

Magnesium vapor nucleation in phase transitions and condensation under vacuum conditions

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Abstract: Recent findings related to coagulable magnesium vapor nucleation and growth in vacuum were assessed critically, with emphasis on understanding these processes at a fundamental molecular level. The effects of magnesium vapor pressure, condensation temperature, and condensation zone temperature gradient on magnesium vapor nucleation in phase transitions and condensation from atomic collision and coacervation with collision under vacuum conditions were discussed. Magnesium powder and magnesium lump condensates were produced under different conditions and characterized by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). The right condensation zone temperature approach to the liquid transition primarily improved the magnesium vapor concentration rate. The gas–solid phase transition was primarily inhibited by setting a small condenser temperature gradient. Under the right condensation temperature and temperature gradients, increasing magnesium vapor partial pressure improved crystallization and reduced the oxidation rate.

Key words: magnesium vapor; vacuum; phase transition; condensation; nucleation

1 Introduction

Magnesium is the eighth most abundant element on earth (approximately 2.5% by mass). This light weight metal, used in industrial products from cars and planes to electronics, has recently been the object of attention in the metals community. Magnesium production by Pidgeon process in China has been expanding for the last 15 years or so, by the year 2011 with the proportion of 81% of the total magnesium produced, reaching a stage where China effectively controls the supply of magnesium [1]. While Pidgeon process can produce significant quantities of “cheap” magnesium for western consumers, concern over quality and the environmental impact of some of the smaller plants is leading the Chinese government to impose tighter restrictions on them. By 2010 small magnesium plants in Henan and Shanxi Provinces were closed because of pollution

problems and weak prices. So, intensive labor, successively declined price as well as to the huge harm to the environment make more and more researcher pay attention to the carbothermic route, which is a way of more ecological and less power.

A number of processes based on carbothermic reduction have been proposed over the last century including some large-scale industrial trials during World War II [2]. These developments all have concentrated on two process routes: the “quench” route and the “solvent” route. And all of these approaches failed to overcome the central problems of reversion and effective consolidation of fine powders [3]. Current work in the United States [4] and Australia [5,6] is based on the use of Laval nozzles to provide high rate of quenching ($>10^6$ °C/s) to overcome the issue of reversion, that is, Mg(g) and CO(g) recombine during cooling to produce a metal heavily contaminated by MgO. This problem is further complicated by the observation that very rapid cooling of

the gases to avoid reversion will result in the formation of extremely fine powders, which in the case of magnesium is pyrophoric and difficult to handle and process.

Research at the Commonwealth Scientific and Industrial Research Organization (CSIRO), through the carbothermic reduction, is currently focused on step change improvements in the production of metallothermic processes, aiming at lowering energy usage, increasing productivity and reducing the overall environmental impact [7]. CSIRO is currently studying the carbothermic reduction of magnesia with graphite at 1600 °C using a Laval nozzle to quench the resultant magnesia vapor [8–12].

Inferior crystalline morphology of the magnesium condensed from carbothermic route, which has often been the largest industrialization obstacle, led National Engineering Laboratory for Vacuum Metallurgy in China (NELVMC) to explore the carbothermic reduction of magnesia in vacuum condition for many years. And the magnesium vapor condensation and reverse reaction have been studied. Based on the findings of various studies, such as those by ZHONG [13], LI [14], TIAN et al [15], condensation temperature and temperature gradients are found to have a significant impact on the condensation rate of magnesium vapor. Despite the Pidgeon process has been developed for 80 years, but it doesn't have a problem on condensation of singleness magnesium. So, there is very little information on magnesium vapor condensation in vacuum of the carbothermic preparation, and the ready-made data are so seldom [16–18]. Therefore, the role of the heterogeneous gas-phase reaction between CO and magnesium vapor at the condensation conditions under vacuum is important, and the issue is currently the subjects of study at NELVMC; moreover, condensation behaviors of alkali vapor and other metal vapors in vacuum carbothermic are studied. So, the above subjects would be figured out until the condensation mechanism of magnesium vapors can be understood, in the research described in this work, the impact of condensing conditions on unitary magnesium vapor is also quite critical and becomes the basic theme.

2 Theoretical analysis

2.1 Influence of magnesium partial pressure on nucleation

Nucleation is generally defined as the creation of molecular embryos or clusters prior to the formation of a new phase during the vapor→liquid→solid transitions. Physical vapor growth can be achieved through vapor condensation [19]. The main controlling factors influencing the pressure and temperature of vapors

around the solid determine the crystal growth rate, conditions, and morphology [20].

