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ARTICLE

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

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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 (4.5×10^{-6} K^{-1}) and a very good thermal conductivity (110~170 W m^{-1} 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

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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

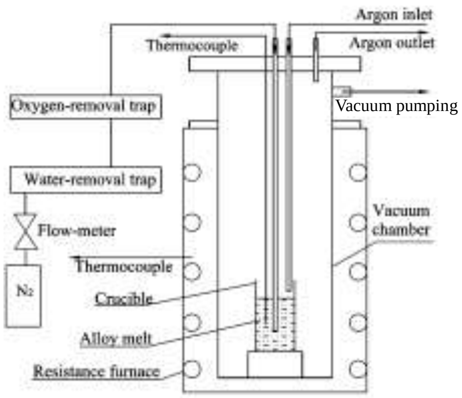

Fig.1 Schematic of experimental setup for the nitridation reaction

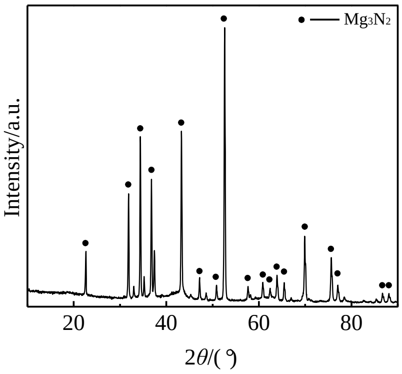

Fig.2 XRD pattern of the greenish-yellow powders reacted at 800 °C for 2 h

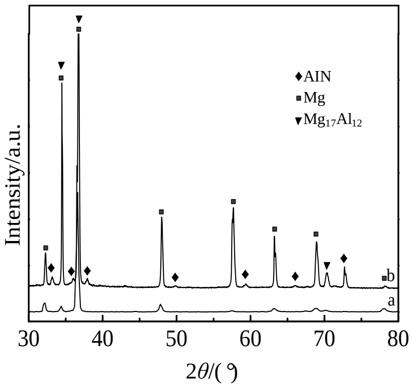

Fig.3 XRD patterns of Mg-9wt%Al alloy ingot (a) and in situ prepared AlN/Mg-9wt%Al composite materials (b)

while Mg_3N_2 phase is not detected, (see Fig.3b), which shows that AlN phase can be formed by bubbling N_2 gas into Mg-Al alloy melt, while the formed Mg_3N_2 phase is transformed into AlN phase completely and AlN phase is more stable than Mg_3N_2 phase in Mg-Al alloy.

Fig.4a shows that the micro-morphologies of the formed reinforcement phases distributed in the grain boundaries have two kinds of morphologies, i.e. fiber and particle. The lengths of the fibers are 20~100 μm, and the sizes of the particle are 2~4 μm. Figs.4b~4d are corresponding mappings of the elements (Mg, Al, N) distribution. It is clear that Mg is distributed in the whole zone, while Al and N are mainly distributed in the formed particles and fiber-like structure. Followed quantitative analysis of EDS for the formed particle which corresponding to a point of the spectrum 1 in Fig.4a shows that the particles are mainly composed of Mg, Al and N elements, whose mass fraction are 33.45%, 41.56%, and 24.99%, respectively, corresponding to atomic ratios of 29.27 at%Mg, 32.77 at%Al, and 37.96 at%N, respectively. While the composition of the matrix is composed of 94.92 wt%Mg, and 5.08 wt%Al, corresponding to atomic ratios of 95.4 at%Mg and 4.6 at%Al, respectively. So combined with XRD analysis results, it can be confirmed that formed reinforcement phases are AlN.

2.3 AlN formation mechanism

For AlN formation mechanism, Ye et al. proposed that the formation of AlN occurred via a two-step reaction: first, the gas-gas reaction process of N_2 and Mg (g) produced Mg_3N_2 particles, i.e. $N_2+3Mg \rightarrow Mg_3N_2$; second, the solid-liquid reaction process of Mg_3N_2 and Al produced AlN particles in the alloy melt, i.e. $Mg_3N_2+2Al \rightarrow 2AlN+3Mg$. The present experiments have also confirmed the formation of Mg_3N_2 powder as an intermediate product. Then Mg_3N_2 powder falls into the Mg-Al alloy melt to form AlN particles with the melt convection irritated by N_2 bubbling.

