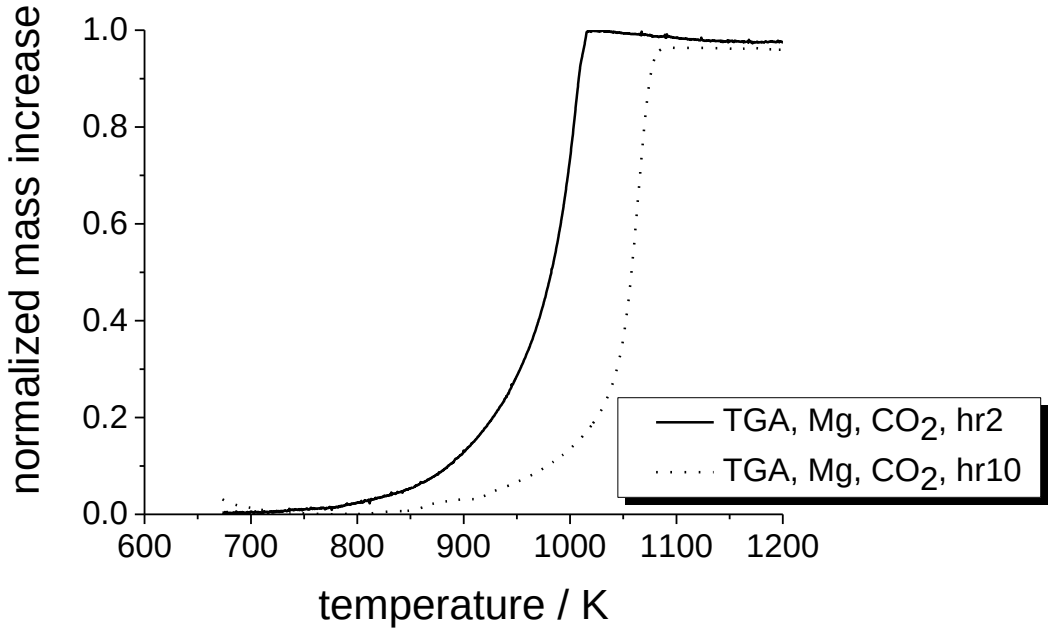

Figure 4: TGAmeasurements of magnesium (-325 mesh) under carbon dioxide with heating rates of 2 and 10 °C·min^{-1}.

In figure 5can be observed that the oxidation of magnesium particles under corgon18 seems to have the same behavior likeunder pure CO_2. The abrupt ending of the oxidation peaks is like in the case of the oxidation under CO_2 (Fig. 4).

