ARTICLE IN PRESS
JID: JMAA [m5+;June 11, 2022;17:21]

Available online at www.sciencedirect.com

ScienceDirect

Journal of Magnesium and Alloys xxx (xxxx) xxx

www.elsevier.com/locate/jma

Full Length Article

Minimizing pest aluminum in magnesium for the production of high-purity titanium

Bo Yang, Rui Zheng, Ge Wu, Zhi-Min Chang, Zhi-Wei Shan*

Engineering Research Center for Magnesium-based New Materials, Center for Advancing Materials Performance from the Nanoscale (CAMP-Nano), State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, PR China

Received 18 January 2022; received in revised form 5 May 2022; accepted 8 May 2022
Available online xxx

Abstract

It is practically difficult to find titanium sponges with low and stable aluminum impurities on the market even though it is the precondition to prepare high-purity titanium. Analysis indicates that almost all the aluminum impurities in the titanium sponge are inherited from the magnesium used to reduce titanium tetrachloride. However, it remains elusive for decades why magnesium produced through the silicothermic reduction method contains a high content of aluminum impurities with large fluctuations. By recourse to thermodynamic calculations and comparative experiments, we demonstrate that fluorite, a material used as a catalyst in the silicothermic reduction method to produce magnesium, is the chief culprit for the pest aluminum and propose a mechanism to rationalize the observed phenomena. Our findings indicate that one practical way to produce qualified magnesium for the production of high-purity titanium is to abandon fluorite during the production of magnesium with the silicothermic reduction method.

Keywords: High-purity titanium; Titanium sponge; Magnesium; Aluminum impurity; Silicothermic reduction.

Magnesium has been chosen as the reducing agent in large-scale commercial titanium sponge production since the 1930s due to its proper reducing activity and relatively low cost [1,2]. High-purity titanium is a crucial fundamental material in IC manufacturing today using titanium sponges as raw materials [3]. Over the past few years, for cost and environmental reasons, an increasing number of titanium manufacturers have been prone to using magnesium produced by silicothermic process (the Pidgeon process) to produce titanium sponges instead of electrolytic magnesium [4]. This presents the manufacturers of high-purity titanium with the following problem: it is difficult for them to find titanium sponges with enough low and stable aluminum impurities. The challenge results from the fact that aluminum and titanium have close deposition voltages and aluminum has a strong affinity to titanium. Consequently, it is very difficult to remove pest aluminum from titanium by the existing purification processes, including molten salt electrolysis refining (MSER [5],[6]) and electron beam melting (EBM[7]). According to our inquiry feedback from Ningbo Chuangrun New Materials Co., Ltd., a leading company concentrated on titanium purification, in order to meet the semiconductor industry requirement, i.e., Al < 1 ppm, the maximum Al content in the titanium sponge (feedstock) should be less than 10 ppm or so.

To pinpoint the source of the aluminum in the titanium sponge, Yang et al. analyzed the data of a leading manufacturer of titanium sponge and concluded that nearly all the aluminum in the titanium is inherited from the primary magnesium [4]. Therefore, producing magnesium containing aluminum impurities that are low and stable enough becomes a prerequisite for the production of high-purity titanium. In this work, we first performed a thorough analysis of the compositional data of the primary magnesium produced by a leading magnesium plant. It was found that aluminum impurity often fluctuates in an uncontrollable way with quite a large amplitude. In addition, few studies can be found to explain the reason. By recourse to thermodynamic

* Correspondence to.
E-mail address: zwshan@xjtu.edu.cn (Z.-W. Shan).

https://doi.org/10.1016/j.jma.2022.05.016
2213-9567/

calculations and comparative experiments, it was surprising to find that fluorite, a material used as a catalyst in the silicothermic reduction method to produce magnesium, is the chief culprit for the pest aluminum. Our findings indicate that one practical way to produce qualified magnesium for the production of high-purity titanium is to abandon fluorite during the production of magnesium with the silicothermic reduction method.

1. Results and discussion

1.1. Large fluctuation of aluminum impurity in primary magnesium

To ascertain the aluminum impurity in primary magnesium produced through silicothermic reduction, we contacted a leading magnesium plant with over 90% of its product reaching the 3N5B level defined by ISO 8287–2011 in 2020. (N is the acronym of the word “nine” and the number before N means the amount of “nine” before the sign of %. For example, 3N5 means that the concentration of Mg should be higher than 99.95%. Moreover, the 3N5B defined by ISO 8287–2011 requires that Al $<$ 150 ppm, Si $<$ 150 ppm, Mn $<$ 150 ppm, Fe $<$ 50 ppm, Cu $<$ 20 ppm, Ni $<$ 10 ppm, Pb $<$ 50 ppm, Sn $<$ 50 ppm, Zn $<$ 100 ppm). This plant represents the best product quality among ~40 magnesium plants in the Yulin area, where nearly 50% of the world’s primary magnesium products were produced in 2020. The recorded data we obtained from this plant enable us to review the aluminum impurity of the primary magnesium they produced in the past 12 months. It was found that aluminum impurities rank the highest of the tested impurities in terms of average content and fluctuation range. In addition, even for a single day, the impurity of aluminum still presented the highest average content and the largest wave range. One typical example is shown in Fig. 1a. Every dashed line with points represents the sampling result of a batch of primary magnesium from one refining furnace which usually has a capacity of approximately 1 ton. The content of aluminum impurity is found to crossover four grades defined by international standards (solid line in Fig. 1a). The amount of aluminum presented the highest average content and largest wave range among the elements tested, blocking the improvement of the overall purity level. Considering that the feedstock quality, operating environment, processing parameters and even testing conditions are relatively stable in the same day, the observed phenomena are unexpected.

