A novel experimental method to study metal vapor condensation/oxidation:

Mg in CO and CO₂ at reduced pressures

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Abstract

A novel method is presented to study magnesium metal vapor condensation/oxidation in CO and CO₂ atmosphere at reduced pressures. Mg(s) was evaporated and mixed with an equimolar amount of CO or CO₂ at 1000°C after which the gaseous mixture flowed through an air cooled tubular condenser. Measurements of the axial temperature profile, calculation of partial pressures and analysis of deposits within the condenser allowed for identification of deposition/condensation onset temperatures, supersaturation ratio and reaction mechanism. In the presence of CO₂, rapid oxidation of Mg(g) has been observed. In the presence of CO, no Mg(g) oxidation was found above 950°C. Mg(g) oxidation observed at lower temperatures is believed to be initiated by CO disproportionation. The proposed mechanism is able to explain the increase in Mg metal yield with decreasing CO partial pressure. At a CO partial pressure <3 mbar, high Mg metal mass yields of >90w% were found. The presented method is applicable to the study of a variety of metal vapor/oxidizer combinations e.g. of interest in metal and solar fuel production.

Keywords: metal vapor, condensation, oxidation, magnesium, carbothermal reduction, solar fuel

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1. Introduction

The study of metal vapor condensation/oxidation is of interest in production processes of volatile metals via carbothermal reduction (CTR) and in metal/metal-oxide redox cycles, e.g. for production of solar fuels. In both cases the produced metal vapor, e.g. Zn(g), Mg(g), Al(g), Si(g) or Ti(g) has to be separated from the reduction by-product, e.g. CO, CO₂ or O₂ [1-6]. When cooling down the gaseous products, the thermodynamic driving force favors undesired reverse reactions. Freezing the equilibrium obtained at high temperatures via rapid cooling/quenching is a common approach to minimize reverse reactions [7, 8]. The goal is to instantly condense the metal phase via homogeneous nucleation. Homogenous nucleation has been achieved using cooling rates in the order of 10^5 - 10^6 K/s which results in formation of fine powders [2, 9, 10]. In practice however, only a limited mass fraction is able to condense via homogeneous nucleation with the remaining fraction condensing heterogeneously as a consequence of freshly created nuclei and instant decrease in partial pressure and supersaturation [11, 12]. Reverse reactions, i.e. oxidation of the metal products, occur simultaneously to the condensation process through gas-gas reactions prior to nucleation or through gas-liquid/solid reactions upon formation of liquid/solid metal. For successful recovery of metal vapor in the presence of oxidizers it is hence crucial to know the mechanism and rate of the various oxidation reactions relative to the metal vapor condensation process.

Here, a novel experimental setup is presented to study metal vapor condensation/oxidation. Similar to previous setups [13-15], a tubular reactor/condenser is used to cool down a mixture of metal vapor/oxidizer. Instead of scraping off the deposits from the tube walls or collecting deposits on individual targets at selected locations, a flexible graphite liner was used to collect and analyze a continuous profile of deposits along the axis of the condenser. The axial distribution and composition of deposits were then correlated as a function of temperature and

partial pressure, allowing identification of the onset deposition/condensation temperatures, supersaturation ratio, and reaction mechanism. Results are shown for the condensation/oxidation of Mg vapor in CO and CO₂ at conditions typical for Mg metal production via CTR.

CTR has been recognized as conceptually the simplest and cleanest route to Mg metal production, but has suffered from technical challenges of development and scale up, primarily related to the back-reaction, $\text{Mg(g)} + \text{CO} \rightarrow \text{MgO} + \text{C}$, upon cool-down [8, 16, 17]. Two recent approaches have successfully minimized back reaction: Mg(g) quenching using a supersonic Laval nozzle and Mg(g) condensation at elevated temperatures and reduced pressures [18-20]. While the first approach results in the formation of fine and pyrophoric powder which raises the need for explosion containments, the latter approach favors formation of large Mg grains. Both approaches have been studied on a rather empirical base without identifying the underlying reaction mechanism. The goal of the present study is to improve the understanding of the various oxidation reactions of Mg in its gas and solid phase and to identify favorable conditions for high Mg metal yields while preventing formation of hazardous powders.

2. Experimental method

Experimental setup

The setup consists of two vertical coaxial Al₂O₃ tubes forming three distinct zones for: 1) Mg evaporation, 2) Mg-oxidizer mixing and gaseous oxidation 3) Mg condensation and condensate oxidation (Figure 1). Mg evaporation rate was controlled by the lower cylindrical furnace (Carbolite, VST 12/200, 1200°C) and monitored by a load cell (Futek LRF 400, 0.25 lb) attached to an Al₂O₃ crucible containing Mg metal pieces (American Elements, 99.9%, 1-10mm). An Argon carrier stream (Airgas UHP, >99.999%) introduced from the bottom of the system swept the evaporated Mg upstream towards the mixing zone. A CO (Airgas UHP, >99.9%) or CO₂

stream (Airgas Instrument, >99.99%) introduced at the top flowed downwards between the two Al_2O_3 tubes while being preheated by the upper cylindrical furnace (CM Furnaces, 1730-10-VT, 1700°C). The hot oxidizer stream mixed with the Mg vapor coming from the bottom. Preheating the oxidizer stream is important to avoid localized cooling and condensation of Mg vapor upon mixing with oxidizer. A fiberglass heat tape in between the furnaces set at 750°C avoided Mg condensation prior to mixing with oxidizer. The Mg-oxidizer mixture then flowed upstream through the inner Al_2O_3 tube which was lined with a removable graphite foil (Mersen, Papyex N998, 0.4mm thick) to collect deposits from Mg condensation/oxidation. A Cellulose Nitrate membrane filter (Thermo Scientific, 0.2 μm) located downstream collected particles entrained in the gas phase.

