Producing High Purity Magnesium (99.99%) Directly by Pidgeon Process

Bo Yang, Fei Liu, Bo-Yu Liu, Zhi-Min Chang, Lu-Yao Mao, Jiao Li, and Zhi-Wei Shan

Abstract

Pure magnesium is the foundation of the entire magnesium industry. Over 90% of the pure magnesium on the market is produced in China using Pidgeon process. Even though the quality of pure magnesium has been improved significantly in the past decades, the majority of them is still suffering the following problems: The purity is only ∼99.9%; there are still too many kinds of harmful impurity elements with their content fluctuating greatly in an uncontrollable manner. The impurities can be passed to magnesium alloys and degrade their properties significantly, especially their corrosion resistance ability. This leaves people an impression that Pidgeon process cannot produce high purity magnesium directly. As a consequence, it has long been accepted that producing high purity magnesium requires additional processes, which is usually costly and time-consuming. After analyzing the impurities' source of the Pidgeon process, we developed a new technique that can produce high purity magnesium (99.99%) directly by Pidgeon process without significantly increasing the costs. The application of this new technique is expected to benefit the entire magnesium industry.

Keywords

High purity • Filtration • Pidgeon process • Low cost

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Introduction

Over 80% of the world's pure magnesium yielded in China in 2018 [1] and more than 95% of them was produced through Pidgeon process. However, by in-depth research in the primary magnesium enterprises, we found that the quality of pure magnesium was worrying in terms of purity. Taking a top primary magnesium enterprise located in Yulin, Shaan Xi, China, for example, near 98% of its products in 2018 could only reach the 99.90% level, which was the second-lowest purity standard *in the Pure Magnesium Standard of China, GB/T 3499-2011*. There are too many kinds of harmful impurity elements with their content fluctuating greatly in an uncontrollable manner and these impurities in raw material can be passed to magnesium alloys, degrading their qualities and having a negative impact on their reputation. High purity magnesium (>99.99%) is not only critical in manufacturing high purity sponge titanium and high-performance magnesium alloys, but also has a trendy application in the fields of Mg-based biomedical implants [2], Mg-based anodes in batteries [3].

It has long been accepted that Pidgeon process, with only traditional flux refining method, cannot produce high purity magnesium. Additional processes are necessary for further purification such as vacuum distillation method, which is usually costly and time-consuming. Here we developed a new technique that can produce high purity magnesium (>99.99%) directly through the Pidgeon process without obviously increasing the cost.

The main impurities in primary magnesium are Si, Mn, Al, Ca, Fe, etc. We first investigated the source of these impurities. Traditional Pidgeon process has two main steps, reduction and refinement, which are two possible source of impurities. As-reduced magnesium, also called crude magnesium, is the magnesium extracted from the reactant pellets in the reduction retort. As-refined magnesium is the commercial pure magnesium that refined by flux refining. Comparison of impurity elements content between the

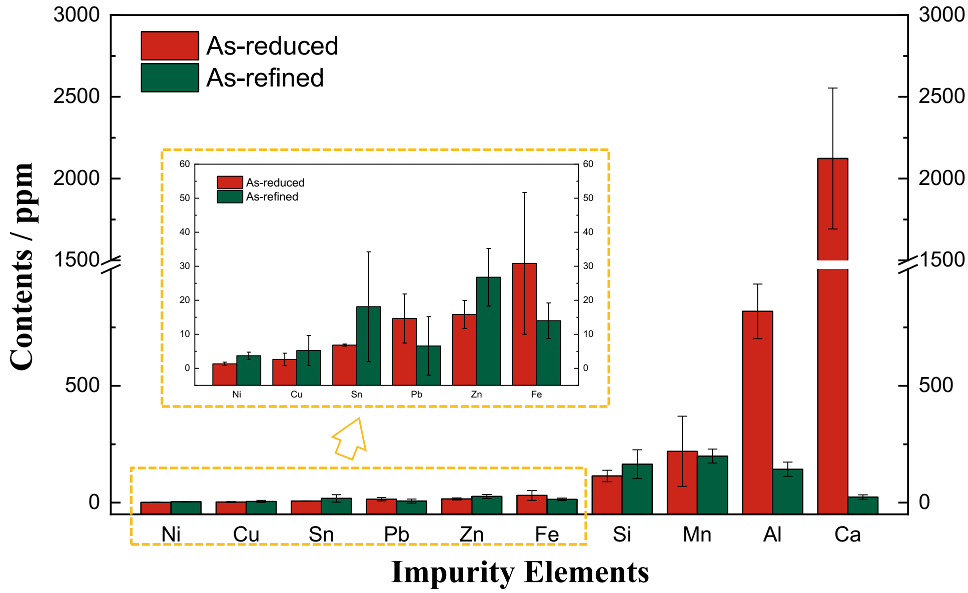

Fig. 1 Comparison of impurity elements content between the as-reduced and as-refined magnesium ingots. Almost all the impurities come from the reduction step, and the flux refining cannot remove all impurities and can even bring in some kinds of impurities