To solve the aforementioned puzzle, we carried out quantitative tracing the of Al source on three feedstocks for Mg production, i.e., calcined dolomite, ferrosilicon and fluorite. Over 1200 groups data from our cooperated primary Mg factories and some other data from previous reports [8] were analyzed (Fig. 1b-c). The weight percentages of the average Al content among the total Al in ferrosilicon, calcined dolomite and fluorite are approximately 73 mass%, 23 mass% and 4 mass%, respectively (Fig. 1b). Notably, the content distributions of Al and Al_2O_3 for different batches of ferrosilicon and calcined dolomite can be very different, as shown in Fig. 1c. The Al content in ferrosilicon shows a normal distribution, with the highest counts at ~0.3 mass% and an upper limit of ~0.6 mass%. The Al_2O_3 content in calcined dolomite matches well with a lognormal distribution, showing the highest counts at ~0.2 mass% and an upper limit of ~0.9 mass%. Consequently, it appears reasonable to speculate that the large fluctuation of Al impurities in raw magnesium stemmed mainly from calcined dolomite and ferrosilicon. However, surprisingly, both thermodynamic analysis and the following well-designed experiments indicate that fluorite instead of calcined dolomite and ferrosilicon is the chief culprit for the pest aluminum in magnesium.

1.2. Thermodynamic analysis for the origin of pest aluminum

To single out the source of the pest aluminum in primary magnesium, thermodynamic calculations were employed first. Based on the aforementioned facts, it is quite natural to think of the aluminum in ferrosilicon as the first suspect because of its high content and large fluctuation (Fig. 1b and Fig. 1c). To verify this speculation, we calculated the equilibrium compositions of a typical reacting system, i.e., 1200 °C and 10 Pa, mimicking the practical fabrication process of the primary Mg products. The only variable is the Al content. The peak counts at 0.3 mass% and the maximum of 0.6 mass% (Fig. 1c) were chosen for comparison. We expected to see a significant change in aluminum in the equilibrium compositions. However, to our surprise, when the content of Al was changed by two times, i.e., from 0.3 mass% to 0.6 mass%, no apparent impurity fluctuation was yielded for the given testing system (Fig. 2a), including Mn, Fe, O, Ca, Si and Al. This suggested that the content of Al in ferrosilicon should not be the primary reason for the observed pest aluminum phenomena, i.e., high content and large fluctuation (Fig. 1a).

After ruling out ferrosilicon, calcined dolomite became the first suspect naturally. On average, the Al_2O_3 in calcined dolomite contributes ~23 mass% of the aluminum amount in the feedstock (Fig. 1c). Under the given reaction conditions, Al_2O_3 could be reduced to aluminum by silicon. We first used Al_2O_3 as the variable and chose its average (0.2 mass%) and highest (0.9 mass%) content as the input parameter. Again, no significant change was found from the yielded aluminum and other impurities (Fig. 2b). We then checked the effect of Si content and obtained similar results, as shown in Fig. 2c. Calculation details are shown in the Methods section. In summary, the dramatic change in Al, Al_2O_3 and Si in the feedstock did not yield significant fluctuations in Al and other impurities. In addition, it is worth noting, that the content of the gaseous Al impurity is significantly lower than that of other impurities in all three calculations. This is against the data gained from the magnesium plants. There must be other factors contributing to the observed phenomena that have not yet been considered.

Among the three feedstocks of Mg production, only fluorite has not been considered yet by far. The main compo-