Vacuum-tight connections between Al_2O_3 and metal tubes were achieved through combination of compression ports, KF fittings, Viton O-rings and Swagelock fittings. Gas streams were controlled by analog, elastomer-sealed mass flow controllers (MKS, 1179A, 200($\pm$ 2) sccm for the oxidizers and 2000($\pm$ 20) sccm for Ar). System pressure was measured by two absolute capacitance manometers (MKS, 626B, 0-133($\pm$ 0.3)mbar and 0-1333($\pm$ 3.3)mbar) and controlled via an exhaust throttle valve (MKS, T3BI) attached to a multi-roots dry pump (Adixen, ACP28G). For safety reasons, pressure drop across the system was monitored by a differential capacitance manometer (MKS, 226A, 0-27($\pm$ 0.1)mbar). Gas concentrations of CO and O_2 were measured by a non-dispersive infrared analyzer (California Analytical Instruments, ZRE NDIR, 0-10($\pm$ 0.1)% CO, 0-15($\pm$ 0.15)% CO_2) and a trace oxygen analyzer (Advanced Micro Instruments, Watchdog, 0-1($\pm$ 0.01)% O_2) located downstream of the vacuum pump. Prior to entering the gas analyzers the gas stream was diluted with Ar to correspond with the NDIR measurement range. Axial temperature profiles of the condensation/oxidation zone were collected by moving a K-type

thermocouple (Omega, KQXL-116G-28, $1250(\pm 1.1 \text{ or } 0.4\%)^{\circ}\text{C}$) along the center line of the inner Al_2O_3 tube.

Figure 1: Schematic of Mg evaporation-condensation system with distinct zones for (1) Mg evaporation, (2) Mg-oxidizer mixing and gaseous oxidation and (3) Mg condensation and condensate oxidation.

Experimental procedure

For each run 5 ± 0.1 g of Mg pieces were loaded into the Al_2O_3 crucible. The system was considered to be leak-free if an ultimate pressure, i.e. system pressure at no gas flow, of < 0.1 mbar was achieved, consistent with the ultimate achievable pressure by the vacuum pump. The

system was flushed with 0.5 sl/min Ar until the measured O₂ concentration was < 100 ppm. Experiments were carried out with either CO or CO₂. System pressure and gas flows were set to constant values of $p = 2.5, 10$ or 40 mbar, $\dot{V}_{\text{oxidizer}} = 0.05$ sl/min and $\dot{V}_{\text{Ar}} = 0.05\text{-}0.75$ sl/min resulting in gas velocities of $0.1\text{-}1.7$ m/s and cooling rates in the order $10^2\text{-}10^4$ K/s. The upper furnace was heated to 1000°C at a heating rate of $20^\circ\text{C}/\text{min}$ and kept at temperature for three hours before starting the Mg evaporation to ensure steady state conditions in the condensation/condensate oxidation zone. In preliminary experiments carried out with CO the upper furnace temperature was varied between $850\text{-}1300^\circ\text{C}$ which changed the axial position of the deposits. However, no influence on onset condensation temperature, supersaturation ratio or reaction mechanism was found and hence the upper furnace temperature was found to be insignificant to the experimental results. Depending on the selected system pressure and gas flows, the temperature setpoint of the lower furnace was varied between $690\text{-}890^\circ\text{C}$ as a means of adjusting the evaporation rate, $\dot{m}_{\text{Mg, evap}}$, such that a molar ratio of $\text{Mg}:\text{oxidizer} = 1\pm 0.2$ was achieved.

Figure 2 and Figure 3 show typical runs performed with CO and CO₂, respectively. The start of Mg evaporation was determined by a decrease in oxidizer concentration, which was more sensitive than the load cell signal. Termination of Mg evaporation was registered by the load cell signal leveling off. Within a few minutes after all the Mg had evaporated, oxidizer gas flow was switched to Ar to prevent further oxidation of Mg condensates. With CO, gas consumption was small (few percent) and responding slowly to changes in $\dot{m}_{\text{Mg, evap}}$. With increasing time and Mg deposits a slight increase in CO consumption has been observed. Conversely, with CO₂, almost complete reduction to CO was observed and CO₂ consumption and CO production immediately responded to changes in $\dot{m}_{\text{Mg, evap}}$, e.g. in the initial heat up period (time = 295-310 min), when

adjusting the evaporation temperature to maintain the molar Mg:CO ratio (time = 370 min) and at the end of the experiment (time = 390 min).