However, it is interesting that there are some fiber-like AlN phase besides small AlN particles in the prepared composites, as shown in Fig.4a and Fig.5, which indicate that there is another different AlN formation mechanism besides the two-step reaction mechanism. In particular, it has been found that the fiber-like AlN phase is formed along with the grain boundaries and its amount decreases with the increase of reaction temperature and time. In Fig.5, the nitridation reaction temperatures and time are 700 ^{o}C, 0.5 h (Fig.5a), 750 ^{o}C, 1 h (Fig.5b), 750 ^{o}C, 2 h (Fig.5c) and 800 ^{o}C, 2 h (Fig.5d). On the contrary, the amount of particle-like AlN phase increases, which indicates that the morphology change of AlN phase can not affect the AlN phase forming. Fig.4a and Fig.6 show the magnified microstructures of particle-like and fiber-like AlN phase. It is obvious that the particle-like AlN phase is composed of small AlN particles, while the fiber-like

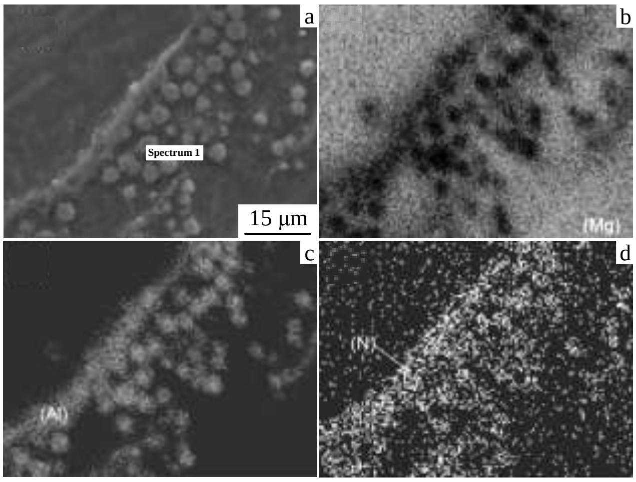

Fig.4 Microstructure (a) and corresponding elements distribution of Mg (b), Al (c), and N (d) for in-situ prepared alloy sample with in-situ formed reinforcement particles

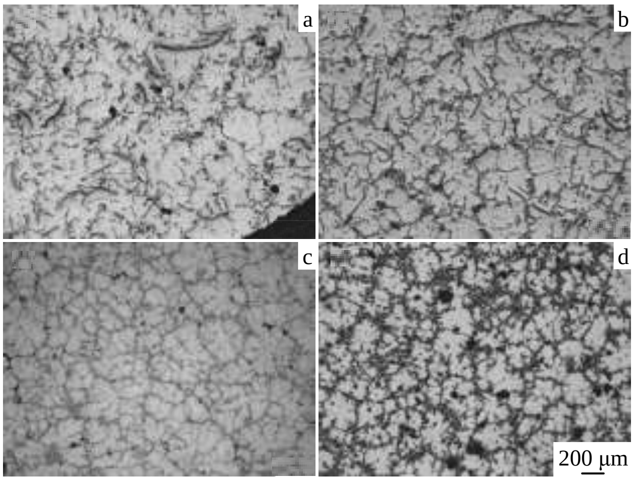

Fig.5 Microstructures of in-situ prepared AlN/Mg-Al composition material with different nitridation reaction temperatures and time: (a) 700 ^{o}C, 0.5 h; (b) 750 ^{o}C, 1 h; (c) 750 ^{o}C, 2 h; (d) 800 ^{o}C , 2 h

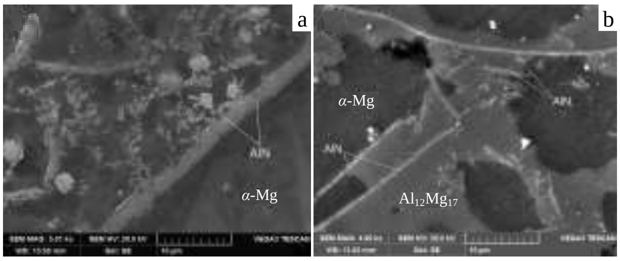

Fig.6 Magnified morphologies of fiber-like AlN phases

AlN phase is composed of small AlN fibers, in which some fiber-like AlN exist alone in the grain boundaries (Fig.6a), while another smaller fiber-like AlN exist on the $Mg_{17}Al_{12}$ phase in the grain boundaries (Fig.6b).