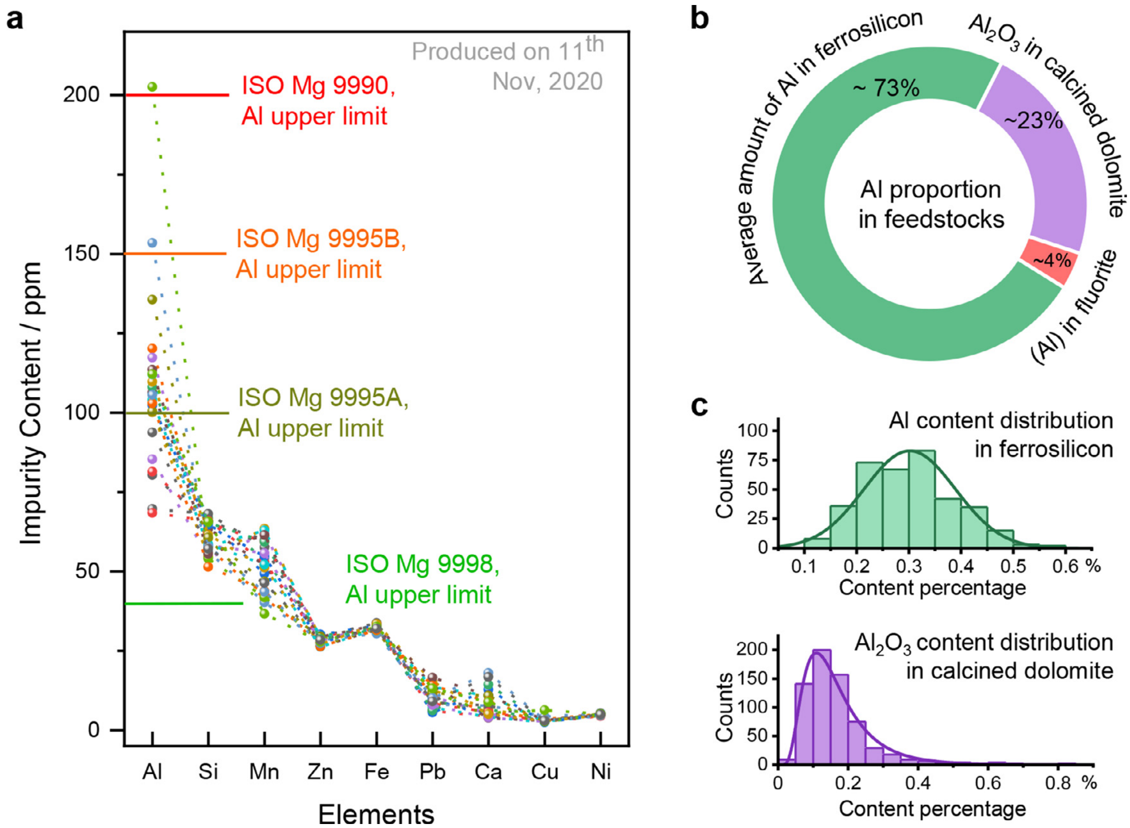

Fig. 1. **The contents of impurities in primary Mg products and the source analysis of Al.** (**a**) Impurities' content fluctuation in Mg products fabricated by a leading Mg producer, from the data in a single day. The amount of Al presents the highest average content and largest wave range among the elements tested, blocking the improvement of the overall purity level. (**b**) Quantitative Al source tracing of the three main feedstocks in Mg reduction. Al and Al_2O_3 are the main Al sources in ferrosilicon and calcined dolomite, containing 73 mass% and 23 mass% of the total Al content, respectively. (**c**) Content distribution of the main Al sources. The average weight percentage of Al in ferrosilicon is ~0.3 mass% and its upper limit is ~0.6 mass%. The average weight percentage of Al_2O_3 in calcined dolomite is ~0.2 mass%, with an upper limit of ~0.9 mass%.

nent of fluorite is CaF_2. It has been used as a catalyst in the silicothermic reduction process. Generally, catalysts only accelerate the reaction but will not affect the reaction equilibrium. Because there were truly no other factors we could try, we used the content of CaF_2 as the variable to determine whether it can alter the content of aluminum impurities significantly. As shown in Fig. 2d, compared with CaF_2-free condition (blue color), adding 3 mass% CaF_2 can dramatically change the content of Al and F (red color) in the gaseous phase, making the content of Al comparable to that of the other impurities such as Si and Ca. Detailed analysis found that compared with CaF_2 free, several other fluorides formed with the addition of CaF_2, including AlF, MgF, CaF and MgF_2 (Fig. 2d). The content of AlF is much higher than that of other fluorides. Therefore, at least based on the theoretical calculation, it can be concluded that after performing a wide range of thermodynamic searches, we identified CaF_2 as the chief culprit for the production of pest aluminum phenomena during the silicothermic reduction process.

1.3. Experimental verification of the effect of fluorite

To verify the effect of fluorite on the pest aluminum phenomena, a miniaturized furnace was set up in our lab. Its schematic diagram is shown in Fig. 3a. This furnace mainly consists of the following parts: temperature control system, vacuum system, stock bin, filter and crystallizer. For simplicity, only the last three parts are shown in Fig. 3a. The temperature of the stock bin and that of the crystallizer are set to 1250 °C and 550 °C, respectively. The filter consists of six specially designed baffles spaced the same distance from each other. Because of the temperature gradient, baffle 1 has the highest temperature (1156 °C) and baffle 6 has the lowest temperature (730 °C). The purpose of this filter design is to separate the substances produced during the silicothermic reduction process with different condensation temperatures. Both the morphology and the chemical composition of materials condensed on different baffles are affected not only by temperature, but also by fluorite addition. The magnesium produced from fluorite-free pellets has very low aluminum contents, i.e., lower than 5 ppm (Fig. 3b, blue color), a value very close to the detection limit of the instrument we used. Comparatively, the magnesium produced from 3 mass% fluorite added pellets has a much higher aluminum content, and three parallel experimental results were 28.6 ± 4.5 ppm, 170.0 ± 15.7 ppm and 70.2 ± 9.2 ppm, respectively (Fig. 3b, red color). This fits well with the theoretical predictions, i.e., the addition of fluorite can substantially increase the content

