Analysis of the behavior of magnesium and CO vapor in the carbothermic reduction of magnesia in a vacuum

Cheng-bo Yang\textsuperscript{a,b,c}, Yang Tian\textsuperscript{a,b,c,*}, Tao Qu\textsuperscript{a,b,c}, Bin Yang\textsuperscript{a,b,c}, Bao-qiang Xu\textsuperscript{a,b,c}, Yong-nian Dai\textsuperscript{a,b,c}

\textsuperscript{a} National Engineering Laboratory for Vacuum Metallurgy, Kunming University of Science and Technology, Kunming 650093, China
\textsuperscript{b} Key Laboratory for Nonferrous Vacuum Metallurgy of Yunnan Province, Kunming 650093, China
\textsuperscript{c} State Key Laboratory Breeding Base of Complex Nonferrous Metal Resources Clear Utilization in Yunnan Province, Kunming 650093, China

Received 16 January 2014; revised 14 February 2014; accepted 17 February 2014
Available online 14 April 2014

Abstract

The aim of this paper is to experimentally investigate the behavior of magnesium and carbon monoxide vapor in the carbothermic reduction of magnesia at condensing zone temperatures ranging from 923 K to 1223 K. The phase, surface morphology, and composition of the condensates obtained were examined by means of scanning electron microscopy and energy-dispersive X-ray spectroscopy. The main findings of this paper include: the reverse reaction products, carbon and magnesium oxide, were formed following the process of magnesium vapor condensation, preventing two metal clusters from mutually combining. Moreover, the nearer the temperature of the condensation zone approached the liquid transformation temperature (810–910 K), the lower the rate of the reverse reaction between carbon monoxide and magnesium vapor. Decrease in the rate of the reverse reaction of magnesium was possible by controlling the condensation temperature.

1. Introduction

Carbothermal reduction has been recognized as conceptually the simplest and cleanest route to produce magnesium metal [1]. Winand [2] first discussed the process of producing magnesium vapor through the reduction of magnesia by carbon; however, the experimental conditions and condenser setup necessary to condense the vapor into liquid or solid magnesium were not elucidated. Various experiments to obtain magnesium by carbothermal reduction have failed due to clogging [3]. Direct extraction of magnesium from magnesia by carbothermic reduction in a vacuum has been extensively studied [4,5]. Such a process requires less energy than previous methods and economically more efficient, but the products obtained have a poor crystalline morphology and the method cannot easily be adapted to large-scale industrialization [6]. And most of the researchers believed that the
developments on the condensation of magnesium produced by carbothermic reduction just concentrated on two process routes: the “quench” route and the “solvent” route [7]. Among significant improvements in this field, the work by CSIRO successfully demonstrated a technology that used supersonic quenching of magnesium vapor (the MagSonic™ process), resulting in rapid coagulation of magnesium vapor, and reduced magnesium vapor and CO responses [8,9]. We have also explored the carbothermic reduction of magnesia in vacuum for many years [10,11], and rather than “quench” or “solvent” route additional process is needed and we aim to directly get the qualified product from condenser located inside the vacuum chamber through control condensation requirement. While we speculate that reversion reactions between magnesium vapor and CO are unavoidable [12], there is still no way of knowing the role of uncoagulable CO vapor in the carbothermic reduction of magnesia, as well as the products of the reverse reaction. In this work, we aim to control the phase transition and formation of magnesium crystals in a vacuum system by a new type of condenser and reduce the rate of the reverse reaction simultaneously. Reports on such topics are scarce and this study is undertaken to bridge these gaps in the literature.

2. Theoretical analysis

The rate at which nucleation occurs is related to the chemical makeup of the critical nucleus and the gas concentration of the nucleating species is an important variable in nucleation of vapor in vacuum condensation. Nucleation from the vapor phase is homomolecular when a single type of gas is involved in the formation of a critical nucleus and heteromolecular when several types of gases are involved in the formation of a critical nucleus [13]. In the absence of existing heterogeneities, homomolecular nucleation requires an extremely high supersaturation. Magnesium vapor cluster formation is closely linked with the gas phase reaction because the abundances required for nucleation to occur are achieved through a gradual increase in concentration of the nucleating vapors produced from carbothermic reduction [14].