In the in-situ synthesis process, it is necessary that N_2 gas is bubbled into the alloy melt firstly. Then the bubbles of N_2 gas will move up to the melt surface. Herein, it is very evident that the motion trace of the N_2 bubbles and the morphology of fiber-like AlN phase are very similar, so it can be deduced that the fiber-like AlN phase is formed through a direct reaction of N_2 and Al (i.e. $N_2 + 2Al \rightarrow 2AlN$) during the N_2 bubbles being moved to the melt surface. However, Ye and Zheng et al. investigated the AlN formation in Mg-Al and Al-Mg alloys adopting an in-situ synthesis method, and they considered that the direct reaction of N_2 and Al to form AlN could take place only when the nitridation reaction temperature was above 900 ^{o}C [7,8]. In the present experiments, the nitridation reaction temperatures are 700~800 ^{o}C only. Then it is impossible seemingly to take place for a direct reaction of N_2 and Al. Whereas, in terms of the interrelation between gas bubbles and liquid, when the gas bubbles are introduced into the alloy melt, on the one hand, they will induce a convection of the alloy melt during floating up to the surface of the liquid pool. On the other hand, these bubbles will grow and explode (collapse). In particular, under the proper conditions, these bubbles can undergo a violent collapse, which will generate very high pressures and temperatures. This process is called cavitation[9]. Based on this, the research results of Yang et al. showed that during collapse of a single cavitation bubble induced by ultrasonic in Al-Si alloy melt, the strong impact coupled with locally high temperatures in a very short time could remelt the primary Si phase [10]. While in the organometallic reactions, the effective temperature reached during cavity collapse of a gas bubble was 5200 K [9]. Compared with the gas bubbles induced by ultrasonic, the inert gas bubbles from outside input have also been used to refine grains during solidification of alloy melt, and a fully grain-refined structure was obtained by a combination of localized chill with vigorous convection[11]. However, in the present work, a reaction gas (N_2) is bubbled into the alloy melt from outside. On the one hand, N_2 gas is deoxidized by a deoxidization furnace at a work temperature of 800 ^{o}C, at which copper turnings are filled in the working chamber to deoxidize the N_2 gas. So the N_2 gas bubbles with a temperature of 800 ^{o}C would enter the alloy melt. And the N_2 gas bubbles would also distend during floating up to the surface of the alloy melt with the increase of inside gas pressure. Once the N_2 gas bubbles reach a critical size, a violent collapse would take place, which will induce a cavitation effect similar to that induced by ultrasonic in the melt. Herein, it is necessary to control the flow rate of N_2 gas to make sure the N_2 gas bubbles having enough time in the alloy melt. Thus, the N_2 gas bubbles can react directly with Al atoms in Mg alloy melt due to a high temperature induced from a cavitation effect, which is different from the inert gas bubbles (eg. Ar) in the alloy melt to refine grains through thermal shock force on the dendrite. So the direct reaction of N_2 and Al takes place with the N_2 gas bubbles floating upward continually, and the reaction product AlN is formed along with the reaction track (i.e., motion trace of N_2 bubbles) like a fiber. Once the alloy melt is solidified, the parts of fiber-like AlN will be attached in the surface of the formed $Mg_{17}Al_{12}$ phase, which can not grow rapidly and are not dispersed to particles due to the restraint of $Mg_{17}Al_{12}$ phases, while some fiber-like AlN existing alone in the grain boundary break off from the fibers and are dispersed into the matrix due to the convection of melt and the impact of gas bubbles (see Fig.6a). Though Mg_3N_2 enters the melt through the convection of melt and reacts with Al atom to form AlN, and then the formed AlN moves with the gas bubble floating upward, it is impossible to form a fiber-like AlN because the AlN attaching on the gas bubbles, on the one hand, will move to the surface of melt, on the other hand, will be dispersed in the melt with the collapse of gas bubbles. So it is reasonable that the fiber-like AlN is formed by a direct reaction of N_2 gas and Al. In addition, Fig.5 shows that the amount of fiber-like AlN phase decreases with the increase of reaction temperature and time. It is indicated that the strong convection of melt and the impact of gas bubbles collapse make the more fiber-like AlN break off and become AlN particles. At the same time, an indirect reaction proposed by Ye et al to form AlN particles also takes place in the alloy melt.