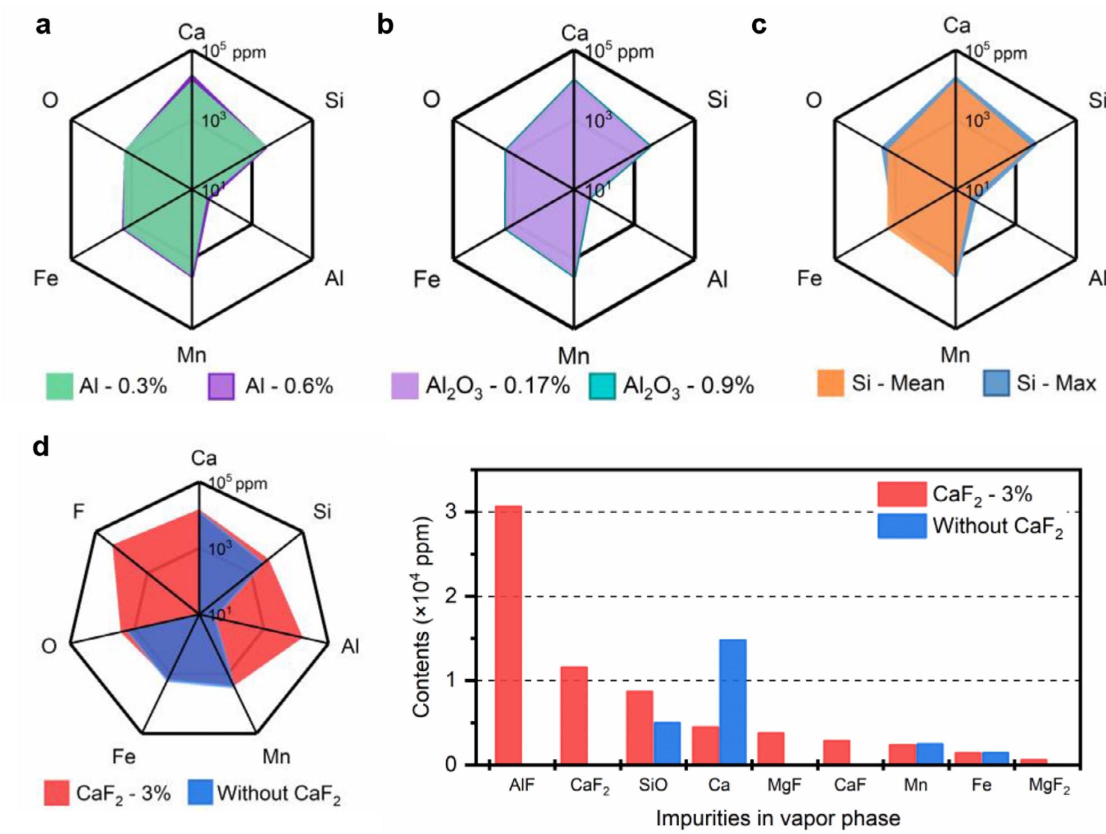

Fig. 2. **Thermodynamic analysis for the origin of Al impurities in primary Mg products.** (**a** ∼ **c**) The gaseous equilibrium elemental compositions calculated under the practical reduction conditions (1200 °C and 10 Pa) have little change with the content fluctuations of Al (**a**), Al_2O_3 (**b**) and the reducing agent, Si (**c**), in the reactants; fluorite was ignored at first for its conventional role as a catalyst that did not affect the reaction equilibrium. All calculated results show that the content of the generated gaseous Al is far less than that of the other impurities. (**d**) Upon the addition of CaF_2, the quantity of Al and F in the gaseous phase dramatically increases, mainly attributed to the formation of AlF.