Under a vacuum pressure of 60 Pa, a number of possible reversion reactions can take place during cooling of an Mg/CO/inert gas mixture.

Gas phase reversion reaction:

\[ \text{Mg}(g) + \text{CO}(g) = \text{MgO}(s) + \text{C}(s) \] (1)

Liquid phase reversion reaction:

\[ \text{Mg}(l) + \text{CO}(g) = \text{MgO}(s) + \text{C}(s) \] (2)

Solid phase reversion reaction:

\[ \text{Mg}(s) + \text{CO}(g) = \text{MgO}(s) + \text{C}(s) \] (3)

The Gibbs free energy reactions (1)–(3) at different temperatures and pressures were evaluated, and the results are reported in Fig. 1. Thermodynamically, these reversion reactions were exothermic; the gas phase reversion will commence as soon as a saturated gas mixture was cooled. When magnesium steam enters the condensation area, so long as the condensation temperature on the temperature of magnesium gas–liquid transition is controlled, the reverse reaction should be decreased because the reaction between CO and liquid-magnesium is harder than solid phase reaction. After the vapor liquefaction, magnesium vapor will nucleate in the liquid phase and bulk magnesium with large grain size will be obtained. This indicates a means to fundamentally solve the effective consolidation of fine powders in the carbon thermal reduction process.

2.1. Gas–liquid phase transitions

The dew-point temperature is defined as the temperature when the pressure of metal vapor produced by the reaction of different reduction temperatures is equal to the saturated vapor pressure of pure metal [15].

For the carbothermic reduction of magnesia, that is, the following reaction:

\[ \text{MgO}(s) + \text{C}(s) = \text{Mg}(g) + \text{C}(s) \]

The relationship between the different reduction temperatures and partial pressures of magnesium vapor can be obtained using Eqs. (1a) and (2a) shown below:

\[ \Delta G^0 = 648101 + 30.87 \lg T - 403.55T \] (1a)

\[ \lg P_{\text{Mg}} = \frac{-\Delta G^0}{4.606RT} \] (2a)
where $\Delta G^0$ is Gibbs free energy, $P_{Mg}$ is the partial pressure of magnesium vapor and $T$ is the reduction temperature.

The saturated vapor pressure of magnesium can be calculated using Eqs. (3a) and (4) [14]:

\[
\lg P^* = -7780/T - 0.855\lg T + 13.535 \quad (298 \text{ K} - 923 \text{ K})
\]

\[
\lg P^* = -7750T^{-1} - 1.411\lg T + 14.915 \quad (923 \text{ K} \text{ and higher})
\]

where $P^*$ is the saturated vapor pressure of magnesium and $T$ is the temperature.

Fig. 2 indicates the relationship between the saturated vapor pressure and partial pressure; the pressure increases with increasing $T$. The partial pressure of magnesium vapor exceeds that of the saturated gas at higher evaporation temperatures, increasing the likelihood of a reunion of magnesium atoms through collisions, which is beneficial to the condensed nucleation of magnesium atoms and magnesium vapor condensation.

Fig. 3 indicates the relationship between the minimum condensation temperature ($T_{\text{min}}$) and the dew-point temperature. In Fig. 3, increasing the partial pressure also increases the dew-point temperature, which partly reflects the minimum temperature necessary for magnesium vapor crystals to nucleate and grow in the liquid phase.

2.2. The possible gas–liquid phase transition

The lifetime of cluster is extremely short, but since a dramatically large number of clusters form and dissociate at any time, a few can reach the critical size and continue to grow spontaneously to form larger particles [16,19]. From an energetic perspective, the free energy of cluster formation increases with cluster size prior to but decreases after the critical nucleus, reaching a maximal value at the critical size [17,20]. Hence, the critical nucleus can be identified if the free energy surface leading to liquid nucleation growth is available [18].