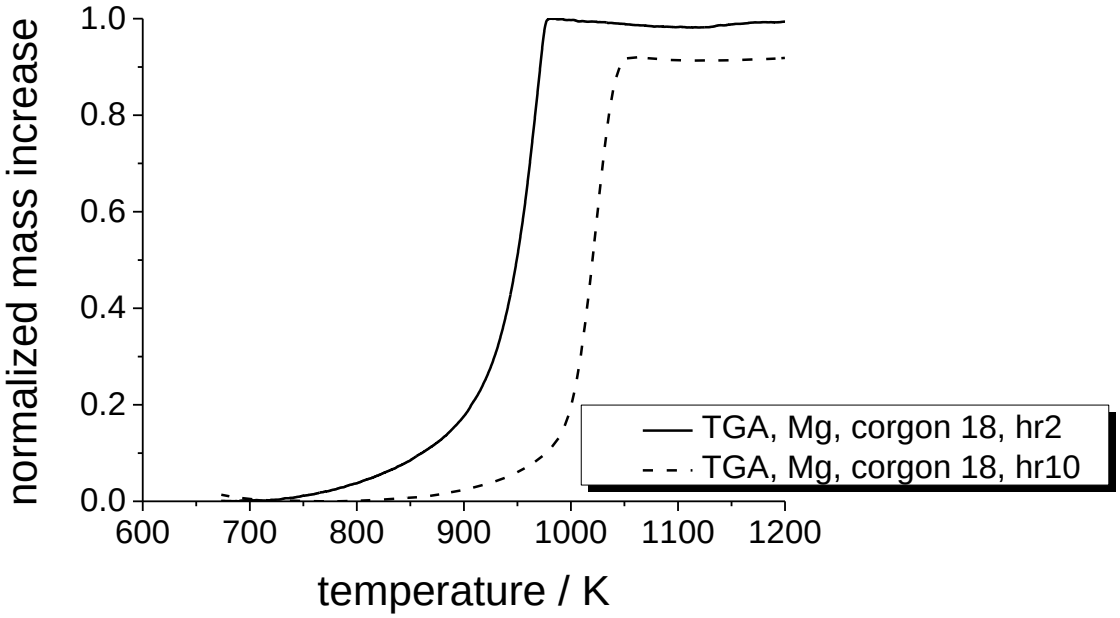

Figure 5: TGAmeasurements of magnesium (-325 mesh) under corgon 18 with heating rates of 2 and 10 °C·min^{-1}.

A comparison of the TGA curves underboth air and carbon dioxide atmospheres with their different ending of the oxidation curves is shown in figure 6. Figure 7 reveals the comparison of the TGA curves under carbon dioxide and corgon 18 atmospheres.

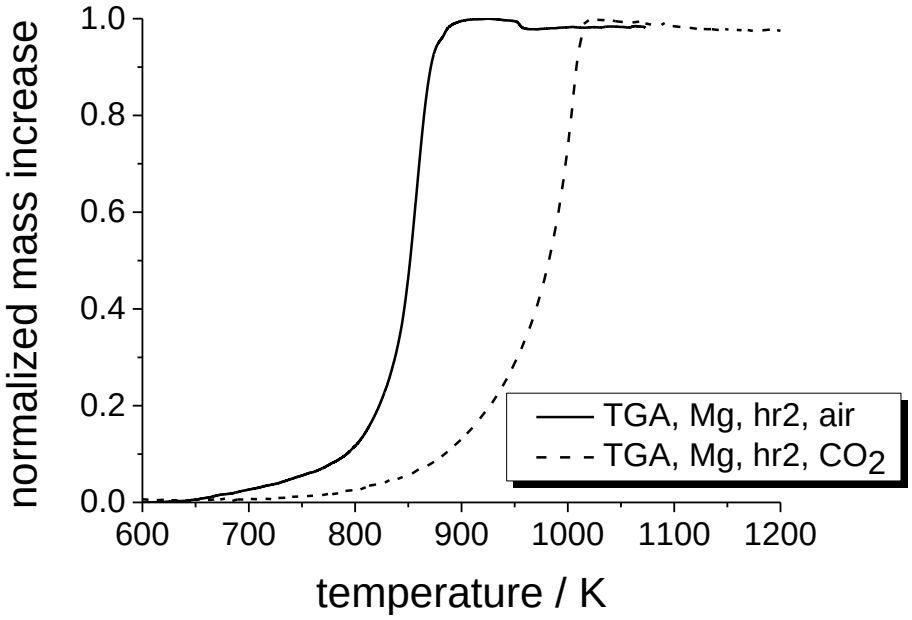

Figure 6: TGA-curves of magnesium (-325 mesh) under carbon dioxide atmosphere in comparison with the behavior showed when oxidized under air atmosphere.