Then, it is convenient and practical to identify in-situ formation of AlN phase from the morphology of fiber. However, the amount of AlN phase changes with the temperature and the time of in-situ reaction. Though at a high temperature, the nitridation reaction for AlN formation is more avail to take place, the volatilization of Mg is extremely serious, which will waste more Mg and reduce the service life of crucible. As described above, upon the nitridation reaction at 800 ^{o}C for 2 h, more Mg_3N_2 particles are formed, but the serious volatilization of Mg and rapid emission of N_2 gas bubbles will block the formed Mg_3N_2 particles to fall into the alloy melt, and the direct contact time of N_2 gas and Al is also reduced. As a result, the AlN phases formed at 800 ^{o}C for 2 h are fewer than that formed at 750 ^{o}C for 2 h. In addition, more

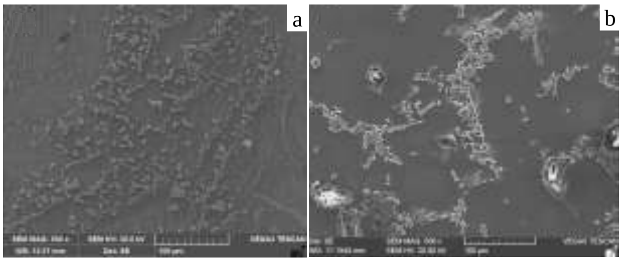

Fig.7 Microstructures of the in-situ prepared alloy samples with AlN phase by the bubbling N2 gas method at different reaction temperatures for 2 h: (a) 750 °C and (b) 800 °C

defects and coarse grains are induced due to a higher temperature, as shown in Fig.7. So from an industrial point of view, the nitridation reaction at 750 °C is more effective to form AlN phase, while the reaction time depends on the alloy weight, and it is necessary to keep a reasonable reaction time for more AlN phase to form in the Mg-Al alloy.

It is also important for a uniform distribution of AlN phase to enhance the alloy properties. Though a direct reaction to form AlN can take place in the alloy melt, the reaction of Mg_3N_2 as an intermediate product with Al mainly proceeds in the top of melt. Thus besides convection and stirring of gas bubbles, the remelting is also effective for a uniform distribution of AlN phase, i.e., after the nitridation reaction, the melt temperature decreases to 600 °C, the solidified ingot is remelted rapidly to 720 °C in a few minutes, which can make AlN phase distributed uniformly without aggregation. In regard to the relation of properties and microstructure of AlN reinforced Mg-Al alloy, it will be discussed in detail in the later paper.

3 Conclusions

1) AlN phases can be in-situ synthesized by bubbling N_2 gas into Mg-Al alloy melts. There are two kinds of nitridation reaction mechanisms to form AlN phase, i.e., the direct nitridation reaction of N_2 and Al and the indirect nitridation reactions of ($3Mg + N_2 \rightarrow Mg_3N_2$) and ($Mg_3N_2 + 2Al \rightarrow 2AlN + 3Mg$).

2) A direct nitridation reaction of N_2 and Al to form AlN takes place due to a cavitation effect of N_2 gas bubbles during a violent collapse.

3) The nitridation reaction temperature of 750 °C is more effective to form AlN phases in situ. While a rapid remelting of the ingot after the nitridation reaction can make AlN phases distributed uniformly.

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Mg-Al 合金中 AlN 颗粒的原位合成机制研究

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摘　要：采用在合金熔体中通入氮气的方法在镁铝合金中原位生成了 AlN 颗粒增强相。合金微观组织的研究分析表明，AlN 相不仅可通过间接氮化反应（$3Mg+N_2 \rightarrow Mg_3N_2$，$Mg_3N_2 +2Al \rightarrow 2AlN + 3Mg$) 形成，而且可在熔体中由 Al 和 N_2 直接反应形成。控制氮化反应温度在 750 ℃，且合金熔体凝固后的快速重熔可在合金中获得分布均匀的 AlN 相。

关键词：原位合成法；AlN；镁合金；形成机制；最优工艺

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