Based on the uniform nucleation theory, which affected by the surface tension, resulted in the liquid nucleus of globularity shapes. According to Kelvin’s formula, different metals have different critical nucleation radii [15], which can be determined by Eq. (5) with respect to $r_k$.

\[
r_k = \frac{2\sigma_{lv} M}{\rho R T \ln(p_r/p_0)}
\]

where $\sigma_{lv}$ is the coefficient of surface tension, $M$ is the relative atomic weight, $\rho$ is density, $R$ is Boltzmann constant, $T$ is temperature, $p_t$ and $p_0$ are the vapor pressure of the curved surface and the vapor pressure of the surface, respectively.

The number of nucleation atomic in liquid metal $N$ can be calculated according to the following expression:

\[
N = \left(\frac{4}{3}\pi r_k^3 \rho}{(M/N_A)}
\]

where $r_k$ is the critical nucleation radius that we have obtained by Eq. (5), $N_A$ is Avogadro constant.

As Table 1 shows, on the basis of analyzing the relationship between surface tension and temperature, respectively, we got the relationship between $T$ and $r_k$, $r_k$, and $N$. When magnesium vapor is in the stage of condensation, the heat exchanging between vapor and walls occurs simultaneously, magnesium vapor is being saturated gradually while the temperature of system decreases. Then reach the advantageous conditions for the formation of liquid nucleus. The number of atoms needed for nucleation will gradually decrease with the gradual increase in the supersaturation of magnesium vapor. From
1, it is known that the critical radius of the liquid core decreases with the increasing condensing temperature and nucleation requires fewer atoms. When the temperature was close to 810 K, the liquid nucleation radius of magnesium vapor reaches a minimum. According to related references [15], if there is condensation when nucleation, the metal vapor would coagulate at relatively lower saturated degree. So through above analysis, under our vacuum experimental conditions, as long as the condensation is controlled at the right temperature, the magnesium vapor approached to nucleation and growth from liquid phase was possible.

3. Experimental

Materials were vacuum distilled using an internally heated vacuum furnace (Fig 4a). Comparative experiments were done with constant magnesium vapor concentration of 1 and varying CO mole ratio from 1/4 to 3/4, and these processes could be achieved by double evaporation apparatus, in which the top reaction crucible controlled the CO concentration through raw material ratios, and the lower Mg sublimation crucible controlled the rest of magnesium vapor concentration by evaporating pure magnesium, thus maintaining the overall magnesium vapor concentration at 1.

The longitudinal section of the multistage condenser is shown in Fig. 4b. The temperature gradient between evaporation area and the first condensation area of the multi-level condensing collection devices was $\Delta T_1 = 7$ K/mm, temperature gradient between the first level and the second was $\Delta T_2 = 6$ K/mm, temperature gradient between the second level and the third was $\Delta T_3 = 0.5$ K/mm, and temperature gradient between the third level and the last was $\Delta T_4 = 0.3$ K/mm.

Influences of condensation temperature, temperature gradient and the partial pressure of magnesium vapor on the metal magnesium condensation were investigated. Fig. 5(a)–(d), respectively, indicates the collection efficiency of the four condensation layers with $T_{\text{min}}$ at 923, 1023, 1123, and 1223 K. The results reflect the ability of the condensing layer with different temperatures to catch magnesium steam at different condensate temperatures. The higher the evaporation temperature of metal magnesium, the larger energy the magnesium steam will carry when running into the condenser. Thus, a moderate temperature gradient eases the phase transition from gas $\rightarrow$ liquid $\rightarrow$ solid. As shown in Fig. 5, with increased condensation temperature, the magnesium collection ratio is increased. At the maximum collection ratio level, the condensation temperature is relatively closer to the gas–liquid transition temperature and the temperature gradient also decreases compared to the former layer. The closer the condensation temperature is to the gas–liquid phase transition temperature and the smaller the temperature gradient is, the smaller the probability of reaction between magnesium and CO. Thus, magnesium vapor condensation through liquid phase transformation is easier and a higher quality of condensed magnesium is obtained.