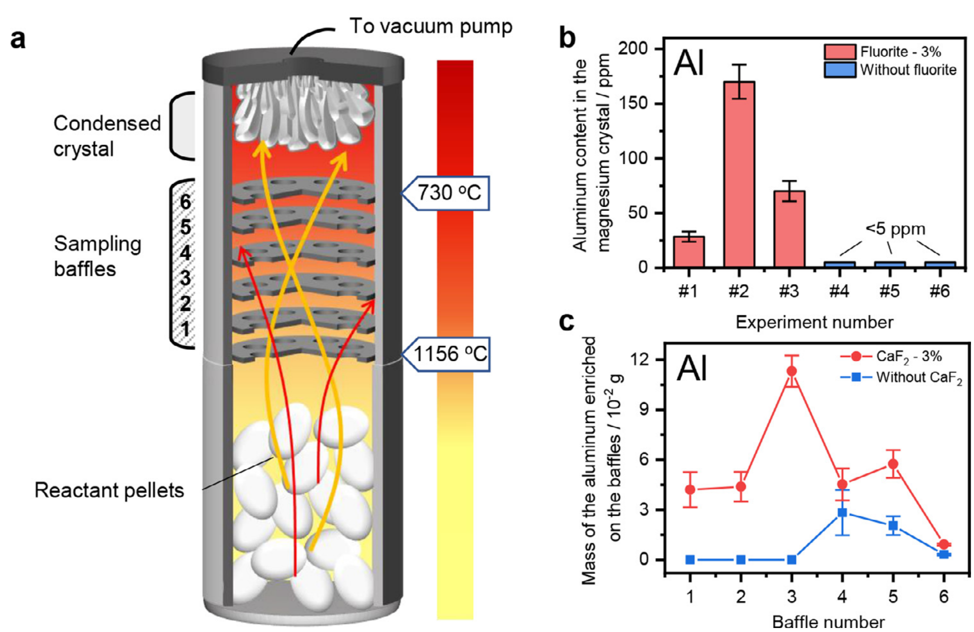

Fig. 3. **Comparison of the Al contents in the reaction products released from fluorite-free and fluorite-added reactants.** (**a**) Experimental setup of a silicothermic reduction method, showing that Al impurity is formed in two ways, pre-deposition on the baffles and t co-condensation in the Mg crystal. (**b**) Al content is always higher in the Mg fabricated with fluorite than in those fabricated without fluorite. (**c**) Al contents on the sampling baffles also show an obvious increase after adding fluorite (comparison between experiment #3 and #4).

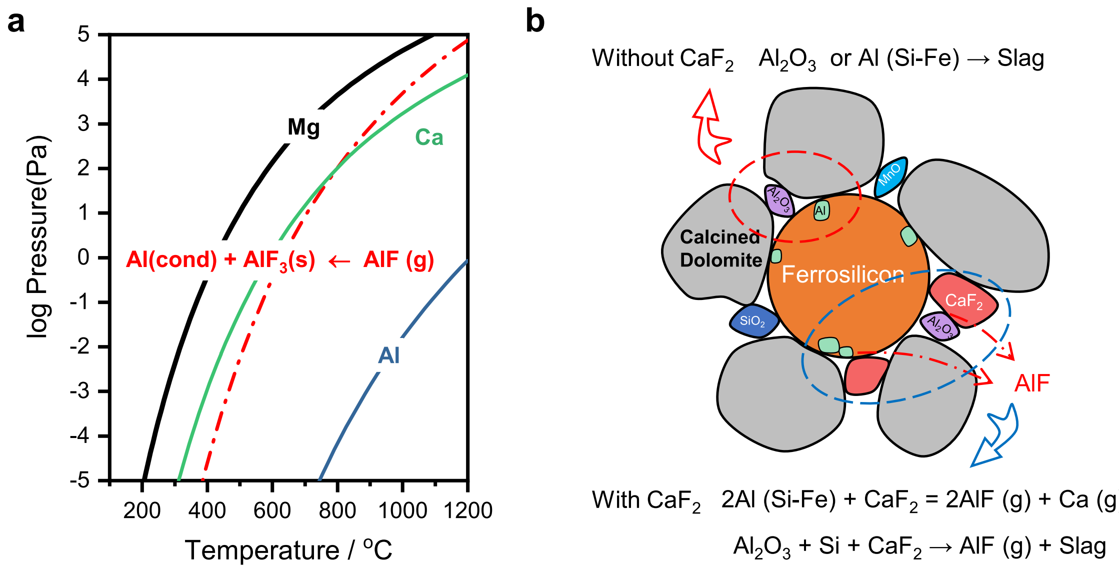

Fig. 4. **Formation mechanism of the pest Al.** (**a**) Equilibrium vapor pressure of AlF with respect to the saturated vapor pressure of Mg, Ca and Al. AlF's equilibrium vapor pressure, controlled by its disproportion reaction, is much higher than the saturated vapor pressure of Al and close to Mg (comparable with Ca), which indicates that AlF and Mg have very close condensation temperatures. This indicates that Al, in the form of monofluoride, is easier to deposit together with Mg. (**b**) Schematic diagram of the reaction. Unlike other oxide impurities, Al oxide cannot be directly reduced by forming Al vapor from the reaction with Si; instead, it is slagged under the reduction conditions. Similarly, most of the Al introduced from the ferrosilicon may serve as a reducing agent, eventually being incorporated into the slag. By adding CaF_2, reactions that involve Al sources to form AlF are thermodynamically favored during the silicothermic reduction reaction with a temperature of ∼1250 °C. The uneven distributions of CaF_2 in the reactants result in an intrinsic generation instability of AlF.

of Al impurities. However, it is worth noting that even though all the experimental parameters were very well controlled, the Mg produced from fluorite added pellets still exhibited large fluctuations in Al impurities, consistent with the phenomenon observed in magnesium plants. Therefore, there must be other factors affecting the amount of aluminum impurities.