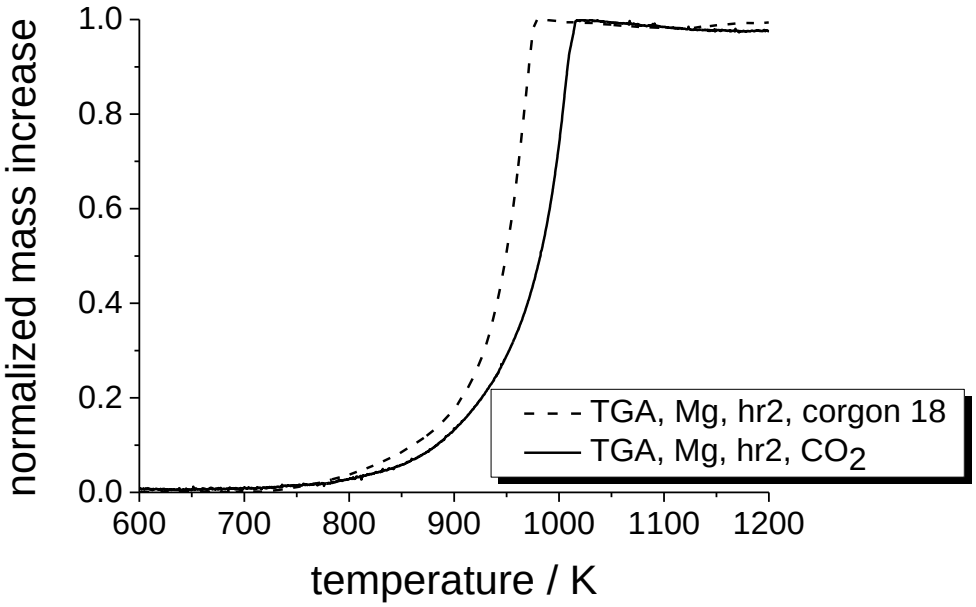

Figure 7: TGA-curves of magnesium under carbon dioxide atmosphere in comparison with the behavior showed when oxidized under corgon18 atmosphere.

The oxidation reaction of magnesium under corgon18 atmosphere takes place at higher rates than the oxidation under carbon dioxide atmosphere.It appears to have a relation with the carbon dioxide content of the present atmosphere, since under corgon atmosphere less CO_2 is available. For less carbon dioxide is available, the oxidation reaction begins at lower temperatures (Fig. 7).

If the results obtained using air and CO_2 atmospheres are compared (Fig. 6), the curves reveal important differences. Thesharp rate increase after a slow beginning of the oxidation reaction and the abrupt ending of the oxidation curve in carbon dioxide could be an indication of an autocatalytic reaction. Autocatalytic reactions are those where one or more of the products are at the same time reactants. Autocatalytic reactions are defined by slow rates that are greatly accelerated as the reactant is consumed and the auto-catalyst produced [7]. In this case the auto-catalyst could be the carbon formed when the equilibrium reaction starts (Eq. 4). Unbound atoms of carbon are highly reactive.

The TGA curves obtained when oxidizing the different magnesium particle sizes under carbon dioxide atmosphere are shown in figure 8. In this case the comparison of the reaction in relation to the particle size reveals the behavior of a diffusion-controlled reaction. In case of an autocatalytic reaction the particle sizes should not play a role but figure 8 shows that for smaller particles the reaction starts earlier, which is an indication of a diffusion controlled reaction.

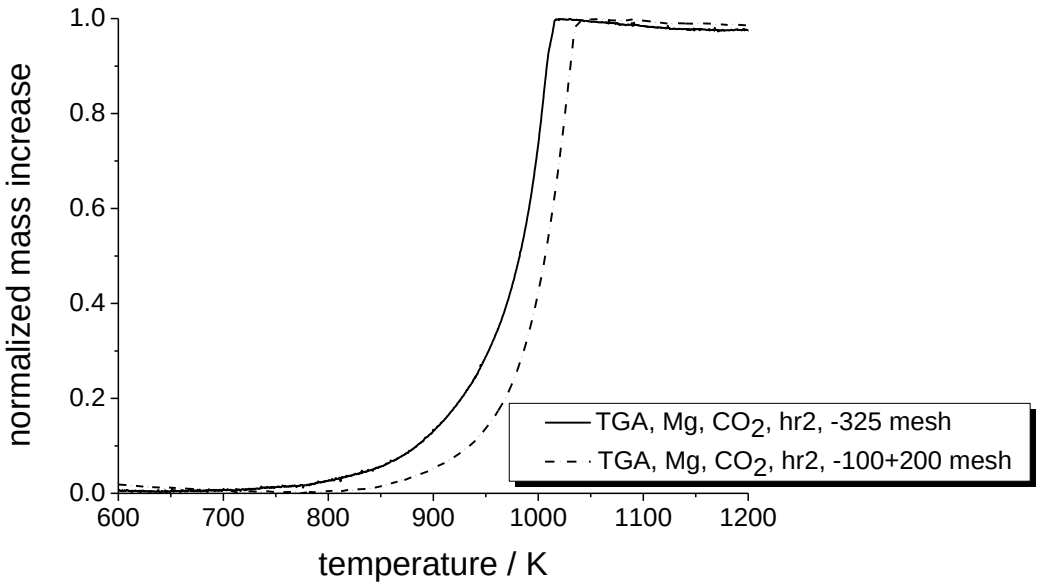

Figure 8: TGA-curves of different magnesium particle sizes under carbon dioxide atmosphere.