4. Results and discussion

We compared the results of the condensates of magnesium vapor at the same condensing condition. Fig. 6 shows scanning electron microscopy (SEM) micrographs of magnesium vapor condensates collected in the third condenser level when $T_{\text{min}} = 923$ K at a magnesium vapor concentration of 1. Fig. 7

<table>
<thead>
<tr>
<th>Temperature (T/K)</th>
<th>Critical radial ($r_k$/m)</th>
<th>Atomic number ($N$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>770</td>
<td>$1.02 \times 10^{-3}$</td>
<td>174,617</td>
</tr>
<tr>
<td>790</td>
<td>$2.95 \times 10^{-3}$</td>
<td>4123</td>
</tr>
<tr>
<td>810</td>
<td>$-4.07 \times 10^{-3}$</td>
<td>–</td>
</tr>
<tr>
<td>830</td>
<td>$-1.15 \times 10^{-3}$</td>
<td>–</td>
</tr>
<tr>
<td>850</td>
<td>$-1.80 \times 10^{-3}$</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 4. The experimental equipment: (a) schematic diagram of vacuum furnace; and (b) the longitudinal section of the multistage condenser.
shows SEM micrographs of condensed products collected in the third condenser level when $T_{\text{min}} = 923$ K at a magnesium vapor concentration 1 and CO mole ratio of 1/2.

Fig. 7 shows irregular shaped condensation products with a non-compact structure that features numerous small openings where carbon can be seen. In contrast, distillation products in Fig. 6 show irregular shapes with a compact structure and good crystallinity.

Loosely crystallized magnesium in Fig. 7 was due to the carbon and magnesia produced by the reverse reaction. The

![Graph showing collection ratio of four condensation layers at different $T_{\text{min}}$.](image)

**Fig. 5.** The collection ratio of the four condensation layers at different $T_{\text{min}}$: (a), $T_{\text{min}} = 923$ K; (b), $T_{\text{min}} = 1023$ K; (c), $T_{\text{min}} = 1123$ K; (d), $T_{\text{min}} = 1223$ K.

![SEM images of condensates of pure magnesium when $T_{\text{min}} = 923$ K at a magnesium vapor concentration of 1: (a) magnified 30 times; and (b) magnified 200 times.](image)

**Fig. 6.** SEM images of condensates of pure magnesium when $T_{\text{min}} = 923$ K at a magnesium vapor concentration of 1: (a) magnified 30 times; and (b) magnified 200 times.
carbon and magnesia obtained by the reverse reaction block the aggregation of nucleating vapors and prevent coalescence, thereby decreasing the rates of magnesium nucleation and crystal growth. Analysis of the difference in vapor condensation between pure magnesium vapor and a combination of CO and magnesium vapors showed that uncoagulable CO vapor decreases the partial pressure and concentration of magnesium vapor above the condensation surface, decreases the rate of collisions and nucleation between magnesium atoms, shortens the mean free path of magnesium atoms, and is involved in the reaction of magnesium vapor. Large and thermodynamically stable clusters formed during a nucleation event must grow quickly so that they are not scavenged by coagulation through collisions with existing larger particles. While the uncoagulable CO vapor, as an existing heterogeneity, could be helpful for nucleation at extremely low supersaturation; the nucleated magnesium vapor clusters were covered with the reverse reaction products of C and MgO such that two clusters are prevented from combining mutually.

4.1. Influence of condensation temperature and the temperature gradient on the reverse reaction

Metal magnesium with different crystal morphologies and impurity contents were obtained from the 1st to 4th layer of the multi-level condenser when the minimum outer layer temperatures \(T_{\text{min}}\) of the condenser were held at 923, 1023, 1123, and 1223 K, respectively, at an average vacuum pressure of 60 Pa. We found that at different \(T_{\text{min}}\), the nearer the temperature of the condensation zone approached the temperature of liquid transition, the lower the rate of the reverse reaction between CO and magnesium vapor; this observation was in accordance with the theoretical analysis. Figs. 8 and 9 show X-ray diffraction (XRD) results and SEM images, respectively, of the condensates from the 1st to the 4th condensation level when \(T_{\text{min}} = 923\) K at a CO mole ratio of 3/4. Fig. 8 shows that the intensities of the XRD peaks for magnesium increased with decreasing condensation temperature and difference in temperature gradient. The intensities of the XRD peaks for magnesium oxide showed marked changes, i.e., the intensity of diffraction peaks of magnesium oxide significantly decreased in the first layer of the condenser, which had the largest temperature gradient, and then almost completely disappeared in the third layer of the condenser, where the condensation temperature approached the liquid transition temperature and the peaks of magnesium increased sharply.