1.4. Generation of the Al impurity and its large fluctuation

Our experiments confirmed the following phenomena, i.e., the addition of fluorite can result in a large and uncontrollable increase in aluminum content. Most external conditions (feedstock quality, temperature and operation) were relatively well controlled in the lab work; however, the Al in Mg metal still presented large fluctuations, making us focus more on the internal factors. Through systematic and careful analysis, we found that the phenomenon can be rationalized as follows: without the addition of fluorite, most of the aluminum in the pellets will simply become a part of magnesium slag. However, once fluorite is added, it will react with aluminum in ferrosilicon or aluminum oxide and silicon to form AlF. AlF is an unusual metastable material in the gaseous phase that form during high temperature (1050 K) treatment of the stoichiometric Al and AlF_3 mixture [9]. It decomposes into Al and AlF_3 upon cooling down the temperature (the disproportion reaction). We calculated the equilibrium vapor pressure of the decomposition reaction of AlF versus temperature and found that it is much higher than the saturated vapor pressure of Al, comparable to that of Ca and close to that of pure Mg (Fig. 4a). In a real production system, the actual partial pressure of AlF should be much lower than that of Mg because of its very low content. Consequently, its actual condense temperature should shift to a lower range and make the condense temperature range of AlF and Mg, in terms of the pure substance, overlap with each other. As a consequence, it is challenging to separate the gaseous monofluoride from vapor Mg, resulting in high Al contents in the deposited Mg crystal.

Undoubtedly, silicothermic reduction is mainly a solid reaction that requires direct contact between different solid reactants [10,11]. Considering the amount, particle size and processing technology of the pellets, a schematic diagram of the spatial distribution of the main runners is shown in Fig. 4b. A large ferrosilicon particle (orange color) with embedded Al tiny particles is surrounded by a number of calcined dolomite particles (gray color). Some small oxide impurities, such as SiO_2 (dark blue), MnO (light blue) and Al_2O_3 (purple), are randomly distributed in the spaces among the larger particles. Since the amount of the added fluorite is much less than that of the main reactants, only a few fluorite particles (red color) distribute unevenly in the space between the larger particles. Binary redox reactions can occur under silicothermic reduction conditions between Si and some oxide impurities, such as CaO [12], ZnO [13], and SiO_2 [14]. However, Al_2O_3 cannot be directly reduced to become Al vapor by reaction with silicon. In the absence of CaF_2, both Al_2O_3 and the Al in ferrosilicon can form aluminates and eventually enter the slag under the reduction conditions [15,16]. Consequently, little gaseous Al can be generated and deposited in crude magnesium. This is supported by thermodynamic analysis (Fig. 2a and Fig. 2b) and the following experimental verification (Fig. 3b and Fig. 3c).

However, in the presence of CaF_2, it becomes a different story. In the CaF_2-enriched areas, reactions including the ternary reaction among Al_2O_3, Si and CaF_2 as well as the direct binary reaction between Al and CaF_2, are both thermodynamically favored (Fig. 4b). Consequently, the uneven distribution of CaF_2 can be an intrinsic reason for the fluctuation of pest aluminum. The uneven degree of CaF_2 might be intensified in the lab work, because the calcining process of dolomite, crushing and mixing of all feedstocks were all manually carried out in a very small batch in the laboratory. However, this does not mean that the uneven distribution of CaF_2 is the sole reason for the Al fluctuation in the industrial mass production Mg. There are many factors that may influence the Al concentration in Mg in actual production, such as the variation in feedstocks' quality, the difference of worker's operation habit, the fluctuation of the furnace temperature and so on.

All these external variations should be relatively stable in one day; however, large fluctuation of Al among different bathes in a single day is often observed in the Mg factory (Fig. 1a), even though every batch is already a mixture of over 30 crude magnesium ingots and refined by the flux refining process. (Flux refining could reduce a certain amount of the Al in the Mg melt [17]). Therefore, it is reasonable to suspect that the uneven distribution of CaF_2 played a role in this case. The randomness and inhomogeneity of CaF_2 distribution can be caused by many factors, such as the variation in batching, mixing and the actual content of CaF_2 in fluorite.

Even though the addition of CaF_2 can cause pest Al in magnesium, it has been proven that CaF_2 can also improve the efficiency of the reducing reaction and increase the yield of Mg per unit time [18,19]. Considering the high price of raw magnesium today, the addition of CaF_2 is very attractive for magnesium plants because it can increase their yield and therefore profits. In addition, for those applications that are insensitive to aluminum impurities, e.g., being used as the raw materials of alloys with aluminum as one of their alloying elements, the addition of CaF_2 is also harmless. However, for applications that are sensitive to aluminum impurities, e.g., to produce titanium sponges with aluminum impurity concentrations as low as possible, it is better to reduce or eliminate the usage of CaF_2 during the silicothermic reduction process. Although this can lead to a decrease in magnesium yield and therefore increase the price of magnesium, considering the high additional value and the importance of high-purity titanium, it is still an economic and efficient approach.