These results indicate that the oxidation of magnesium takes place through an autocatalytic reaction, where the autocatalytic reactant would be the carbon formed during the process. In contrary, for higher CO_2 concentrations and therefore higher formation of carbon, the reaction takes place at lower velocities. This could be explained by means of the different chemical reactions taking place in the process. The formation of magnesium oxide is not dependent on the presence of carbon; it only depends on the presence of a source of oxygen. But the presence of carbon leads to the formation of a secondary process, the formation of magnesium carbides. This carbide formation is an autocatalytic reaction. Carbon is a reactant in the magnesium carbide formation (Eqs. (6) and (7)), and it is simultaneously a product (Eq. (8)). This presence of two reactions, a diffusion-controlled reaction and an autocatalytic reaction, can explain the different effects observed.

Assuming that there is as well a diffusion-controlled reaction, the influence of the particle size on the process is not a surprise. The TGA curves of figure 8 are incorrelation with the results obtained from the BET method. Due to theirlarger surface area the smaller particles react faster than the bigger ones and point to a diffusion controlled reaction.

A kinetic model of Jander´s Diffusion was used to obtain the kinetic parameters of the oxidation kinetics. A comparison to an autocatalytic model for non-isothermal curvesas described in [16] was made.The assumption of Jander 3D diffusion controlled reaction doesn´t fit for the oxidation behavior of magnesium in carbon dioxide. The following measurements show the kinetically adjustment of the TGA curves by procedures of Wolfram Mathematica (FindMinimum) and using an own Fortran code for an autocatalytic least squares fit.

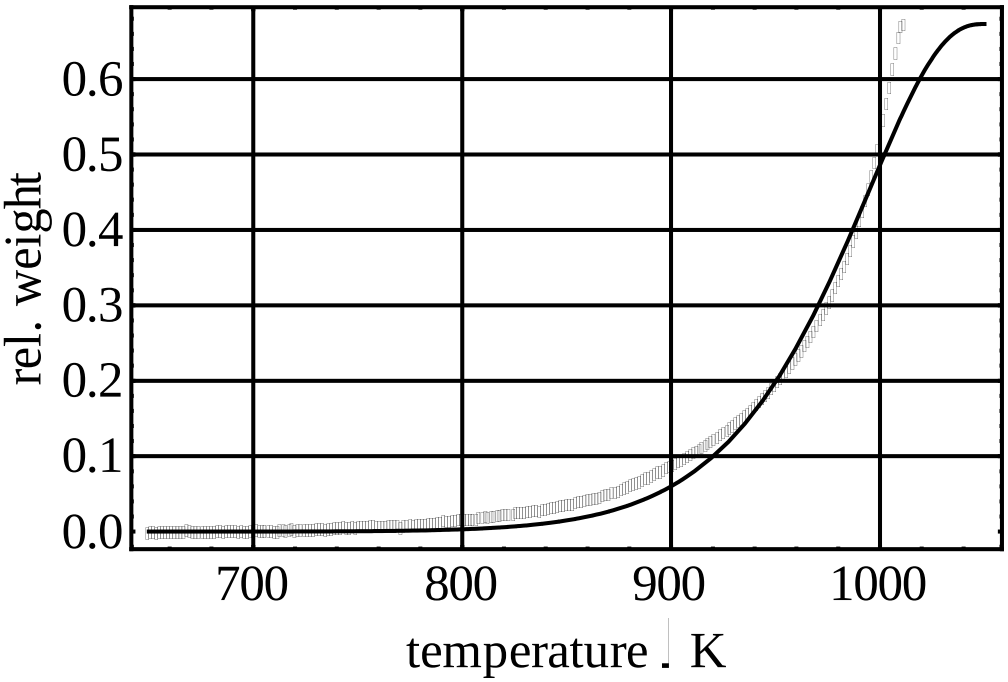

Figure 9: Kinetic adjustment of the TGA-curve by Jander 3D by FindMinimum of Mathematica;TGA-curve of magnesium under carbon dioxide with heating rate of 2°C·min^{-1}.