After cooling down, the system was opened and exposed to ambient air. The graphite liner with Mg, MgO and C deposits was removed from the inner Al₂O₃ tube and compared to the axial temperature profile (Figure 4). The deposits showed sections of black, white and metallic gray colored deposits. The appearance of the first black deposits marks the deposition onset temperature T_{deposit} , while the presence of crystalline Mg marks the Mg condensation temperature, T_{condens} . T_{deposit} was always found to be higher than T_{condens} , indicating that some reaction occurred prior to Mg condensation. Deposits were scraped off the graphite foil in axial sections of equal appearance, weighed, and analyzed for atomic C and O content using LECO elemental analyzers (TC-600, C200). Elemental magnesium and magnesium oxide were calculated assuming that all elemental oxygen is bound as magnesium oxide. Deposit morphology was characterized by Field Emission Scanning Electron Microscopy and Energy Dispersive X-ray Spectrometry (FESEM/EDS, JEOL JSM-7401F). Chemical composition was further analyzed with X-Ray powder Diffraction (XRD, Bruker D2 Phaser). Deposit surface area was calculated by BET analysis (Micromeritics, Gemini 2380).

Figure 2: Gas evolution and Mg evaporation from crucible as measured by NDIR and the load cell, respectively, for an experiment performed with CO at $p = 40$ mbar, $\dot{V}_{\text{CO}} = \dot{V}_{\text{Ar}} = 0.05$ sl/min resulting in $p_{\text{CO}} = 13.2$ mbar.

Figure 3: Gas evolution and Mg evaporation from crucible as measured by NDIR and the load cell, respectively, for an experiment performed with CO₂ at $p = 10$ mbar, $\dot{V}_{\text{CO}_2} = 0.05$ sl/min and $\dot{V}_{\text{Ar}} = 0.15$ sl/min resulting in $p_{\text{CO}_2} = 2$ mbar.

Figure 4: Graphite foil liners with deposits from experiments performed with CO ($p_{\text{CO}} = 13.2$ mbar) and CO₂ ($p_{\text{CO2}} = 2$ mbar) along with the corresponding axial temperature profile.

Two criteria are defined to assess the successful condensation of Mg: The Mg metal mass yield, Y_{Mg} , defined as the mass ratio of Mg metal deposits to total deposits (eq. (1)) and the mass fraction, W_{condens} , deposited below temperature T_{condens} (eq. (2)). The latter criterion is considered to be important for potential industrial applications where deposits are desired to be formed in a dedicated condensation zone operating at $T < T_{\text{condens}}$.

$$Y_{\text{Mg}} = \frac{m_{\text{Mg}}}{m_{\text{total}}} = \frac{m_{\text{Mg}}}{m_{\text{Mg}} + m_{\text{MgO}} + m_{\text{C}}} \quad (1)$$

$$W_{\text{condens}} = \frac{m_{\text{condens}}}{m_{\text{total}}} = \frac{m_{\text{condens}}}{m_{\text{Mg}} + m_{\text{MgO}} + m_{\text{C}}} \quad (2)$$

m_{Mg} , m_{MgO} and m_{C} are estimated based on NDIR measured oxidizer consumption/production (see Appendix A). m_{condens} is the mass of deposits collected at $T < T_{\text{condens}}$. CO, CO₂ and Mg

partial pressures are obtained using Raoult's Law, eq. (3), with pressure and molar flows determined by the manometers, load cell, mass flow controllers and composition of deposits.

$$p_i = p \cdot \frac{\dot{n}_i}{\dot{n}_{\text{CO}} + \dot{n}_{\text{CO}_2} + \dot{n}_{\text{Ar}} + \dot{n}_{\text{Mg}}} \quad i = \text{CO}, \text{CO}_2, \text{Mg} \quad (3)$$

Supersaturation is estimated by eq. (4) with the equilibrium vapor pressure, $p_{\text{Mg,eq}}$, calculated by eqs. (5) and (6) [21].

$$S = \frac{p_{\text{Mg}}}{p_{\text{Mg,eq}}(T)} \quad (4)$$

$$p_{\text{Mg,eq}}(\text{bar}) = 10^{\frac{-7780}{T(\text{K})} + 11.41 - 0.855 \cdot \log(T(\text{K}))} \cdot 1.333 \cdot 10^{-3} \quad \text{for } T < 923\text{K} \quad (5)$$

$$p_{\text{Mg,eq}}(\text{bar}) = 10^{\frac{-7550}{T(\text{K})} + 12.79 - 1.41 \cdot \log(T(\text{K}))} \cdot 1.333 \cdot 10^{-3} \quad \text{for } T > 923\text{K} \quad (6)$$

3. Results and discussion

Figure 5 shows Mg metal mass yield, Y_{Mg} , as a function of partial pressures, p_{CO} and p_{CO_2} . Experiments performed with CO showed a decrease in Y_{Mg} with increasing p_{CO} . High $Y_{\text{Mg}} > 90\text{w}\%$ were observed for $p_{\text{CO}} < 3 \text{ mbar}$. In contrast, experiments with CO_2 resulted in low $Y_{\text{Mg}} < 10\text{w}\%$ with no clear dependency on p_{CO_2} . Observed yields and partial pressures agreed well with the results obtained from experimental setups focusing on CTR studies of MgO [5, 6]. Hence, the chosen setup and conditions are able to successfully reproduce gas compositions comparable to those obtained from CTR experiments. Similarly to Y_{Mg} , a decrease in W_{condens} with increasing p_{CO} and low $W_{\text{condens}} < 10\text{w}\%$ in the presence of CO_2 has been observed (Figure 6). A low W_{condens} implies deposits above the Mg condensation onset temperature, T_{condens} , which are visible as black sections in Figure 4.