A broad range pressure of vacuum can be studied, however, in this study, the pressure of 40 Pa was chosen under which the lab equipment can handle without appreciable error. Thus, the system pressure p_s at 40 Pa was fixed to simplify our calculations and yet retain the generalization. The saturated vapor pressure of magnesium can be calculated using the following equations [21]:

$$\lg p^* = -7780/T - 0.855 \lg T + 13.535 \quad (298 \text{ K} \leq T \leq 923 \text{ K}) \quad (1)$$

$$\lg p^* = -7750/T - 1.411 \lg T + 14.915 \quad (T > 923 \text{ K}) \quad (2)$$

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

Figure 1 indicates the relationship between p^* and T . As shown in Fig. 1, p^* increases with increasing T , whereas p_s is constant at 40 Pa. When magnesium vapor pressure $p_{\text{Mg}} = p^* = 40 \text{ Pa}$, $T = 823 \text{ K}$. Generally, the temperature in the high temperature zone is greater than 823 K, so in the high temperature zone with system pressure $p_s = 40 \text{ Pa}$, magnesium vapor does not reach saturation, which does well to magnesium evaporation. While when the vapor enters into the condensing zone with temperature below 823 K, magnesium vapor under the pressure will be in hyper saturated state, which satisfies the condensing condition. So, with specific system temperature, the smaller the system residual pressure p_s is, the larger the magnesium vapor pressure difference between p^* at this temperature is. Namely, super-saturation degree of magnesium vapor is higher and the nucleation is easier.

In case of temperature in high temperature zone T , decreasing the temperature in the condensing zone can also achieve the above effect. According to the above theory, in circumstance with specific operation process,

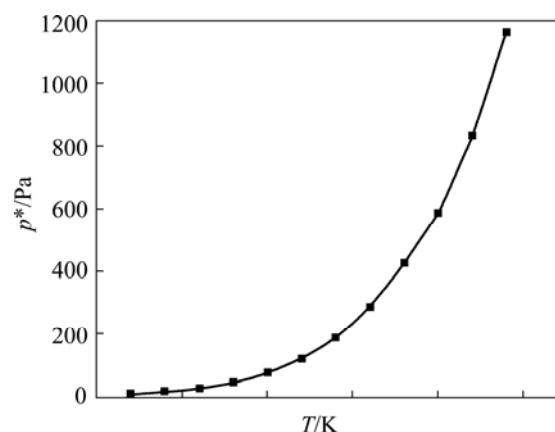


Fig. 1 Relationship between saturated vapor pressure of Mg and temperature

the lower the condensing temperature is, the better it is. However, the fact is not so. Because the crystallized magnesium powder with extremely high oxidation rate will generate if the condensing temperature is too low. It is when the condensation temperature is higher that magnesium crystalline grain is bigger, dense and its oxidation rate is relatively lower. Therefore, it can be known that it is related to not only the pressure but also the condensation temperature.

2.2 Influence of temperature on magnesium vapor nucleation and condensation

2.2.1 Influence of condensation temperature

The formation of molecular clusters occurs through the random collisions and rearrangements of atoms or molecules of the pre-existing phase. The thermal velocity and collisions among atoms could precede clustering and nucleation. The number of atomic collisions is an important factor influencing nucleation rate and magnesium clustering [22].

The relationship between temperature, pressure, and the number of atomic collisions per unit of time can be obtained using the following expression [23]:

$$Z = \frac{\sqrt{2}\pi d^2 P \bar{v}}{RT} \quad (3)$$

where Z is the number of atomic collisions per unit of time; d is the diameter of the magnesium atomic; \bar{v} is the average speed of the magnesium atomic; R is the Boltzmann constant; and T is temperature.

Figure 2 indicates the relationship between Z and T when $p=p^*$. In the high temperature zone with temperature higher than 823 K, magnesium vapor is in superheated state and has larger kinetic energy, and the collision frequency of atoms actually is more. If the condensing temperature is too low and Z reduces too fast, the rapid growth of the nucleation rate will result in a number of vapor nucleating simultaneously and condensing down. In this way, magnesium powder can be obtained. If magnesium vapor is not in extremely cold state and Z slowly declines, magnesium vapor will go through gas-liquid phase changes. After the vapor liquefaction, magnesium vapor will nucleate in liquid phase, and bulk magnesium with large grain size will be obtained. This indicates a method to fundamentally solve the effective consolidation of fine powders in the carbon thermal reduction process. Therefore, the condensing temperature should not be too low because low condensing temperature will lead to a large number of magnesium powders.

2.2.2 Influence of condensation temperature gradient on magnesium vapor nucleation and condensation

Through above analysis, the right temperature of

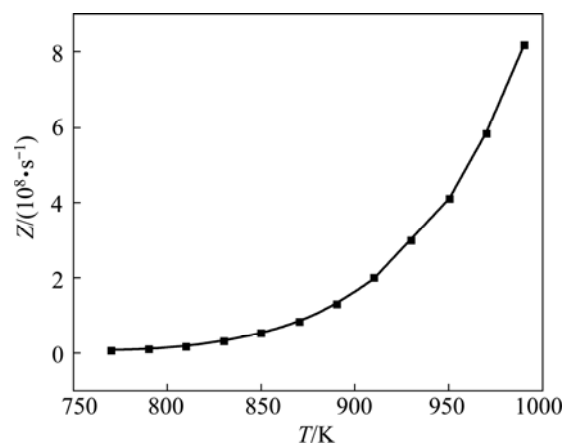


Fig. 2 Relationship between temperature and number of atomic collisions per unit of time

gas-liquid transformation could effectively solve the effective consolidation of fine powders. The lifetime of clusters is extremely short, but because a very large number of clusters form and dissociate at any given time, a few can reach critical size and continue to grow spontaneously to form larger particles [24]. From an energetic perspective, the free energy of cluster formation increases with cluster size first but decreases after the critical nucleus, thus reaches a maximal value at the critical size [25].