as-reduced and as-refined magnesium ingots is shown in Fig. 1. The flux refining significantly decreased the content of Ca, from over 2000 ppm to about 50 ppm, and then Al, from over 800 ppm to about 200 ppm. However, the refining effect on other impurities, like Mn, Fe and Pb, is not significant because the flux does not interact with elements that are less chemical active than Mg [4]. Surprisingly, the content of some other impurities even increased after refining, such as Ni, Cu, Sn and Si. The above analyses suggest that almost all the impurities come from the reduction step, and the flux refining cannot remove all impurities and can even bring some impurities. Therefore, if the impurities can be removed from the magnesium vapor during the reduction step, a much better refining effect can be expected.

Experimental Setup

We then investigated how to purify magnesium vapor in the reduction process. Figure 2a is a schematic diagram of the reduction retort. It is divided into three parts according to the temperature difference: heating zone, gradient cooling zone and condenser. Most part of the reduction retort belongs to the heating zone, where the reduction reaction happens under an average temperature of around 1250 °C and a vacuum of 13 Pa. The part covered by the recycled coolant jacket is the condenser, where magnesium condensation takes place. Gradient cooling zone is the region between these two parts. The temperature gradually decreases along the gradient cooling zone. The magnesium vapor and impurities generate from the heating zone, migrate along the gradient cooling zone and finally all stop in condenser. These impurities generally have two states, condensed state and gas state. The impurities in condensed state, like small particles of reactant, are carried into the condenser by the airflow when pumping starts or by the metal vapor stream during reaction. For these impurities, the best place to set filter is the gradient cooling zone. For impurities in gas state, we use commercial thermodynamics software, Factsage, to predict their condense behaviors. Based on the calculate results, we find that some impurities should condense or deposit at a high temperature, while others will condense or deposit at a relative lower temperature. The first kind of gaseous impurity might be effectively blocked by the filter. For the second kind gaseous impurity, specially designed filter core is needed.

A specially designed filter was placed in the gradient cooling zone (marked by blue-dashed frame, Fig. 2a). The filter consists of three parts, a case, a filter core and a baffle (Fig. 2b). A special structure of the case was designed to make sure that the filter could be fixed onto the proper position in the gradient cooling zone. Two kinds of filter core were selected to capture the impurities. The baffle can protect the filter core from direct thermal shock from magnesium vapor stream in high temperature. Figure 2c shows the cross-section structure of the filter. Vapor flow could be disturbed by this twisted inner structure and mixed intensively so that the temperature field could be more uniform. All the experiments were carried out in the magnesium plants of Fugu JingFu Coal Chemical Co. LTD.

