Rare Metal Materials and Engineering
Volume 45, Issue 1, January 2016
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2016, 45(1): 0018-0022.

ARTICLE

In Situ Synthesis and Formation Mechanism of AlN in Mg-Al Alloys

Yang Changlin, Lü Hebin, Chen Guiyun, Liu Feng

State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, China

Abstract: In-situ synthesis of AlN-Mg composite materials by the gas bubbling method was investigated using nitrogen as the gaseous precursor in the temperature range of 700 °C to 800 °C. The proofs of a direct reaction of N_2 and Al to form AlN in Mg-Al alloy melt were found. Microstructure analysis confirms the formation and the uniform distribution of AlN phases in the alloy. An optimum process to form in situ AlN phase in Mg-Al based alloys has been obtained.

Key words: in-situ; AlN phase; magnesium alloy; formation mechanism; optimum process

Magnesium alloys have attracted much attention in recent years because of their low density which is approximately two thirds of that of aluminum, one quarter of zinc, and one fifth of steel[1], as well as other beneficial properties such as good damping capacity, excellent castability and superior machinability. However, the magnesium alloys have relatively low strength, especially at high temperatures. In order to improve the mechanical properties of the magnesium alloys, the magnesium matrix composites with some reinforcement particles such as SiC, TiC, TiB and Mg_2Si have been developed. These composites materials are most prepared by conventional methods such as stir casting, squeeze casting, or powder metallurgy, and the reinforcements were added into the alloy melt from the outside[1]. Whereas the more recently developed in-situ synthesis process is considered a potential method for high strength of magnesium matrix composites, in which the reinforcements are formed in the matrix by the controlled reactions where one of the elements is usually a constituent of the molten matrix alloy while other elements may be externally-added fine powders or gaseous phases.

The in-situ metal matrix composites technologies are classified into four kinds of processes including liquid-gas reactions, e.g., Ti-Al(l) reacts with nitrogen to precipitate one or more nitrides (TiN, AlN) within the matrix; liquid-solid reactions, e.g., Zr-ZrC/ZrB_2 composites by directed metal reaction; solid-gas reactions and solid-solid reactions self-propagating high-temperature synthesis or SHS[2]. Among the various in-situ routes, the gas bubbling is considered a promising method that reactive gases are bubbled into the melt and the reinforced particulates are formed during the reaction between the gas or its decomposition product and the melt or its alloying elements. Gas introduced method was first developed by Koczak and Kumar in which reactive gases were introduced into the melt and the reinforcement was formed through the reaction between the gas or its decomposition product and the melt or its alloying elements[3]. By means of this technology it is possible to form uniformly distributed fine reinforcing particles and clean interfaces between particles and matrix which provide superior properties such as the hardness, the ultimate tensile strength and the high temperature creep. Compared with other reinforcements, AlN as a novel ceramic material has a low density (3.026 g/cm^3), a low coefficient of thermal expansion ($4.5\times10^{-6}\ K^{-1}$) and a very good thermal conductivity (110~170 $W\cdot m^{-1}\cdot K^{-1}$) [4]. Moreover, AlN is stable which does not react or decompose in molten magnesium alloys. Therefore, AlN could provide an improved interfacial bond between matrix and reinforcement, and thus the interfacial reactions and the problems associated with poor

Received date: January 25, 2015
Foundation item: the Research Fund of State Key Laboratory of Solidification Processing (NWPU), China (41-QP-2009, 60-TP-2010); National Key Basic Research Development Program of China ("973" Program) (2011CB610403)
Corresponding author: Yang Changlin, Ph. D., Associate Professor, State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, P. R. China, Tel: 0086-29-88460622, E-mail: ycl@nwpu.edu.cn

interface are out of consideration. Thus the in-situ synthesis of AlN particles in magnesium melt can enhance the modulus, the strength, the hardness, the wear resistance of magnesium matrix composites. In addition, AlN has a simple hcp structure with lattice parameters of a=0.3114 nm and c=0.4986 nm (JCPDS-International Centre for Diffraction Data, PCPDFWIN v. 2.3, 2002), which are very close to the lattice parameters of the Mg matrix with hcp structure of a=0.3209 nm and c=0.5211 nm. So it can be a potential grain refiner for magnesium alloys. H. M. Fu has approved that AlN could reduce the grain size of Mg-3wt% Al alloy from 450 μm to 120 μm [5]. And the wear resistance of magnesium matrix composites reinforced by in-situ AlN particles has been improved obviously [6]. However, at present the reinforcing effects are still limited due to lacking the knowledge of the uniform distribution, the morphology control and the formation mechanism of AlN particles in the matrix.