According to the uniform nucleation theory, vapor nucleation is affected by surface tension and results in a globular liquid nucleus. According to the Kelvin equation, different metals have different critical nucleation radii [18], which can be determined by the following equation with respect to r_k :

$$r_k = \frac{2\sigma_{lv} M}{\rho RT \ln(p_r/p_0)} \quad (4)$$

where σ_{lv} is the surface tension coefficient; M is the relative atomic mass; ρ is the density; R is the Boltzmann constant; T is the temperature; and p_r and p_0 are the curved surface vapor pressure and surface vapor pressure, respectively.

The metal vapor pressure is p_1 when reduction temperature is T_1 , the temperature drops to T_2 with the vapor pressure p_2 when the vapor enters into the condensing zone. So,

$$p_2 = \frac{p_1}{T_1} T_2 \quad (5)$$

where p_2 equals to the pressure of vapor at temperature T_2 ,

$$p_2 = p^* \quad (6)$$

where the temperature T_2 is the dew-point temperature.

From the above Eqs. (1), (2), (5) and (6), it can be

calculated that when the experimental temperature is 1473 K, the corresponding dew point of magnesium vapor is 1062 K, namely magnesium vapor starts to condense when the temperature is below 1062 K. At this time, the corresponding dew point of temperature in the high temperature zone is higher than the melting point of magnesium 920 K. Therefore, if the condensing temperature is lower than the dew point temperature while higher than the melting temperature, the condensation product is liquid, and if the condensing temperature is lower than the melting temperature, the condensation product is solid. From Table 1, it is known that the critical radius of liquid core decreases with the increasing condensing temperature, and nucleation requires fewer atoms. When the temperature is close to 810 K, the liquid nucleation radius of magnesium vapor reaches minimum. So, the obtained condensing interval is 810–1062 K.

Table 1 Critical radii atoms contained in critical fluid core at different temperatures

| Temperature, T/K | Critical radius, r_k/m |
|--------------------|--------------------------|
| 770 | 1.02×10^{-8} |
| 790 | 2.95×10^{-9} |

Through the above theoretical analysis, for the same condenser, the probability of the condensation nucleation of magnesium atoms increases through time and space dependent collision and nuclear growth. Moreover, the design and temperature control would allow a smaller condenser temperature gradient and extend the transfer time of the magnesium atoms into the condenser. The probability of crossing the phase area is quite small for metal vapor condensation, and obtaining a massive and compact magnesium particle is easy. If the condenser temperature gradient is bigger, the metal magnesium steam will pass through the liquid phase area considering the shortened motion time from high to low temperature area. At this time, obtaining powdered magnesium will be easy. Therefore, the design of condenser's temperature gradient is important to fine block product.

3 Experimental

3.1 Experimental procedure

The materials used for vacuum distillation are included in an internally heated vacuum furnace. The longitudinal section of the multilayer condenser is shown in Fig. 3.

Figure 4 shows the relationship between the temperature difference of every condensation layer and the distance to the distilling zone (temperature gradient in condenser). And the gradient between the evaporation

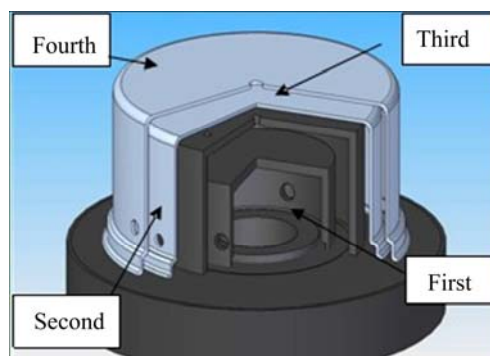


Fig. 3 Longitudinal section of multilayer condenser

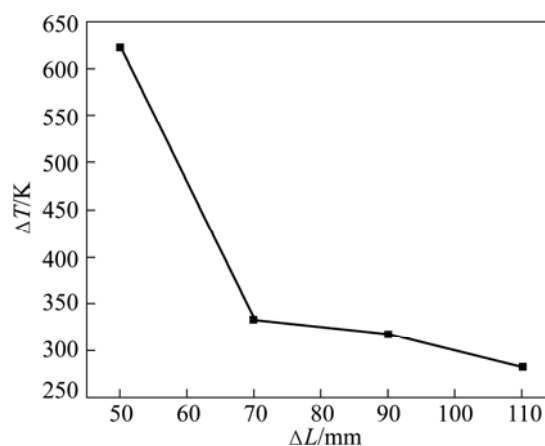


Fig. 4 Relationship between temperature difference of every condensation layer and distance to distilling zone

area and the first condensation area of the multi-level condensing collection devices is $\Delta T_1 = 7$ K/mm. The temperature gradient between the first and second levels is $\Delta T_2 = 6$ K/mm, whereas that between the second and third levels is $\Delta T_3 = 0.5$ K/mm. Meanwhile, the temperature gradient between the third and last levels is $\Delta T_4 = 0.3$ K/mm.