Figure 5: NDIR based Mg metal yield, Y_{Mg} , as a function of CO and CO₂ partial pressures. Dashed line represents the exponential fit of the CO results between $p_{CO} = 0.6 - 13.2$ mbar.

Figure 6: Deposits below Mg condensation onset temperature, $W_{condens}$, as a function of CO and CO₂ partial pressures.

Figure 7 shows axial mass distribution of deposits with LECO determined MgO and C content for experiments carried out with CO and CO₂ at $p_{\text{CO}} = 2$ mbar, $p_{\text{CO}} = 13.2$ mbar and $p_{\text{CO}_2} = 2$ mbar. The uncertainty represents the 95% confidence interval of the LECO measurements. The difference between MgO+C and total deposits represents the amount of condensed Mg. Above T_{condens} , deposits consisted of MgO and C while below T_{condens} they are a mixture of Mg, MgO and C.

With CO, no deposits were found between the Mg-CO mixing zone and T_{deposit} . According to equilibrium diagrams obtained by Gibbs free energy minimization, formation of deposits, i.e. MgO and C, are expected below $T = 1288^\circ\text{C}$ for $p_{\text{CO}} = 2$ mbar and below 1424°C for $p_{\text{CO}} = 13.2$ mbar (Figure 8). The fact that first deposits were found at considerably lower temperatures, i.e. at $T_{\text{deposit}} = 794^\circ\text{C}$ for $p_{\text{CO}} = 2$ mbar and at $T_{\text{deposit}} = 934^\circ\text{C}$ for $p_{\text{CO}} = 13.2$ mbar, indicates that Mg(g) and CO can coexist in a metastable phase. A similar result has previously been found for Zn(g) and O₂ [13].

At $p_{\text{CO}} = 2$ mbar, few MgO/C deposits have been found between T_{deposit} and T_{condens} while the bulk of deposits, mainly Mg, has been found below T_{condens} resulting in a high $W_{\text{condens}} = 97.4$ w% and high $Y_{\text{Mg}} = 94.4$ w%. Increasing p_{CO} and hence p_{Mg} axially shifts the deposits and increases T_{deposit} and T_{condens} . At $p_{\text{CO}} = 13.2$ mbar, a significant amount of MgO and C deposited above T_{condens} resulting in $W_{\text{condens}} = 77.2$ w%. Higher p_{CO} also increased the MgO/C deposits below T_{condens} which reduce Y_{Mg} to 71.2 w%.

With CO₂, most deposits were found above T_{condens} consisting of MgO and C. No T_{deposit} could be identified because deposits were extending all the way towards the Mg-CO₂ mixing zone. Hence, unlike CO, upon mixing, CO₂ readily oxidizes gaseous Mg resulting in a low $W_{\text{condens}} = 2$ w% and low $Y_{\text{Mg}} = 0.3$ w%. Rapid vapor-phase combustion of Mg in CO₂ has been previously observed at temperatures above 700°C resulting in formation of MgO and small amounts of

carbon [22]. The products of magnesium combustion can form small MgO particles in the gas phase and/or condensates on a surface [23, 24]. SEM/EDS and XRD analysis of deposits collected above T_{condens} confirm formation of μm -sized polycrystalline MgO (Figure 9). Similarly, structured MgO films have been previously obtained by chemical vapor / atomic layer deposition using various precursors [25-27]. MgO growth orientation was found to be highly dependent on deposition temperature, flow rates and pressure. Deposits collected below T_{condens} at various axial positions are shown in Figure 10. Hexagonal Mg prism and dendrites in the μm -range accompanied with submicron whiskerlike Mg/MgO agglomerates have been found.

The observed Mg prism are typical for heterogeneous vapour-solid nucleation [28, 29]. Experimentally determined Mg condensation onset temperature, T_{condens} , was found to be $24 \pm 14^\circ\text{C}$ below its evaporation temperature (Figure 11) corresponding to low supersaturation ratios of $S = 1.7 \pm 0.5$ typical for heterogeneous nucleation. For the $p_{\text{CO}} = 2$ mbar experiment, supersaturation ratios of $S = 2-7$ at $x = 292-316$ mm and $S = 9-14$ at $x = 329-339$ mm were estimated. These values are below the reported thresholds for homogeneous Mg vapor nucleation [21]. Generally, S increased with axial position and decreasing temperature consistent with the observed decrease in particle size and change in morphology from discrete, well-formed crystals to dendritic crystals [29]. As a consequence, in the $p_{\text{CO}} = 2$ mbar experiment, specific surface area increased from $0.5 \text{ m}^2/\text{g}$ at $x = 292-316$ mm to $1.7 \text{ m}^2/\text{g}$ at $x = 329-339$ mm. The fact that large Mg particles were formed despite the presence of oxidizers indicates that under the given conditions, Mg condensation is much faster than oxidation of condensed Mg. Based on gas velocity, Mg condensation was taking place in less than one second. Below the Mg melting point, oxidation has been reported to be slow. After exposure of Mg samples to O_2 , CO or CO_2 for several minutes, formation of few nanometer thick oxide films were observed [22, 30-33].