The present paper aims at producing magnesium matrix composites using in situ synthesized AlN particles via bubbling pure N_2 into the molten melts. The size, the morphology, the distribution and number density of AlN particles as functions of reaction temperatures and time were investigated. Finally, the optimum process parameters for forming AlN were obtained according to the microstructures of the composites.

1 Experiment

Mg-9wt%Al alloys were used as the matrix alloy. The in-situ synthesis was performed in a vacuum chamber as schematically shown in Fig.1. The chamber was firstly evacuated to 0.01 MPa and then filled with Ar gas to 0.2 MPa before melting. Herein, Ar gas was used to protect the melt from oxygen. After the matrix alloy of 1 kg was melted in a 304 stainless steel crucible and the temperature detected by the thermocouple arrived a designed value, N_2 gas purified by the drier and the deoxidization was bubbled into the melt for a designed time through a 304 stainless steel tubing with an inner diameter of 3 mm. The flow rates of N_2 and Ar were kept at 300 mL/min and 200 mL/min, respectively. The pressure of the vacuum chamber was kept at 0.2 MPa. After the reaction the melt was cooled down to 600 °C, then the alloy was remelted rapidly at 750 °C, and subsequently the melt was solidified to room temperature. In order to study the effect of the temperature and time on the nitridation reaction, the experiments were divided into two groups, i.e., the reaction temperatures were 700, 750 and 800 °C, with the same reaction time of 2 h, and the reaction time was 0.5, 1, 1.5 h, at the same reaction temperature of 750 °C.

The microstructure of the ingot was investigated by an Olympus PMG optical microscope and a Tescan Mira 3 XMU scanning electron microscope (SEM) with an INCAX-sight energy-dispersive spectrometer (EDS). The samples were also examined by X-ray diffraction analysis using a Panalytical X'pert MPD Pro X-ray diffractometer.

2 Results and Discussion

2.1 Formation of Mg_3N_2

In the present experiments, it was obvious that a great amount of greenish-yellow powder was found on the inside and outside wall of the crucible from the top to the bottom once the nitridation reaction took place at 800 °C for 2 h. The formed greenish-yellow powder became less with reducing the reaction temperature and time. Only a few of powder was formed at 700 °C for 0.5 h. As shown in Fig.2, XRD analysis confirms that the greenish-yellow powder is Mg_3N_2. So it indicates that the Mg_3N_2 powder is the product of gaseous phase reaction and then falls on the wall of the crucible or into the melt.

2.2 Formation of AlN particles

Based on Mg-Al binary diagram, Mg-9wt%Al alloy is hypoeutectic structure, i.e., the primary phase (α-Mg) and eutectic structure (α-Mg/$Mg_{17}Al_{12}$). Fig.3 is the XRD analysis results of Mg-9wt%Al alloys ingot and in situ prepared AlN/Mg-Al composite materials. It has confirmed that Mg-9 wt%Al alloys are composed of α-Mg and $Mg_{17}Al_{12}$ phases as shown in Fig.3a. In the in situ prepared composite materials, besides phases α-Mg and $Mg_{17}Al_{12}$, AlN phase is also detected

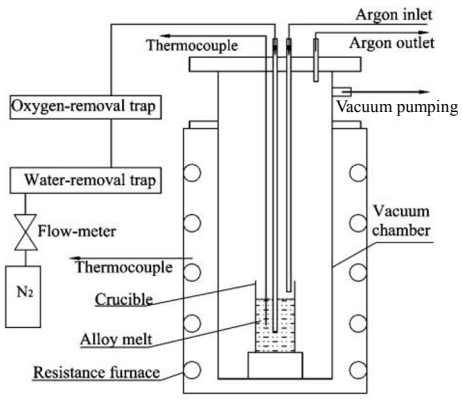

Fig.1 Schematic of experimental setup for the nitridation reaction

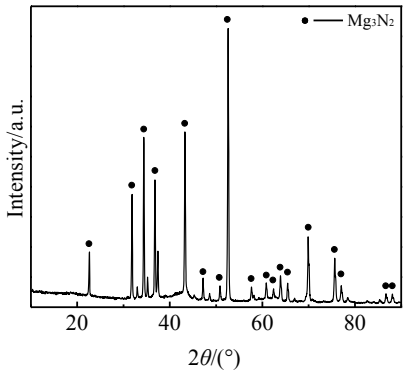

Fig.2 XRD pattern of the greenish-yellow powders reacted at 800 °C for 2 h