Under vacuum conditions, evaporation–cooling method (without inert gases) was used for sample preparation. Small magnesium beads (chemical composition given in Table 2) were used as raw materials for heating distillation in graphite crucibles. By controlling the raw material quantities, the mole ratios of magnesium vapor (C_V) were varied from 1/2 to 2. With an average vacuum degree of 40 Pa, the minimum temperatures (T_{\min}) of the condenser used were 673, 773, 873, and 973 K, respectively. Heat preservation was performed for 1 h. With increasing magnesium vapor concentration, condensation temperature and condensation temperature gradient, magnesium steam pressure correspondingly increased. Under circumstances guaranteeing certain magnesium vapor concentrations, with the condensation temperature changes and the multi-level condensation design, the magnesium steam

situation at different condensate temperatures can be ascertained, as well as the influence of the temperature gradient on magnesium steam condensation at certain concentrations and condensation temperatures.

Table 2 Chemical compositions of magnesium materials (mass fraction, %)

| Mg | Fe | Cu | Si | Mass loss ratio |
|------|------|------|------|-----------------|
| 98.0 | 0.01 | 0.05 | 0.05 | 5.0 |

3.2 Results and discussion

3.2.1 Metal magnesium distillation

Metal magnesium with different crystal morphologies and impurity contents was obtained from the first to fourth layer of the multi-level condenser when the minimum temperatures T_{\min} of condenser outer layer were maintained at 673, 773, 873, and 973 K, respectively, at an average vacuum degree of 40 Pa. Heat preservation was performed for 1 h. Figures 5(a)–(d) indicate the collection efficiency of the four condensation layers with T_{\min} at 673, 773, 873, and 973 K, respectively. The results reflect the ability of the condensing layer with different temperatures to catch magnesium steam at different condensate temperatures.

A physical map of magnesium vapor condensation was gained under the same concentration at different condensation temperatures and under the same temperature at different concentrations. Figures 6 (a)–(d) show condensation products of magnesium vapor with $C_V=1$ in the condenser obtained from the second and third levels at $T_{\min}=873$ K (Figs. 6(a) and (b)) and $T_{\min}=973$ K (Figs. 6(c) and (d)). Figures 6(e)–(h) show condensation products of magnesium vapor with $C_V=2$ in the condenser obtained from the second and third levels at $T_{\min}=873$ K (Figs. 6(e) and (f) and $T_{\min}=973$ K (Figs. 6(g) and (h)).

3.2.2 Magnesium powder from vacuum distillation experiment

At $T_{\min}=873$ K and 973 K, magnesium powder was obtained at the first layer of the condenser at certain magnesium vapor concentrations. The oxidation rate was high, the crystal morphology was poor, and particles were also tiny and easily burned. It is concluded that following the principle that atomic steam always moves toward the direction of low temperature, the magnesium steam first rises along with the conduit into the first condenser layer, which has the largest temperature gradient. The temperature difference in the section is