As shown in Fig. 9, the crystal morphologies and impurity contents of magnesium crystals varied with decreasing condensation temperature and gradient. In the first layer, where a large amount of heat exchange and heat loss occurs...
because of the large gradient, magnesium vapor crossed the liquid phase and directly condensed into solid powder. Thus, we obtained flocked magnesium, which has a higher degree of oxidation. We can see from Fig. 10 that something like a flocking substance was the product of the reverse reaction of magnesium. Bulk magnesium began to appear in the second condensation layer, but some flocking floe products remained. We obtained the best condensation products from the third layer. The phenomenon of supersaturation steaming through liquid phase uniform growth was even more apparent after the liquid–gas phase transformation, forming clear crystal boundaries and compact structures without obvious oxidation.

Fig. 9. SEM images of the condensed products when \( T_{\text{min}} = 923 \) K at magnesium concentration of 1 and CO mole ratio of 3/4 from 1st level to the 4th level (a–d): (a) 1st level; (b) 2nd level; (c) 3rd level; and (d) 4th level.

Fig. 10. SEM images of flocked substances in the condensed products: (a) magnified 2000 times; and (b) magnified 10,000 times.
Bulk magnesium was still obtained, but it was oxidized by CO in the last layer. And some similar results were obtained after comparing the results of others at different $T_{\text{min}}$.

Thus, control of the condensation temperature and the gradient in the condensation zone tends to change the rate of the reverse reaction of magnesium.

4.2. Influence of the vapor partial pressure on the reverse reaction

After confirming that the condensation temperature and gradient may decrease the rate of the reverse reaction, we tested the effect of the partial pressure on the condensation of CO and magnesium vapors. Keeping the magnesium vapor concentration constant at 1, decreasing the concentration of CO increased the corresponding partial pressure of magnesium in the condensation system. In contrast to Fig. 9, Fig. 11 shows SEM images of the condensates from the first to the fourth condensation levels at the same $T_{\text{min}}$ but different CO mole ratios.

From the results obtained, we found that the morphology of magnesium crystals significantly changed from irregular growth with rough interfaces to regular growth with large, fused clusters as the magnesium vapor concentration increased. The oxidation rate decreased with increasing crystallization quality. The increase in concentration improves the partial pressure of magnesium steam on the condensing surface. Thus reduced the likelihood of collisions between magnesium steam and carbon monoxide atoms. Consequently, the oxidation rate decreases to yield higher-purity crystallized magnesium.

5. Conclusion

(1) At a vacuum pressure of 60 Pa, after the oversaturation of magnesium vapor, the likelihood that available magnesium atoms will collide with each other and agglomerate increases. If magnesium vapor condenses at temperature lower than those that pass the liquid phase, it will directly condense to the solid phase.

(2) The quality of condensed magnesium was associated with the concentration of CO. Under the appropriate condensation temperature and temperature gradient conditions, increasing the magnesium vapor concentration could decrease the rate of the reverse reaction of magnesium. This phenomenon explains why we obtained products with
a decentralized structure and low metal luster. Thus, a method to separate the magnesium vapor from the carbon monoxide must be determined. Such a method could be a key to obtain a better crystalline structure.

(3) Controlling the temperature of the condensation zone at $810 \sim 910 \text{ K}$ such that it approaches the temperature of liquid transition and setting a smaller temperature gradient at $\Delta T = 0.5 \text{ K/mm}$ not only decreases heat loss but also increases the liquid nucleation rate and improves the magnesium steam concentration. Consequently, crystal quality was also improved. Moreover, it helps to avoid rapid solidification while extending the fusion time of the magnesium clusters.

References