The observed Mg/MgO agglomerates became more dominant with increasing axial position. Formation of two distinct products, i.e. large particles with nearly pure Mg and smaller particles/agglomerates containing Mg and MgO have been previously observed [6, 34]. Typically, small nuclei and agglomerates are formed in the gas phase via homogeneous nucleation at high supersaturation ratios [29]. Submicron MgO particles and agglomerates have been found as a result of condensed MgO(g) formed in the gas phase during combustion of Mg in CO₂/CO mixtures [22, 35].

Figure 7: Axial mass distribution of deposits with MgO and C content from experiments with CO and CO₂ at partial pressures of $p_{\text{CO}} = 2 \text{ mbar}$, $p_{\text{CO}} = 13.2 \text{ mbar}$ and $p_{\text{CO}_2} = 2 \text{ mbar}$.

Figure 8: Chemical equilibrium diagram of the systems representing the experimental conditions at $p_{\text{CO}} = 2$ mbar ($\text{Mg} + \text{CO} + 3\text{Ar}$, $p = 10$ mbar) and $p_{\text{CO}} = 13.2$ mbar ($\text{Mg} + \text{CO} + \text{Ar}$, $p = 40$ mbar) obtained by Gibbs free energy minimization [36].

Figure 9: SEM/EDS and XRD analysis of deposits collected above T_{condens} from experiments carried out with CO_2 at a partial pressures of $p_{\text{CO}_2} = 2$ mbar (left) and CO at a partial pressure of $p_{\text{CO}} = 13.2$ mbar (right).

Figure 10: SEM/EDS analysis of deposits collected below T_{condens} at various axial positions x from an experiment carried out with CO at a partial pressures of $p_{\text{CO}} = 2$ mbar.

Besides Mg and MgO, small amounts of carbon were found in the collected deposits. In the experiment performed with CO_2 at $p_{\text{CO}_2} = 2$ mbar, 0.64 g C was collected. Based on the gas species balance (equation A.6) a production of 0.33 g C from the gas phase was estimated. Hence, beside carbon likely collected from the graphite foil liner during scraping off deposits, some carbon was formed by either $\text{Mg} + \text{CO} \rightarrow \text{MgO} + \text{C}$ and/or the CO disproportionation reaction, $2\text{CO} \rightarrow \text{C} + \text{CO}_2$.

Experiments performed with CO showed a logarithmic increase of T_{deposit} with p_{CO} (Figure 12). Similar temperatures and pressure dependence on p_{CO} were found for CO disproportionation [35, 37]. Moreover, a recent study has shown that at high temperatures ($>850^\circ\text{C}$) metal oxides can act as efficient substrates for carbon deposits via CO disproportionation [38].

Figure 11: Experimentally determined Mg condensation onset temperature, T_{condens} , as a function of Mg partial pressures, p_{Mg} . Black solid lines indicate phase boundaries between solid, liquid and gaseous Mg. First Mg condensation deposits were observed at supersaturation ratios of $S = 1.7 \pm 0.5$.

Figure 12: Deposit onset temperature, T_{deposit} , as a function of CO partial pressure, p_{CO} . Dashed line represents the logarithmic fit between $p_{\text{CO}} = 0.6 - 13.2$ mbar.

Proposed mechanism

In agreement with previous studies, CO₂ was found to rapidly oxidize Mg vapor in the gas phase via $\text{Mg(g)} + \text{CO}_2 \rightarrow \text{MgO} + \text{CO}$ [22, 35]. The observed deposits, polycrystalline MgO and submicron MgO particles are believed to be formed from MgO vapor deposition and homogeneous nucleation, respectively. Possible mechanism for carbon deposits are the heterogeneous reactions $\text{Mg(g)} + \text{CO} \rightarrow \text{MgO} + \text{C}$ and $2\text{CO} \rightarrow \text{CO}_2 + \text{C}$ which may take place on the reactor walls/deposits and small particles entrained in the gas flow [35, 38].

In the absence of CO₂, Mg(g) and CO were found to coexist in a metastable phase at high temperatures. Only at a temperature low enough, i.e. below T_{deposit} , oxidation of Mg(g) was observed and resulted in similar deposits as in experiments with CO₂. It is therefore suggested that formation of CO₂ via CO disproportionation below T_{deposit} is responsible for the break-down of the Mg-CO metastability. Once CO₂ is produced, it immediately reacts with Mg(g) to form MgO and carbon deposits as schematically shown in Figure 13. CO disproportionation further explains the observed dependence on partial pressures: With increasing p_{CO} , CO disproportionation is shifted towards higher temperatures (Figure 14) and hence higher CO₂ reaction rates which result in the observed reduction of Y_{Mg} and increase in T_{deposit} .