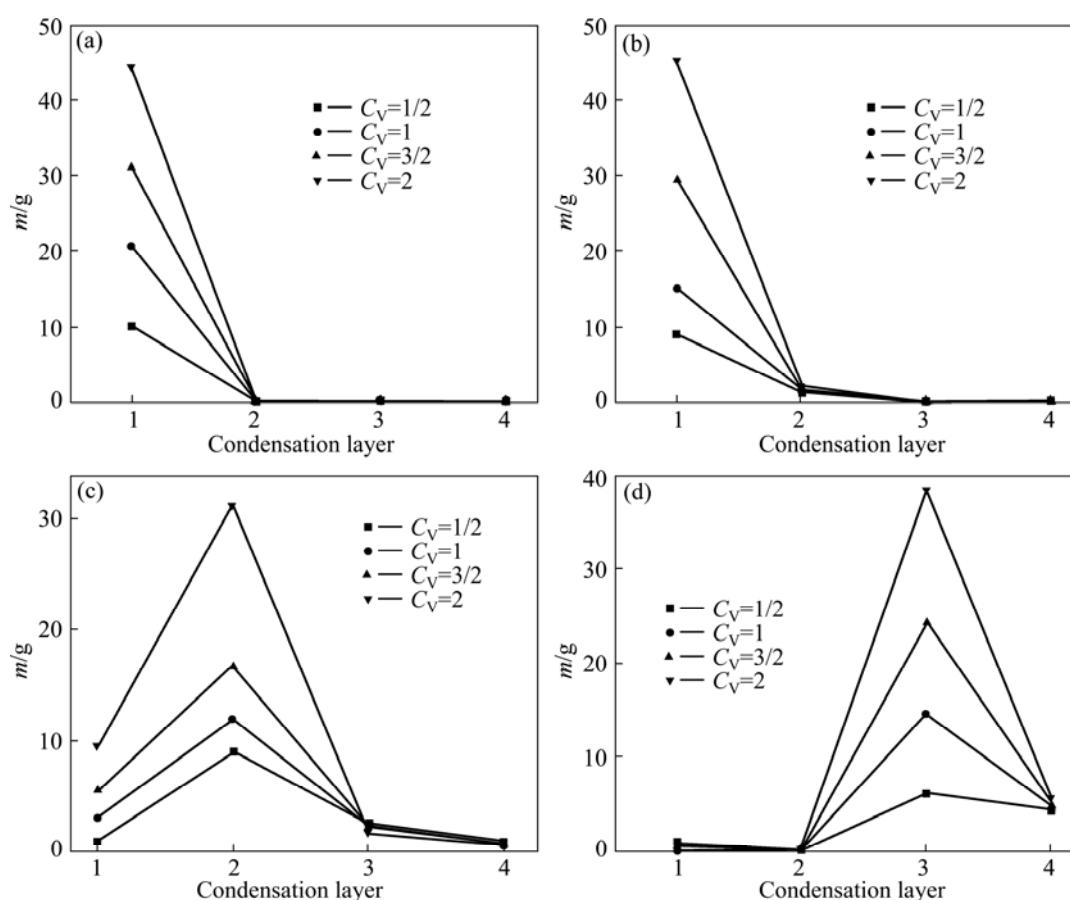


Fig. 5 Collection efficiency of four condensation layers at different T_{\min} and different C_V : (a) $T_{\min}=673$ K; (b) $T_{\min}=773$ K; (c) $T_{\min}=873$ K; (d) $T_{\min}=973$ K

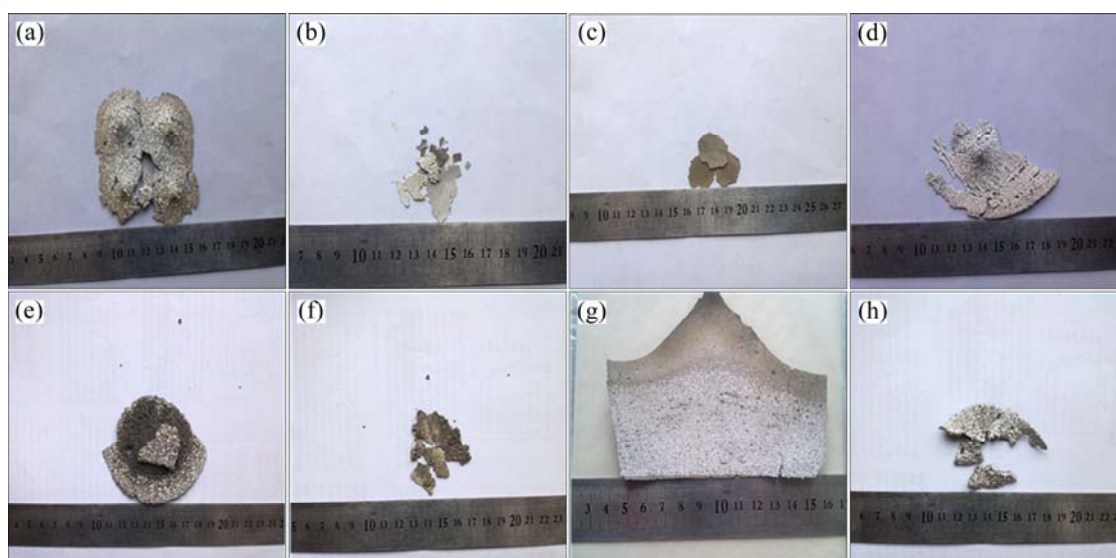


Fig. 6 Condensation products of magnesium vapor with different concentration at different T_{\min} : (a) $C_V=1$, 2nd layer, $T_{\min}=873$ K; (b) $C_V=1$, 3rd layer, $T_{\min}=873$ K; (c) $C_V=1$, 2nd layer, $T_{\min}=973$ K; (d) $C_V=1$, 3rd layer, $T_{\min}=973$ K; (e) $C_V=2$, 2nd layer, $T_{\min}=873$ K; (f) $C_V=2$, 3rd layer, $T_{\min}=873$ K; (g) $C_V=2$, 2nd layer, $T_{\min}=973$ K; (h) $C_V=2$, 3rd layer, $T_{\min}=973$ K

also the largest. Steam atoms with large kinetic energy and large amount of heat enter into the strongly cooling environment, and create sharp collisions with the condenser wall and with one another, resulting in numerous heat exchanges and losses. A small proportion of the steam atoms begin cooling down rapidly on the condenser wall when the critical nucleation size is not obtained through collision reunion and solid particle formation. This generation of solid granules increases the contact area between the magnesium group and the remaining oxygen in the system, thereby increases oxidation rate. Particles are gathered on the surface of the condensation plate through intermolecular force; thus, powdered magnesium in the form of tiny particles is obtained.