2. Summary

The initial motivation of this work was to solve the problem of aluminum impurity removal in the production of high-purity titanium. By sorting the entire industrial chain, it was found that titanium sponges with a low aluminum impurity content can effectively reduce the difficulty of the subsequent production of high-purity titanium. To produce titanium sponges with a stable low aluminum content, the aluminum impurity content in magnesium used as reducing agent of titanium sponges should be as low and stable as possible. However, studies of the suppliers found that even the leading producers of raw magnesium have pest aluminum in their products, i.e., high content and large fluctuation. By recourse to the combination of thermodynamic analysis and experimental verification, we found that calcium fluoride is the chief culprit for the pest aluminum in the raw magnesium produced by silicothermic reduction and thus solved a problem that has plagued the magnesium industry for decades. Our findings suggest the following facts: first of all, for applications that are sensitive to aluminum impurities such as titanium sponges, raw magnesium with very low aluminum impurities can be obtained by reducing or discarding the usage of calcium fluoride. Secondly, when solving industrial problems, one may find the lowest comprehensive cost solution by tracing the source of the problem in the upstream industry chain.

3. Methods

3.1. Thermodynamic calculation

Under fixed temperature and pressure conditions, the equilibrium composition of a closed system can be determined based on the 2nd Law. Here we took the common chemical composition of the raw materials in practical production, according to the data from the Mg plants, as the basic input of the thermodynamic calculation. The weight ratios of the three main raw materials (calcined dolomite, ferrosilicon and fluorite) were 80 mass%, 17 mass% and 3 mass%, respectively. The contents of Al, Al_2O_3 and Si in the reactants, which were suspected to be related to the introduction of aluminum impurity, were deliberately changed to calculate new equilibrium compositions to see whether the change in the composition of its product was consistent with our expectation.

The Equilib Module of the commercial software *FactSage* was used to calculate the equilibrium compositions under 10 Pa and 1200 °C, to mimic the actual Mg reduction in the Pidgeon process. To cover the content fluctuation of the Al source in the raw materials, the average and the maximum content of the three suspects were chosen for comparison, i.e., 0.3 mass% and 0.6 mass% for Al, 0.2 mass% and 0.9 mass% for Al_2O_3 (Fig. 1c), and 12.87 mass% and 13.26 mass% for Si. Compound databases including FactPS and Solution Database including FTOxide-MeO, FToxide-bC2S, FToxid-aC2S, FToxide-Merw and FToxide-SLAGA were used in this study, covering all the possible products, even the uncommon substances, in the silicothermic reduction. Taking aluminum fluoride as an example, not only AlF_3 and AlF, but also other uncommon fluorides, such as AlF_2, were taken into calculation. After trying all kinds of combinations of possible substances, the computer finally gave us a product composition that has the lowest total Gibbs free energy and viewed it as the equilibrium state of the system under the constraints we set. Therefore, the calculated product composition shown in

Fig. 2d has already been the most thermodynamically favorable product under the given reaction conditions.

Moreover, to provide a clearer presentation of the differences between the systems we studied, the equilibrium vapor phase compositions were separately picked out to make comparison, as shown in Fig. 2b-d.

3.2. Silicothermic reduction experiments

The silicothermic reductions of calcined dolomite were conducted in the laboratory, mimicking the practical production of Mg as much as possible. The ordinary calcined dolomite and ferrosilicon directly delivered from the production site, Fugu JingFu Coal Chemical Co. LTD, ShaanXi, China, were crushed and milled to 100 mesh powder, while the fluorite was crushed and milled to 200 mesh. Powders were mixed together with the formula mentioned above and the control group did not add any fluorite powder. The mixed powder was then pressed into small cylinders of 25 mm in diameter and 10 to 15 mm in height under 70 $\sim$ 85 MPa. Approximately 250 g of briquettes were charged into the graphite crucible and reduced in a tube muffle furnace. To ensure that the reaction temperature reached and was maintained at 1250 °C, the furnace temperature was set slightly higher, at 1300 °C. The vacuum of the tube was maintained below 10 Pa during the two-hour constant temperature stage. Each experiment was repeated three times.

3.3. Impurities' content quantitative measurement

The co-condensed impurities in Mg crystals were directly tested by OES (Optical Emission Spectrometer, S5, GNR). The produced Mg crystal was remelted into ingots for impurity homogenization, lathed to a fresh flat surface and then tested by OES. To maintain the accuracy of the equipment, every time before testing, a standard cleaning process was carried out, including cleaning of the electrode, spark room and lens and standard global calibration using three standard samples.

The pre-deposited impurities on the sampling baffles were weighed and then characterized by SEM and EDS. Uniformed morphology and chemical composition were observed on each baffle. Radial 5-point sampling EDS testing was conducted on all 6 baffles. The data used in Fig. 3c were from two experiments, #3 (3 mass% fluorite) and #4 (without fluorite). A quick glance of the baffles from the other experiments was made and we are confident that Al contents on the sampling baffles also show an obvious increase after adding fluorite.