Figure 9 shows the adjustment of the TGAdata curve of magnesium oxidation in carbon dioxide by a procedure of Wolfram Mathematica and the Jander 3D model. The steep increase close to 1000 K is remarkable and cannot be reproduced by the Jander 3D model with the best parameters $Log_{10}A = 14.4168$; $E_A = 350$ kJ mol^{-1} resulting in a standard deviation approximately of 10 %.

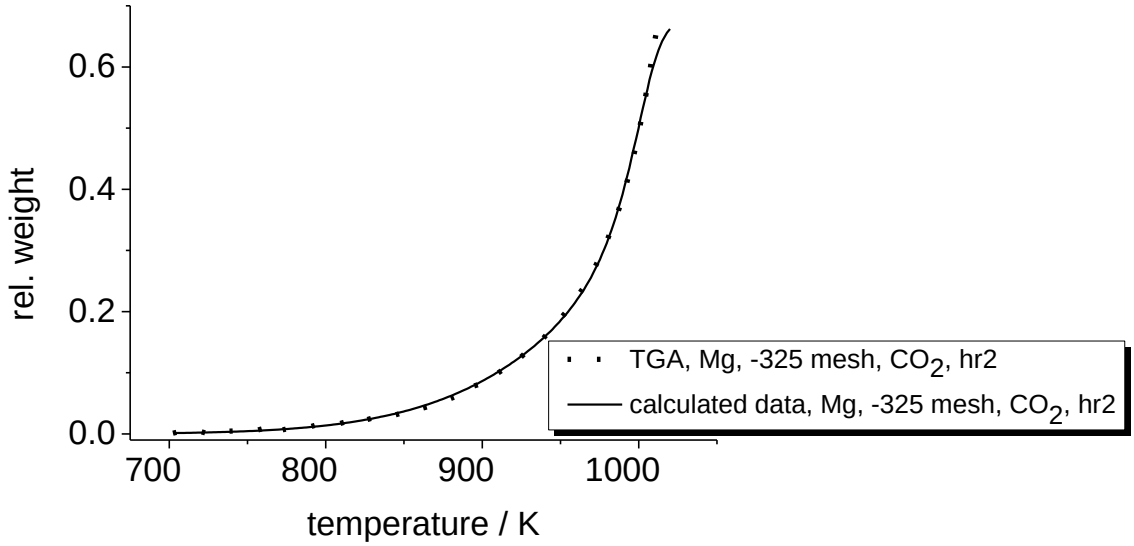

Figure 10: Kinetic adjustment of the TGA-curveby the Fortran code of an autocatalytic model; TG-curve of magnesium under carbon dioxide with heating rate of 2°C·min^{-1}.

Figure 10 shows the adjustment by a fit procedure of Fortran using the analytical solution for the autocatalytic 1st order model [16]. Close to 1000 K there arise also higher residuals but

the standard deviation is below 1 % favoring an autocatalytic model. The kinetic parameters are $Log_{10}A_1$ = 3.155, E_{A1} = 100.3 kJ mol^{-1}, $Log_{10}A_2$ = 22.77, E_{A2} = 459.8 $kJmol^{-1}$.