Below T_{condens} , the remaining Mg vapor condenses on the reactor walls and entrained MgO particles forming μm -sized Mg crystals and submicron Mg/MgO agglomerates, respectively. The well known surface oxidation of solid Mg deposits ($\text{Mg(s)} + \text{CO}_2 \rightarrow \text{MgO} + \text{CO}$ and $\text{Mg(s)} + \text{CO} \rightarrow \text{MgO} + \text{C}$) turned out to be much slower than the competing diffusion-phoretic driven condensation process discussed in detail in [39].

Figure 13: Schematic representation of dominating reactions and deposits when cooling down a stream of Mg(g) and CO.

Figure 14: Chemical equilibrium diagram of the Boudouard reaction $2\text{CO} \leftrightarrow \text{CO}_2 + \text{C}$ for a pressure of 0.8 mbar (solid lines) and 13.2 mbar (dashed lines) obtained by Gibbs free energy minimization [36].

4. Conclusions

A novel method to study metal vapor condensation/oxidation is presented. The experimental setup allows the study of metal vapor/oxidizer combinations at temperatures up to 1700°C and pressures as low as 0.1 mbar. It is hence suitable to study a variety of back reactions of interest in production processes of volatile metals as well as in metal/metal-oxide redox cycles. Measurements of the axial temperature profile, calculation of partial pressures and analysis of deposits within the condenser allowed for identification of deposit/condensation onset temperatures, supersaturation ratio and reaction mechanism. Experiments carried out with Mg(g)-CO₂ and Mg(g)-CO mixtures confirmed a fast reaction of Mg(g) in the presence of CO₂. In the presence of CO and at low supersaturation ratios ($S < 10$ -100), Mg(g) was heterogeneously condensing at high purity. Hence, under the studied conditions ($p_{\text{CO}} \approx p_{\text{Mg}} = 0.6$ -13.2 mbar, $T = 200$ -700°C) condensation of Mg(g) is much faster than the competing surface oxidation reactions. For successful Mg metal production via CTR, it is crucial to minimize CO₂ formation. Typically this is achieved at CO partial pressures < 3 mbar, resulting in Mg metal yields of $>90\text{w}\%$.

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Appendix A

For experiments carried out with CO, m_{Mg} , m_{MgO} and m_{C} are obtained by eqs. (A.1-A.3) assuming Mg oxidation taking place via $\text{Mg} + \text{CO} \rightarrow \text{MgO} + \text{C}$.

$$m_{\text{Mg}} = m_{\text{Mg,evap}} - \int_{t_0}^{t_{\text{final}}} (\dot{n}_{\text{CO,baseline}} - \dot{n}_{\text{CO}}(t)) dt \cdot M_{\text{Mg}} \quad (\text{A.1})$$

$$m_{\text{MgO}} = \int_{t_0}^{t_{\text{final}}} (\dot{n}_{\text{CO,baseline}} - \dot{n}_{\text{CO}}(t)) dt \cdot M_{\text{MgO}} \quad (\text{A.2})$$

$$m_{\text{C}} = \int_{t_0}^{t_{\text{final}}} (\dot{n}_{\text{CO,baseline}} - \dot{n}_{\text{CO}}(t)) dt \cdot M_{\text{C}} \quad (\text{A.3})$$

For experiments carried out with CO_2 , m_{Mg} , m_{MgO} and m_{C} are obtained by eqs. (A.4-A.6) assuming Mg oxidation taking place via $2\text{Mg} + \text{CO}_2 \rightarrow 2\text{MgO} + \text{C}$ and $\text{Mg} + \text{CO}_2 \rightarrow \text{MgO} + \text{CO}$.

$$m_{\text{Mg}} = m_{\text{Mg,evap}} - \int_{t_0}^{t_{\text{final}}} \left(2 \cdot (\dot{n}_{\text{CO}_2,\text{baseline}} - \dot{n}_{\text{CO}_2}(t)) - \dot{n}_{\text{CO}}(t) \right) dt \cdot M_{\text{Mg}} \quad (\text{A.4})$$

$$m_{\text{MgO}} = \int_{t_0}^{t_{\text{final}}} \left(2 \cdot (\dot{n}_{\text{CO}_2,\text{baseline}} - \dot{n}_{\text{CO}_2}(t)) - \dot{n}_{\text{CO}}(t) \right) dt \cdot M_{\text{MgO}} \quad (\text{A.5})$$

$$m_{\text{C}} = \int_{t_0}^{t_{\text{final}}} (\dot{n}_{\text{CO}_2,\text{baseline}} - \dot{n}_{\text{CO}_2}(t) - \dot{n}_{\text{CO}}(t)) dt \cdot M_{\text{C}} \quad (\text{A.6})$$

$m_{\text{Mg,evap}}$ is the mass of Mg evaporated during the entire experiment. t_0 and t_{final} are the times of start and end of Mg evaporation. $\dot{n}_{\text{CO,baseline}}$ and $\dot{n}_{\text{CO}_2,\text{baseline}}$ are the average molar flows prior to Mg evaporation. $\dot{n}_{\text{CO}}$ and $\dot{n}_{\text{CO}_2}$ are the molar flows measured during Mg evaporation and M_{Mg} , M_{MgO} and M_{C} are the molar masses of Mg, MgO and C.