Figures 7(a) and (b) show SEM micrographs of magnesium powder collected in the first condenser layer at $T_{\min}=873$ K and 973 K with a magnesium vapor concentration of 1. In Figs. 7(a) and (b), the particle size has an uneven distribution and the phenomenon of a larger particle formed from smaller particles is evident. As revealed by EDS, increasing condensation temperature contributes to the fusion and growth of magnesium atoms, and increasing oxidation rate with decreasing particle size.

Figures 8(a) and (b) show SEM micrographs of magnesium powder collected at the first condenser layer at C_V of 1/2 and 3/2, respectively, and at a condensate temperature of 873 K. As magnesium vapor concentration increased, group crystallization morphology changed greatly from irregular growth on

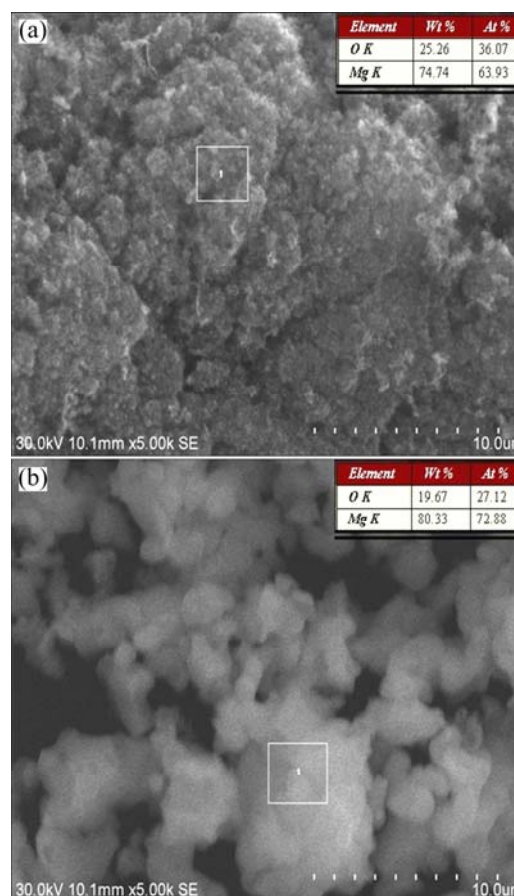


Fig. 7 SEM and EDS images of product in 1st layer at same $C_V=1$ at different T_{\min} : (a) $T_{\min}=873$ K; (b) $T_{\min}=973$ K

the rough interface into regular growth with the fusion of large clusters. Similarly, oxidation rate decreased with increasing crystallization quality.

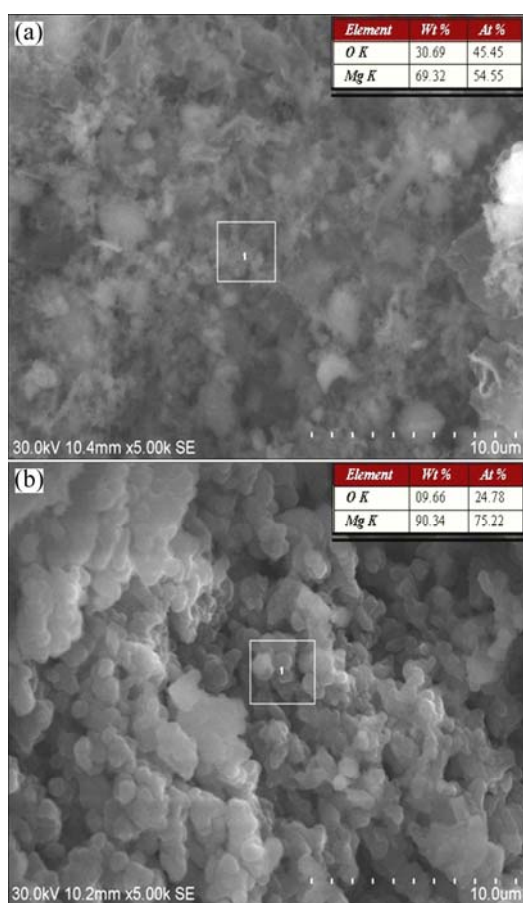


Fig. 8 SEM and EDS images of product in first layer at same $T_{\min}=873$ K at different C_V : (a) $C_V=1/2$; (b) $C_V=3/2$