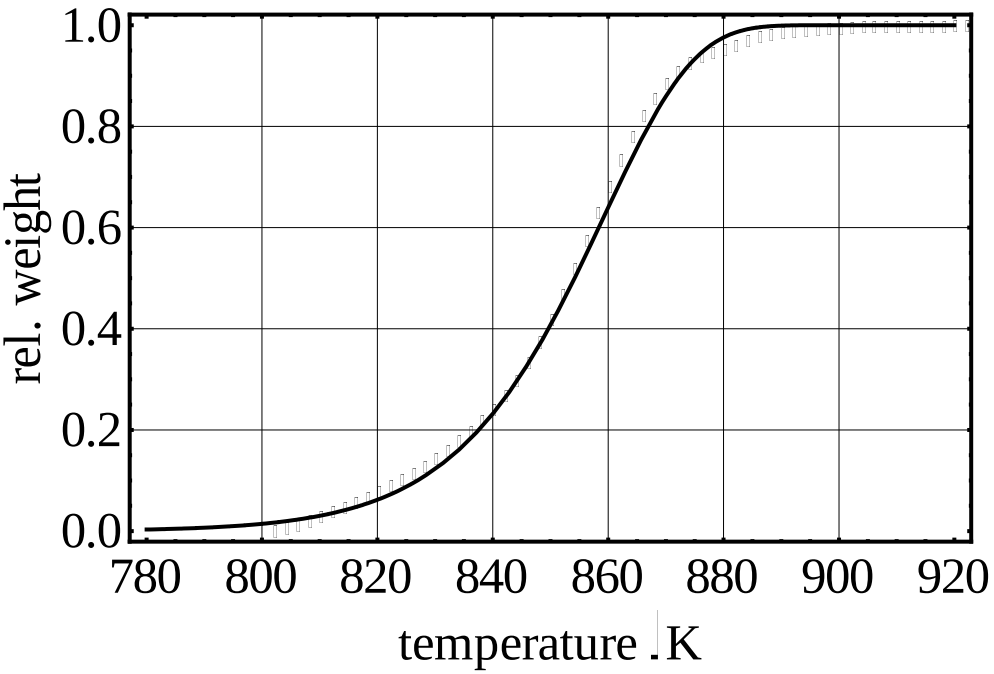

Figure 11: Kinetic adjustment of the TGA-curve by Mathematica; TGA-curve of magnesium under airwith heating rate of 2°C·min^{-1}[12].

A kineticevaluation of magnesium oxidation under air could be definedasa 1st order reaction with sufficient agreement. Figure 11 shows this adjustment of the TGA data curve. For the magnesium combustion under air the activation energy could be calculated with a value of 392.5 KJ mol^{-1} and $Log_{10}A$=21.888[12]. Data evaluation with higher heating rates gave even higher activation energies.

3. XRD

Figure 12 shows the in-situ-high-temperature X-ray diffraction analysis of magnesium in carbon dioxide atmosphere and a temperature range of200 °C to 800 °C.

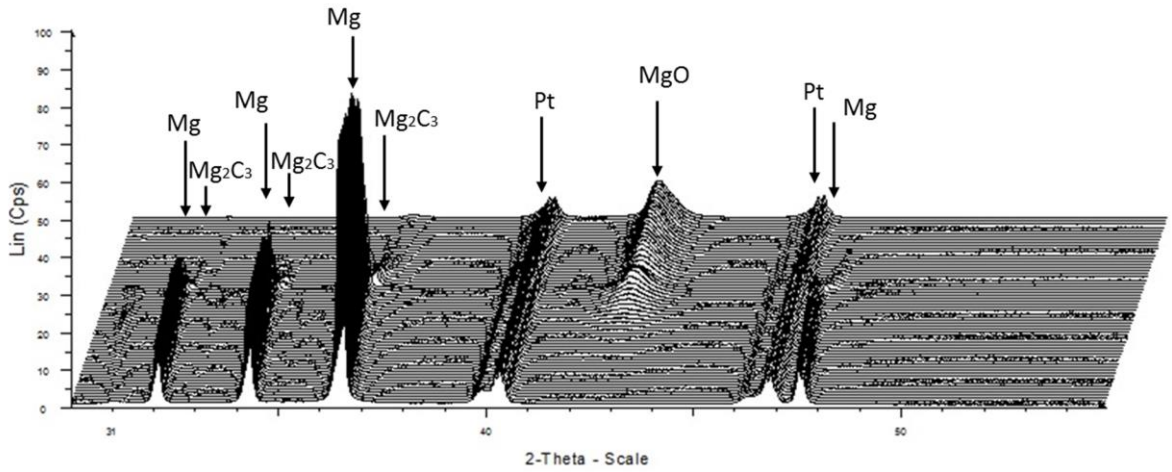

Figure 12: X-ray diffraction series of patterns obtained from the oxidation of Mg within the temperature range of 200 °C to 800 °C under carbon dioxide atmosphere.

At the beginning of the process, in the temperature range of 400 °C to 500 °C, the XRD analysis allows the detection of the mixture of the starting material magnesium, magnesium carbide, the end product magnesium oxide and platinum peaks. The platinum peaks have been detected due to the platinum foil used for heating the sample. The region where the formation of the magnesium carbides is expected is plotted in figure 13.