Nomenclature

m = mass, g

M = molar mass, g mol⁻¹

$\dot{n}$	=	molar flow, mol s ⁻¹
p	=	pressure or partial pressure, mbar
S	=	supersaturation ratio, -
t	=	time, s
T	=	temperature, °C
$\dot{V}$	=	volume flow, sl/min
W	=	mass yield, w%
x	=	axial position, mm
Y	=	metal mass yield, w%

Subscripts

condens	=	condensed
evap	=	evaporated

References

- [1] J.P. Murray, A. Steinfeld, E.A. Fletcher, Metals, nitrides, and carbides via solar carbothermal reduction of metal oxides, *Energy*, 20 (1995) 695-704.
- [2] A. Donaldson, R.A. Cordes, Rapid plasma quenching for the production of ultrafine metal and ceramic powders, *JOM*, 57 (2005) 58-63.
- [3] M. Halmann, A. Frei, A. Steinfeld, Vacuum Carbothermic Reduction of Al₂O₃, BeO, MgO-CaO, TiO₂, ZrO₂, HfO₂ + ZrO₂, SiO₂, SiO₂ + Fe₂O₃, and GeO₂ to the Metals. A Thermodynamic Study, *Mineral Processing and Extractive Metallurgy Review*, 32 (2011) 247-266.
- [4] G. Levêque, S. Abanades, Investigation of thermal and carbothermal reduction of volatile oxides (ZnO, SnO₂, GeO₂, and MgO) via solar-driven vacuum thermogravimetry for thermochemical production of solar fuels, *Thermochim. Acta*, 605 (2015) 86-94.
- [5] B.A. Chubukov, A.W. Palumbo, S.C. Rowe, I. Hischier, A.J. Groehn, A.W. Weimer, Pressure dependent kinetics of magnesium oxide carbothermal reduction, *Thermochim. Acta*, 636 (2016)

23-32.

- [6] I. Vishnevetsky, M. Epstein, Solar carbothermic reduction of alumina, magnesia and boria under vacuum, *Solar Energy*, 111 (2015) 236-251.
- [7] F.J. Hansgirg, Thermal Reduction of Magnesium Compounds, *The Iron Age*, (1943) 56-63.
- [8] G. Brooks, S. Trang, P. Witt, M.N.H. Khan, M. Nagle, The carbothermic route to magnesium, *Jom*, 58 (2006) 51-55.
- [9] D. Gstoehl, A. Brambilla, L.O. Schunk, A. Steinfeld, A quenching apparatus for the gaseous products of the solar thermal dissociation of ZnO, *Journal of Materials Science*, 43 (2008) 4729-4736.
- [10] A. Koo, G.A. Brooks, M. Nagle, Nucleation and growth of Mg condensate during supersonic gas quenching, *J. Cryst. Growth*, 310 (2008) 2659-2667.
- [11] I. Alxneit, Assessing the feasibility of separating a stoichiometric mixture of zinc vapor and oxygen by a fast quench – Model calculations, *Solar Energy*, 82 (2008) 959-964.
- [12] J.H. Nicodemus, J.H. Davidson, Mechanisms of hydrolysis in a transverse jet zinc aerosol reactor, *Chemical Engineering Science*, 122 (2015) 514-522.
- [13] A. Weidenkaff, A. Steinfeld, A. Wokaun, P.O. Auer, B. Eichler, A. Reller, Direct Solar Thermal Dissociation of Zinc Oxide: Condensation and Crystallisation of Zinc in the Presence of Oxygen, *Solar Energy*, 65 (1999) 59-69.
- [14] N.X. Fu, T. Tamagawa, M. Kobayashi, M. Tanaka, Condensation of zinc vapor on solid media in Zn_(g)-CO-CO₂-Ar mixtures, *Metallurgical and Materials Transactions B*, 35 (2004) 625-631.
- [15] L.J. Venstrom, J.H. Davidson, The kinetics of the heterogeneous oxidation of zinc vapor by carbon dioxide, *Chemical Engineering Science*, 93 (2013) 163-172.
- [16] E. Aghion, B. Bronfin, D. Eliezer, The role of the magnesium industry in protecting the environment, *J. Mater. Process. Technol.*, 117 (2001) 381-385.
- [17] S. Das, Primary magnesium production costs for automotive applications, *JOM*, 60 (2008) 63-69.
- [18] L.H. Prentice, M.W. Nagle, T.R.D. Barton, S. Tassios, B.T. Kuan, P.J. Witt, K.K. Constanti-Carey, Carbothermal Production of Magnesium: CSIRO's MagSonic™ 8482; Process, in: S.N. Mathaudhu, W.H. Sillekens, N.R. Neelameggham, N. Hort (Eds.) *Magnesium Technology 2012*, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2012.
- [19] R. Winand, M. van Gysel, A. Fontana, L. Segers, J.-C. Carlier, Production of magnesium by

