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Thermal Decomposition of Mg_2Sn in Vacuum

Abstract: Vacuum distillation of magnesium is considered one of the practical approaches for processing secondary biodegradable alloys of the Mg–Sn system. The process relies on the difference in the partial vapor pressures of magnesium and tin; however, its accurate description requires an understanding of the thermal behavior of the intermetallic Mg_2Sn phase. In the present work, dimagnesium stannide was synthesized, containing 97.8% of the Mg_2Sn phase and 2.8% Sn. The obtained specimen was used to further investigate the decomposition and possible dissociative evaporation of Mg_2Sn to refine the process parameters of magnesium distillation.

Keywords: biodegradable alloy, dimagnesium stannide, magnesium, tin, dissociation, vacuum, dissociation pressure.

Introduction

Magnesium alloys have long attracted the attention of researchers in the fields of materials science, physical chemistry, and metallurgy due to their lightweight, high strength-to-weight ratio, and unique reactivity profiles, which determine their behavior in various environments (Ablakatov et al., 2023). These properties are attributed to magnesium's position in the periodic table as an alkaline earth metal with a low density of approximately 1.74 g/cm³ and a hexagonal close-packed crystal structure, which influences its mechanical properties and alloying potential (Volodin et al., 2024 & Li et al., 2023). In recent decades, the focus has shifted to their biomedical applications, where magnesium-based biodegradable materials offer a novel approach to implants and devices (Chen et al., 2021 & Tamay et al., 2021). Traditionally, metals such as titanium or stainless steel have been used for implants, often requiring secondary procedures for their removal from the body (Wang et al., 2022). In contrast, magnesium alloys naturally degrade in the body, synchronizing with the healing process and minimizing long–term complications (Gan et al.,2021 & Frank et al., 2008).

However, the high reactivity of magnesium with atmospheric gases and its flammability pose safety risks during manufacturing and processing, often requiring inert atmospheres or specialized equipment to prevent oxidation or combustion (Han et al.,2023). Recycling, especially from secondary sources such as used medical implants or industrial waste, remains insufficiently studied despite its environmental, economic, and resource saving importance (Guangling et al., 2007). Traditional remelting can introduce impurities or degrade properties, while the presence of alloying elements complicates separation. This gap is critical for the development of a closed-loop system for biomaterial use, where effective recycling could reduce dependence on primary production and decrease the carbon footprint–recycling magnesium requires only about 5% of the energy needed for primary production (Lipeng et al., 2024)

A promising approach to solving these problems in biodegradable alloys containing tin is vacuum distillation. The method is based on the difference in the partial pressures of the components, which allows selective extraction of the target element followed by its condensation. In the Mg–Sn system, the high volatility of magnesium enables the recycling of magnesium–tin alloys. However, the thermodynamic behavior of the intermetallic phase Mg_2Sn remains insufficiently studied. The compound melts congruently at 770 °C, but data on its behavior at the liquid–vapor boundary and the possibility of its transition into the gas phase without decomposition are lacking. This is critical for correctly constructing the phase diagram, taking into account the evaporation region, and for assessing the risk of magnesium distillate contamination with tin during the potential evaporation of Mg_2Sn.

In light of this, our study aims to experimentally determine the thermal behavior of dimagnesium stannide (Mg_2Sn) upon heating in a vacuum to establish its stability or decomposition in the gas phase and to subsequently optimize the distillation recycling strategy for alloys.

The main part of the research

The object of the study was the synthesized crystalline dimagnesium stannide (Mg_2Sn). Tin with a purity of 99.99 wt.% and magnesium with a purity of 99.99 wt.% (subjected to double distillation) were used as the starting components for the synthesis. For the preparation of the alloy, magnesium and tin were taken in amounts of 23.50 wt.% and 76.50 wt.%, respectively. The synthesis was carried out in an argon atmosphere at a pressure of 500 kPa and a temperature of 1100 °C. The excess pressure was required to prevent the evaporation of magnesium.

X-ray diffraction analysis revealed the presence of a single-phase dimagnesium stannide (97.8 %) in the synthesized sample, along with a small amount of unreacted tin (2.8 %).

The thermal behavior of Mg_2Sn was studied during heating at a constant rate using an apparatus with continuous sample weighing under varying constant gas-phase pressures. During the experiment, it was determined that, upon the decomposition of dimagnesium stannide, elemental magnesium is released and evaporates, which is recorded by the weighing system. Tin, on the other hand, does not evaporate up to 1000 °C due to its low vapor pressure. The temperature at which the sample starts losing mass at this pressure was considered the decomposition temperature of Mg_2Sn.

As a result of a series of experiments, the temperatures for the intense evaporation of the volatile component were determined in the pressure range from 0.13 to 40.00 kPa. The obtained data allowed the development of an approximation equation for the temperature dependence of the dissociation pressure of dimagnesium stannide: $\ln p^D$ [Pa]=26,695 – $21250 \times T^{-1}$

The dissociation temperature at atmospheric pressure was found to be 1401 K (1128 °C). The enthalpy of dissociative evaporation of magnesium was estimated to be 176.7 ± 16.5 kJ/mol, and the entropy was 126.1 ± 11.8 J/(mol·K).

It was established that during dissociative evaporation, Mg_2Sn decomposes into the metals Mg and Sn, as confirmed by the experiment at 850 °C and 0.67 kPa.

Based on the established decomposition behavior, a series of experiments was conducted on the distillation processing of the synthetic Mg–Sn alloy containing the Mg_2Sn phase and magnesium oxidation products. The material was heated at 800 °C and 0.67 kPa for 1 hour to obtain distillates. Two products were obtained: a magnesium condensate with a silvery color (Figure 1a) and a powdery residue with small spherical granules (Figure 1b). The presence of spherical granules indicates the coalescence of tin droplets after magnesium evaporation from the alloy. Overall, the obtained morphological and analytical data are consistent with the dissociative evaporation mechanism of Mg_2Sn that we have established.

X–ray diffraction analysis showed the following phase composition of the condensate: 91.6 % Mg, 1.52 % Mg_2Sn, and 6.95 % SiO_2. X–ray fluorescence analysis revealed magnesium content of 95.35 %, tin content of 0.25 %, and silicon content of 4.84 %. The presence of Mg_2Sn is explained by the entrainment of the original alloy by the magnesium vapor flow during dissociation, while the presence of SiO_2 is attributed to sample contamination during removal from the condenser surface.

a) b)

Figure 1. Magnesium condensate (a) and residue after distillation with spherical tin granules (b)

Conclusions

Thus, the vacuum thermal evaporation of magnesium from dimagnesium stannide confirms the dissociation of the compound into its elements. The dissociation pressure at the melting temperature (770.5 °C = 1043.5 K) is 560 ± 52 Pa (4.2 ± 0.4 mm Hg), which is consistent with the data from the vacuum thermal process. The vapor pressure of pure magnesium at this temperature is estimated to be 258 Pa, illustrating the simultaneous decomposition of the stannide and evaporation of elemental magnesium under the experimental conditions. During vacuum distillation of the Mg–Sn alloy at pressures above 0.67 kPa, the vapor phase primarily consists of elemental magnesium.

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