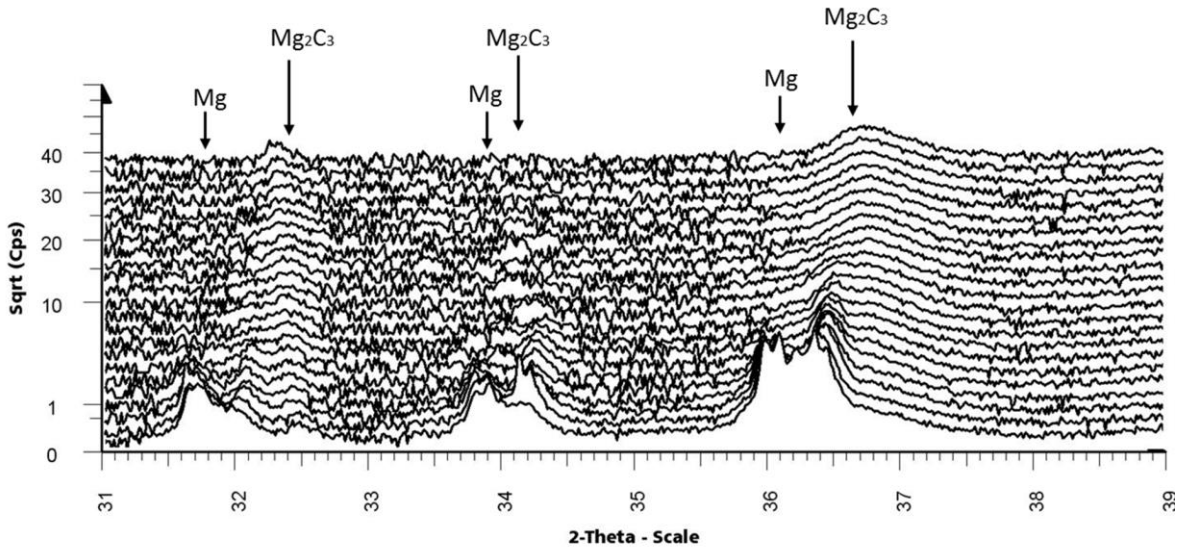

Figure 13: X-ray diffraction series of patterns obtained from the oxidation of Mg within the temperature range of 400 °C to 500 °C under carbon dioxide atmosphere.

The formation and consumption of magnesium carbides takes place during the whole process. For this reason, this intermediate product does not have to be present in the exact moment of the measurement. That some magnesium carbides are detected is enough to confirm the existence of these phases. This confirms as well that, when carbon dioxide is used, the oxidation of magnesium takes place together with the formation of magnesium carbides. This process, limits the magnesium available for the oxidation process at lower temperatures, and therefore it slows down the oxidation reaction to higher temperatures (Fig. 6).

Conclusion and Outlook

The investigation showed that the reaction mechanism of magnesium in air follows a different mechanism than the reaction of magnesium in carbon dioxide. This investigation verifies the formation of magnesium carbides during the combustion of magnesium in atmospheres with carbon dioxide content and shows the analysis of the kinetic of the combustion of magnesium, both in air and carbon dioxide.

The results indicate the presence of an autocatalytic reaction. In case of an autocatalytic reaction carbon could play the role of an auto-catalyst. The decomposition of carbon dioxide forms high reactive carbon which reacts rapidly with the starting material magnesium to magnesium carbide (Eqs. (6) and (7)), and this magnesium carbide was found in the temperature range of 400 °C to 500 °C when the reaction was carried out using HT-XRD. The end product was detected as pure magnesium oxide.

The kinetic of the oxidation of magnesium under air and carbon dioxide is not yet defined. Further investigation on this field is needed. The fact that for less carbon dioxide concentrations the oxidation reaction starts at higher velocities is also an indication of this parallel formation of magnesium carbides and therefore it will hinder the formation of magnesium oxide. XRD measurements under corgon 18 atmosphere could give more information about the formation of magnesium carbides. Especially different carbon dioxide

atmospheres with different concentrations could help for a better understanding of the process. Furthermore investigations in alternative atmospheres e.g. nitrogen are still in progress.

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