- vacuum carbothermic reduction of calcined dolomite, in: Transactions - Institution of Mining and Metallurgy. Section C. Mineral processing & extractive metallurgy, 1990, pp. C105-C112.
- [20] C.-b. Yang, Y. Tian, T. Qu, B. Yang, B.-q. Xu, Y.-n. Dai, Production of magnesium during carbothermal reduction of magnesium oxide by differential condensation of magnesium and alkali vapours, *Journal of Magnesium and Alloys*, 1 (2013) 323 - 329.
- [21] F.T. Ferguson, J.A. Nuth, L.U. Lilleleht, Experimental studies of the vapor phase nucleation of refractory compounds. IV. The condensation of magnesium, *Journal of Chemical Physics*, 104 (1996) 3205-3210.
- [22] E. Shafirovich, A. Varma, Metal-CO₂ Propulsion for Mars Missions: Current Status and Opportunities, *Journal of Propulsion and Power*, 24 (2008) 385-394.
- [23] A.Y. Lukin, A.M. Stepanov, Theoretical investigation of processes of condensed product formation during combustion of metal particles, *Combustion, Explosion and Shock Waves*, 19 (1983) 411-414.
- [24] A. Abbud-Madrid, A. Modak, M.C. Branch, J.W. Daily, Combustion of Magnesium with Carbon Dioxide and Carbon Monoxide at Low Gravity, *Journal of Propulsion and Power*, 17 (2001) 852-859.
- [25] K. Kamata, Y. Shibata, Y. Kishi, MgO films deposited by chemical vapour deposition, *Journal of Materials Science Letters*, 3 (1984) 423-426.
- [26] R. Huang, A.H. Kitai, Preparation and characterization of thin films of MgO, Al₂O₃ and MgAl₂O₄ by atomic layer deposition, *Journal of Electronic Materials*, 22 (1993) 215-220.
- [27] J.-H. Boo, S.-B. Lee, K.-S. Yu, W. Koh, Y. Kim, Growth of magnesium oxide thin films using single molecular precursors by metal–organic chemical vapor deposition, *Thin Solid Films*, 341 (1999) 63-67.
- [28] E.R. Buckle, K.J.A. Mawella, Condensation and morphology of magnesium particles in vapour plumes, *Journal of Materials Science*, 20 (1985) 2647-2652.
- [29] J. Dirksen, T. Ring, Fundamentals of Crystallisation: Kinetic Effects on Particle Size Distribution and Morphology, *Chemical Engineering Science*, 46 (1991) 2389-2427.
- [30] U. Goldshleger, E. Shafirovich, Combustion regimes of magnesium in carbon oxides. 2. Combustion in CO, *Combustion Explosion and Shock Waves*, 36 (2000) 220-226.
- [31] V. Fournier, P. Marcus, I. Olefjord, Oxidation of magnesium, *Surface and Interface Analysis*, 34 (2002) 494-497.
- [32] C. Chen, S. Splinter, T. Do, N. McIntyre, Measurement of oxide film growth on Mg and Al

surfaces over extended periods using XPS, Surface Science, 382 (1997) L652-L657.

[33] M. Kurth, P. Graat, H. Carstanjen, E. Mittemeijer, The initial oxidation of magnesium: an in situ study with XPS, HERDA and ellipsometry, Surface and Interface Analysis, 38 (2006) 931-940.

[34] C.-b. Yang, Y. Tian, T. Qu, B. Yang, B.-q. Xu, Y.-n. Dai, Analysis of the behavior of magnesium and CO vapor in the carbothermic reduction of magnesia in a vacuum, Journal of Magnesium and Alloys, 2 (2014) 50-58.

[35] E.Y. Shafirovich, U.I. Goldshleger, Combustion of Magnesium Particles in CO₂/CO Mixtures, Combustion Science and Technology, 84 (1992) 33-43.

[36] C.W. Bale, A.D. Pelton, W.T. Thompson, FactSage 6.4, in, 2013.

[37] B. Marchon, W.T. Tysoe, J. Carrazza, H. Heinemann, G.A. Somorjai, Reactive and kinetic properties of carbon monoxide and carbon dioxide on a graphite surface, The Journal of Physical Chemistry, 92 (1988) 5744-5749.

[38] M. Kogler, E.-M. Köck, B. Klötzer, T. Schachinger, W. Wallisch, R. Henn, C.W. Huck, C. Hejny, S. Penner, High-Temperature Carbon Deposition on Oxide Surfaces by CO Disproportionation, The Journal of Physical Chemistry C, 120 (2016) 1795-1807.

[39] I.V. Frishberg, Gas-phase method of metal powder production, in: O.D. Neikov, S.S. Naboychenko, G. Dowson (Eds.) Handbook of Non-Ferrous Metal Powders: Technologies and Applications, Elsevier, Oxford, UK, 2009.

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Graphical abstract