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A novel experimental method to study metal vapor condensation/oxidation: Mg in CO and CO_2 at reduced pressures

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ABSTRACT

A novel method is presented to study magnesium metal vapor condensation/oxidation in CO and CO_2 atmosphere at reduced pressures. Mg(s) was evaporated and mixed with an equimolar amount of CO or CO_2 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 CO_2, 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 >90 w% 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.

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, CO_2 or O_2 (Murray et al., 1995; Donaldson and Cordes, 2005; Halmann et al., 2011; Levêque and Abanades, 2015; Chubukov et al., 2016; Vishnevetsky and Epstein, 2015). 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 (Hansgirg, 1943; Brooks et al., 2006). 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 (Donaldson and Cordes, 2005; Gstoehl et al., 2008; Koo et al., 2008). 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 (Alxneit, 2008; Nicodemus and Davidson, 2015). 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 (Weidenkaff et al., 1999; Fu et al., 2004; Venstrom and Davidson, 2013), 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 CO_2 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

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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

challenges of development and scale up, primarily related to the back-reaction, $Mg(g) + CO \rightarrow MgO + C$, upon cool-down (Brooks et al., 2006; Aghion et al., 2001; Das, 2008). 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 (Prentice et al., 2012; Winand et al., 1990; Yang et al., 2013). 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

2.1. Experimental setup

The setup consists of two vertical coaxial Al_2O_3 tubes forming three distinct zones for: (1) Mg evaporation, (2) Mg-oxidizer mixing and gaseous oxidation and (3) Mg condensation and condensate oxidation (Fig. 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 Al_2O_3 crucible containing Mg metal pieces (American Elements, 99.9%, 1–10 mm). 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 CO_2 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, 0.4 mm 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.

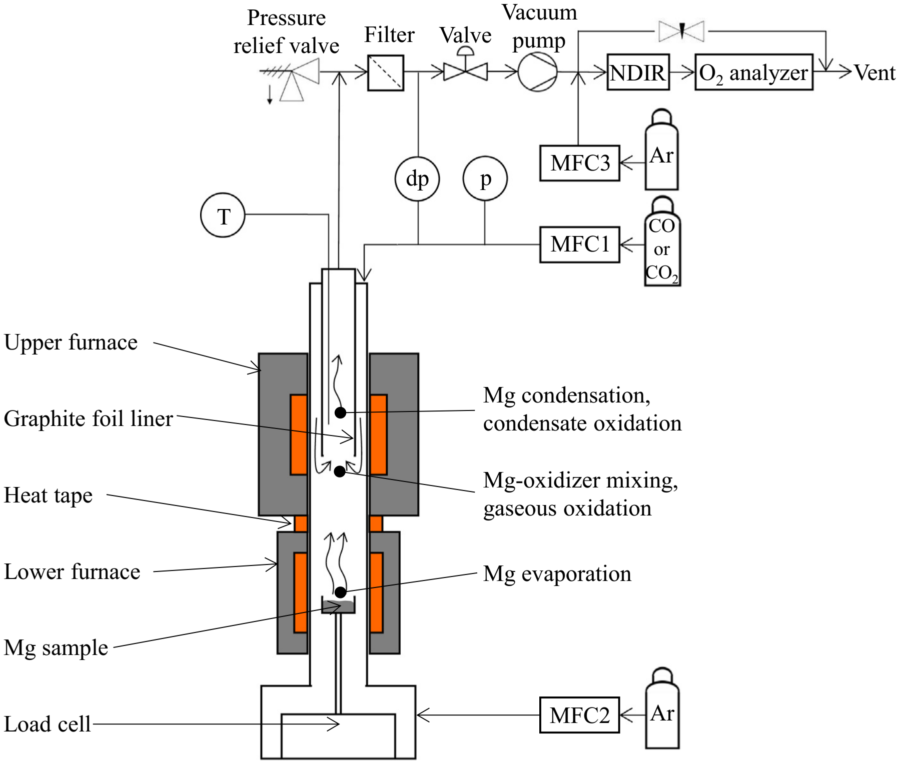

Fig. 1. Schematic of Mg evaporation-condensation system with distinct zones for (1) Mg evaporation, (2) Mg-oxidizer mixing and gaseous oxidation and (3) Mg condensation and condensate oxidation.