3.2.3 Block magnesium from distillation experiment

The higher the evaporation temperature of metal magnesium is, the larger energy the magnesium steam will carry when running into the condenser. Thus, a moderate temperature gradient eases the phase transition from gas→liquid→solid. When $T_{\min}=873$ K and 973 K, at a certain magnesium vapor concentration, a massive magnesium particle with good crystallization and compact structure was collected at the second and third condenser layers. As shown in Figs. 5(c) and (d), with increased condensation temperature, the location of the maximum crystal magnesium concentration moves from the second to the third layer. When $T_{\min}=873$ K, the condensation temperature is about 923 K at the maximum concentration location of the second layer. When $T_{\min}=973$ K, condensate temperature is about 953 K at the maximum concentration location in the third layer. With two condensate temperatures at the maximum concentration level, the condensation temperature is not only relatively closer to the gas–liquid transition temperature, the temperature gradient also decreases compared with the former layer. The closer the condensation temperature is to the gas–liquid phase transition temperature and the smaller the temperature

gradient is, the lesser the heat exchange loss is between magnesium atoms during inter-atomic collision and collision with the condenser wall. Thus, magnesium vapor condensation through liquid phase transformation is easier, and a higher quality of condensed magnesium is obtained.

Figures 9 shows SEM micrographs of massive magnesium particles collected at the second and third condenser layers when $T_{\min}=873$ K and 973 K, respectively, at a magnesium vapor concentration of 1, corresponding to Figs. 6(a) and (b) and Figs. 6(c) and (d). Figures 10(a) and (b) show SEM micrographs of massive magnesium particles collected at the second and third condenser layers when $T_{\min}=873$ K and 973 K, respectively, at a magnesium vapor concentration of 2, corresponding to Figs. 6(e) and (h). In contrast to Figs. 6(a)–(d), the right condensing temperature improves the magnesium steam concentration in the layer. More importantly, the phenomenon of supersaturation of steam through liquid phase uniform growth, as well as a smooth crystal surface and a compact structure without obvious oxidation, become even more apparent after the liquid–gas phase transformation. Based on the SEM contrast chart in Figs. 9(c) and (d) and Figs. 10(a) and (b), temperature is the key to control grain size and crystallization quality. Based on EDS analysis, at a fixed temperature, increased concentration improves the partial pressure of the magnesium steam on the condensing surface, thus reduces the collision probability between magnesium steam and residual gas. Consequently, the oxidation rate is reduced to obtain a higher-purity crystallized magnesium.

4 Conclusions

1) Under a vacuum system, the magnesium vapor is oversaturated after entering the condensation zone. And the collection efficiency of the number of magnesium atoms increases with decreasing temperature at a given time, the association rate on the growth interface increases, the dissociation rate decreases, and the crystal growth rate increases. However, if the condenser temperature gradient is too wide, the magnesium clusters would transform from gaseous to solid state directly after they coagulate below the lowest gas–liquid transition temperature.

2) Under a vacuum system, when the condenser temperature and the temperature gradient are constant, the crystal growth rate increases with increasing partial pressure of magnesium. Unevenness of surface diffusion caused by rapid growth is avoided through the mitigating temperature gradient that helps fuse the magnesium cluster and improves crystal quality while oxidation rate decreases.