Data availability

The data that support the findings of this study are available from the corresponding authors on request.

Conflict of interest

The authors declare no conflict of interest.

CRediT authorship contribution statement

Bo Yang: Methodology, Data curation, Writing – original draft. **Rui Zheng:** Investigation, Writing – review & editing. **Ge Wu:** Writing – review & editing. **Zhi-Min Chang:** Methodology. **Zhi-Wei Shan:** Conceptualization, Supervision, Writing – review & editing.

Acknowledgments

Z. W. Shan and his team members acknowledge the support from the National Natural Science Foundation of China (No. 52031011) and funding from the Science and Technology Departments of Shaanxi and Xi'an, China (Nos. 2021GXLH-Z-015, 2016KTZDGY-04–04 and 201805064ZD15CG48). We acknowledge B. Y. Liu, X. H Cheng, A. W, L. Y. Mao, P. Y. Wang, F. W. Fan, P. C. Zhang, C. W. Guo and P. Zhang (Xi'an Jiaotong University) for assistance in this work. We acknowledge Yong-Liang Yang (Fugu TaiDa Coal Chemical Co. LTD), and Wei-Yin Zhang (Fugu JingFu Coal Chemical Co. LTD) for providing the chemical composition data of raw materials and primary Mg.

References

[1] F. Froes, History and Extractive Metallurgy, in: Titanium: Physical Metallurgy, Processing, and Applications., ASM International, 2015, pp. 1–10.
[2] G.Z. Chen, D.J. Fray, T.W. Farthing, Nature 407 (2000) 361–364, doi:10.1038/35030069.
[3] J.X. Song, et al., Effect of Electrolytic Compositions in Kinetics Mechanism of High-Purity Titanium Electrochemical Extraction Process, Recent Advancements in the Metallurgical Engineering and Electrodeposition, IntechOpen, 2019 (ed. Al-Naib, U. B.). Ch.5, 1–15.
[4] B. Yang, B.Y. Liu, H. Yang, Z.W. Shan, Mater. China 39 (2020) 576–584, doi:10.7502/j.issn.1674-3962.202006033.
[5] Q.G. Weng, et al., Trans. Nonferrous Metals Soc. China 24 (2014) 553–560, doi:10.1016/S1003-6326(14)63095-8.
[6] T.C. Yuan, Q.G. Weng, Z.H. Zhou, J. Li, Y.H. He, Adv. Mat. Res. 284–286 (2011) 1477–1482, doi:10.4028/www.scientific.net/AMR.284-286.1477.
[7] K. Vutova, et al., J. Mater. Process. Technol. 210 (2010) 1089–1094, doi:10.1016/j.jmatprotec.2010.02.020.
[8] N. Xue, Metall. Anal. 41 (2021) 62–67, doi:10.13228/j.boyuan.issn1000-7571.011177.
[9] J.M. Dyke, et al., Chem. Phys. 88 (1984) 289–298, doi:10.1016/0301-0104(84)85286-6.
[10] J.R. Wynnyckyj, W.J Rsukin, Metall. Trans. B 19 (1988) 73–81, doi:10.1007/BF02657756.
[11] R.B. Li, C. Zhang, S.J. Zhang, L.J Guo, Metall. Mater. Trans. B 45 (2013) 236–250, doi:10.1007/s11663-013-9934-5.
[12] J.R. Wynnyckyj, L.M Pidgeon, Metall. Mater. Trans. B 2 (1971) 979–986, doi:10.1007/BF02664228.
[13] C. Yu, K.Q. Qiu, Q.Y. Chen, Acta Phys.-Chim. Sinica 27 (2011) 1312–1318 https://chinesesites.library.ingentaconnect.com/content/apcs/apcs/2011/00000027/00000006/art00009.
[14] E.I. Istomina, P.V. Istomin, A.V. Nadutkin, Russian J. Inorg. Chem. 57 (2012) 1058–1063, doi:10.1134/S0036023612080062.
[15] Y.L. Li, et al., Environ. Eng. Sci. 33 (2016) 290–297, doi:10.1089/ees.2015.0097.
[16] W.X. Hu, et al., Chin. J. Proc. Eng. 10 (2010) 127–132 http://www.jproeng.com/CN/Y2010/V10/I1/127.
[17] B. Yang, et al., Producing High Purity Magnesium (99.99%) Directly by Pidgeon Process, in: J.B. Jordon, et al. (Eds.), Magnesium Technology

2020, Springer International Publishing, 2020, pp. 299–302. https://link.springer.com/chapter/10.1007/978-3-030-36647-6_44.

[18] C. Wang, C. Zhang, S.J. Zhang, L.J. Guo, Int. J. Mineral Process. 142 (2015) 147–153, doi:10.1016/j.minpro.2015.04.017.

[19] J.M. Toguri, L.M. Pidgeon, Can. J. Chem. 40 (1962) 1769–1776, doi:10.1139/v62-271.