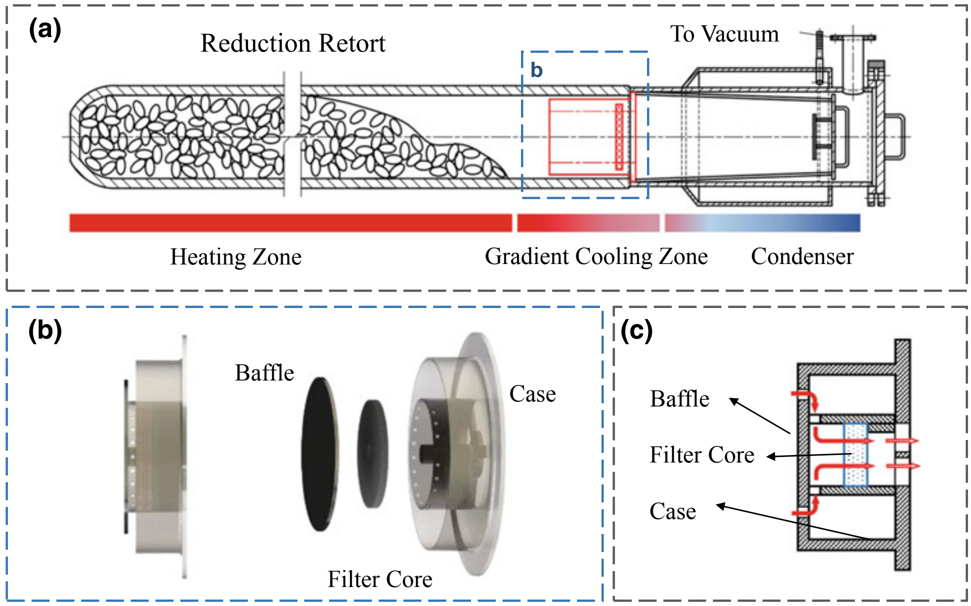

Fig. 2 Details of our filter design. **a** Schematic diagram of a reduction retort. It can be divided into three parts by temperature, heating zone, gradient cooling zone and condenser. **b** The filter consists of three parts, a case, a filter core and a baffle. **c** The cross-section structure of the filter

Results

After a reduction period of about 11 h, condensed magnesium ingots with shinning appearance were obtained. The mass of them is in the range of 25–31 kg, which were comparable to that of the control group without filter. Note that this indicated that impurities did not clog the holes in the filter, otherwise we should see obvious decrease in yield.

In order to minimize the system error, the crude Mg produced next day, using the same reduction retort in the same furnace, was specially selected as the control experiment group. Samples were cut from the same position from both magnesium ingots with or without filter. The purity was measured by optical emission spectrometry (OES, Thermo Scientific ARL3460). Most of the impurities dramatically decreased after the filter was inserted. Figure 3 shows examples of Mn, Si and Al, which are the key impurities in primary magnesium. The content of these elements reached the standard of Mg9999 (*Pure Magnesium Standard of China, GB/T 3499-2011*).

Note that the content of Ca was still more than 1000 ppm, only reduced less than half, but it can be largely removed by the following flux refining process (see in Fig. 1). Moreover, the content of iron was 14 ppm, Sn was 17 ppm and other impurities' content, like Ni, Cu, Pb, etc., was all in very low level, which are not mentioned here.

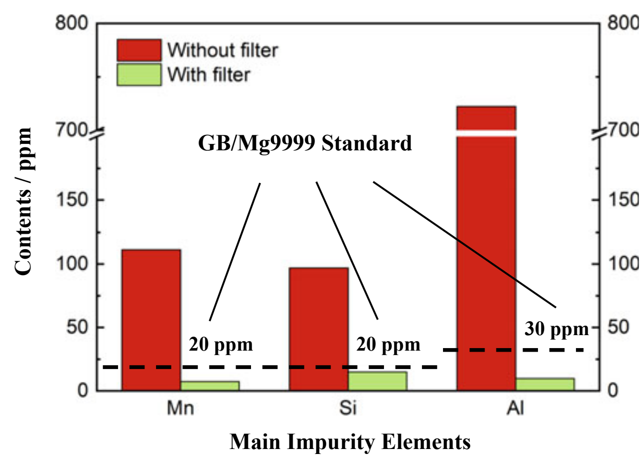

Fig. 3 The contents of key impurity elements can be dramatically decreased by using the filter. The contents of key impurities including Mn, Si and Al, in the magnesium ingot made in our experiment meet the standard of Mg9999

So far it is really difficult to control the content of calcium in the as-reduced magnesium. That is because it is very difficult to obtain the ideal and accurate temperature distribution in the plant with only limited reform, especially when every retort is on its full capacity. It is worth to mention, however, that we achieved the high purity Mg (>99.99%, Ca < 10 ppm, Si < 10 ppm, Fe < 10 ppm, Mn ∼5 ppm, Al undetectable, using OES GNR S5) directly by Pidgeon

Table 1 Chemical component of industrial as-reduced magnesium produced with or without filter and laboratory as-reduced magnesium using filter

	Purity (wt%)	Impurity element content (ppm)									
	Mg	Ca	Al	Mn	Si	Fe	Zn	Pb	Sn	Cu	Ni
Industrial, without filter	99.62	2833	722	111	97	12	11	11	31	<5	<10
Industrial, with filter	99.80	1926	10	7	15	14	6	6	17	<5	<10
Laboratory, with filter	>99.99	<10	<10	5	<10	<10	9	9	10	<5	<10

reduction without any refinement in our lab study, 50 grams per cycle, by accurately controlling the cooling path and using appropriate filters. Analysis results for all elements of the magnesium mentioned above are listed in Table 1.

Summary

Pidgeon process can be a very "clean" method and 99.99% high purity magnesium can be produced directly through the reduction process without costly and time-consuming additional processes.

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