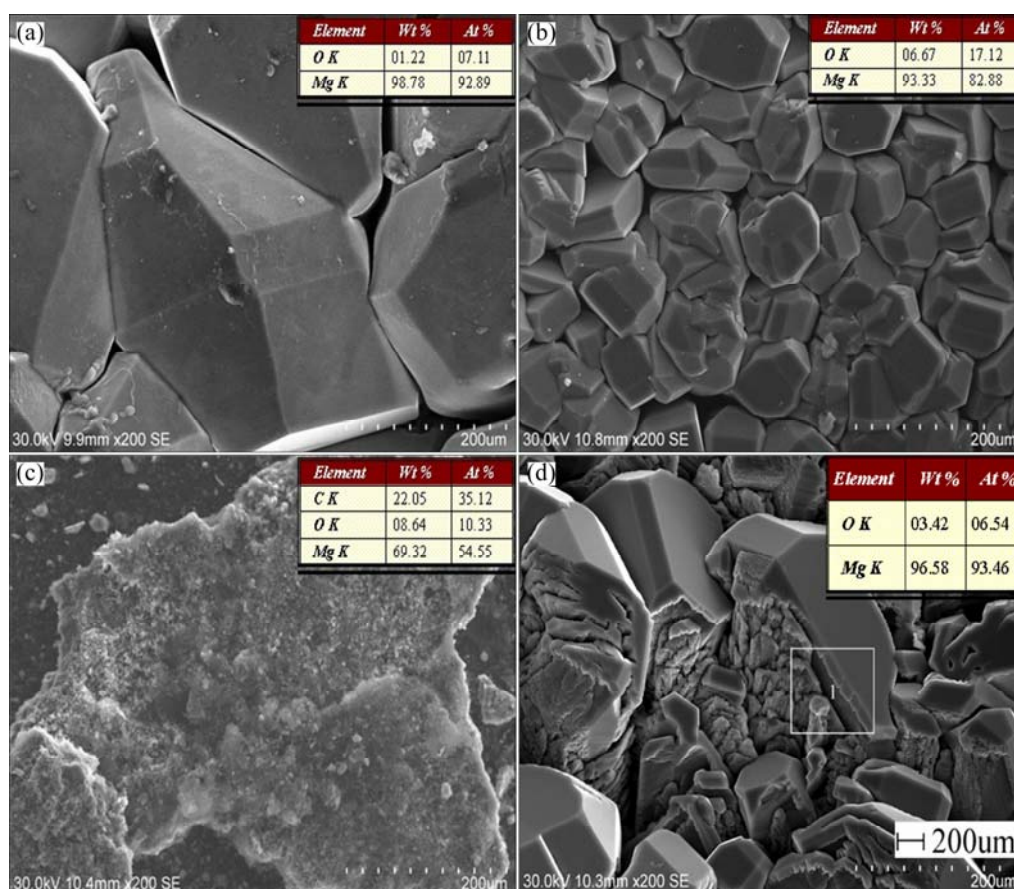


Fig. 9 SEM images and EDS results of product at same $C_V=1$ in different condenser layers and T_{\min} : (a) 2nd layer, $T_{\min}=873$ K; (b) 3rd layer, $T_{\min}=873$ K; (c) 2nd layer, $T_{\min}=973$ K; (d) 3rd layer, $T_{\min}=973$ K

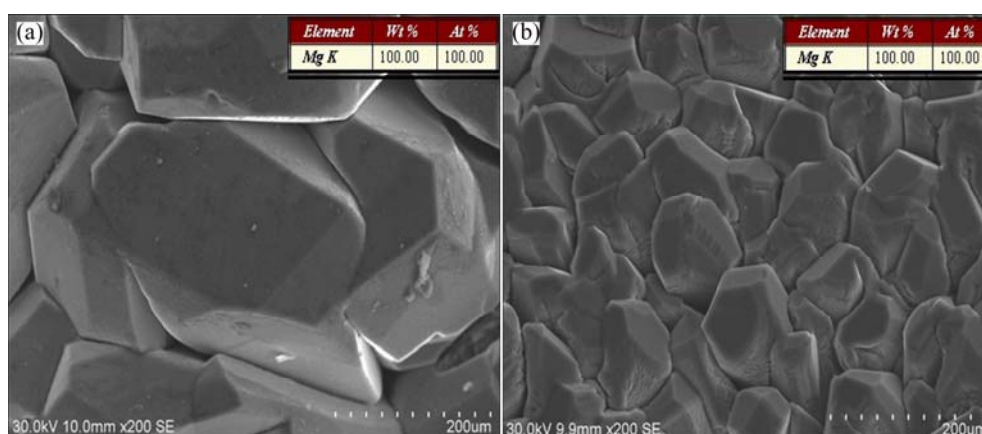


Fig. 10 SEM images and EDS results of product at same $C_V=2$ mol in different layers and T_{\min} : (a) 2nd layer, $T_{\min}=873$ K; (b) 3rd layer, $T_{\min}=973$ K

3) Under vacuum conditions, increased crystal growth rate induces decreased crystal quality. In practice, the two synthesis factors should be considered to guarantee crystal quality and to increase growth rate as much as possible. For this reason, controlling the condensation zone approach to liquid transition and a smaller temperature gradient not only lowers heat loss, but also increases the liquid nucleation rate and improves

magnesium steam concentration. Consequently, crystal quality is also improved. Setting a mitigating temperature gradient helps to avoid rapid solidification while extending the fusion time of the magnesium cluster. At the right condensation temperature and temperature gradient conditions, increased magnesium vapor concentration decreases the magnesium oxidation rate.

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真空条件下镁蒸气相变形核及冷凝

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摘 要: 描述真空条件下可凝镁蒸气的形核与长大, 并从分子水平的研究原理解释这些过程。在平均真空度为 40 Pa 条件下, 分析系统压力、冷凝区温度及温度梯度对镁蒸气冷凝的影响。采用自主设计的多级冷凝设备, 通过真空蒸发冷凝制备块状镁和镁粉。利用扫描电镜(SEM)与能谱(EDS)进行分析。结果表明: 在真空条件下, 适宜的气-液转变温度是提高蒸气冷凝富集率的关键所在; 而较小的温度梯度则是抑制蒸气发生气-固转变的主要途径; 在特定的冷凝温度及温度梯度下, 蒸气分压及浓度的提高可以明显改善镁的结晶形貌, 降低氧化率。

关键词: 镁蒸气; 真空; 相变; 冷凝; 形核

(Edited by Chao WANG)