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Mill setting and microstructural evolution during mechanical alloying of Mg_2Si

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The mechanical alloying behaviour of magnesium and silicon to form the intermetallic compound Mg_2Si and the optimum setting of a planetary ball mill for this task, were examined. For the ductile–brittle magnesium–silicon system it was found that the efficiency of the mill is mostly influenced by the ratio of the angular velocity of the planetary wheel to that of the system wheel and the amount of load. The examination of the kinetics inside the planetary ball mill for different mill settings showed that a ratio of angular velocities of at least 3 is necessary to compensate the reduction of efficiency due to slip. The optimum powder load for the 500 ml vial was found to be 10–20 g. The milling process starts with elemental magnesium and silicon bulk particles. During the milling, the silicon pieces are rapidly diminished and together with the constantly forming Mg_2Si they act as an emery powder for the magnesium bulk pieces. Simultaneous to the diminution of the magnesium, alloying occurs.

1. Introduction

Mg_2Si is an intermetallic compound with low density ($1.95\,g\,cm^{-3}$ [1]) which can be used for structural [2–4] and thermoelectric [5–7] applications. In this paper, on the production of Mg_2Si from elemental bulk magnesium and silicon by mechanical alloying (MA) in a planetary ball mill, is reported. Thus, the oxidation and the concomitant danger during processing are minimized.

The time evolution of the mechanical alloying process starting from a ductile (magnesium) and a very brittle (silicon) bulk component to form an intermetallic compound (Mg_2Si) has been examined in detail as a function of different mill settings. In addition, by means of electron microscopy investigations, the structural formation of the alloy was unveiled. It is shown that in the present case the process is different from the accepted models [8, 9] for the mechanical alloying of a ductile-brittle system.

2. Experimental procedure

The mechanical alloying of the Mg_2Si intermetallic compound was performed in a Retsch PM 400 DLR planetary ball mill [10]. Starting materials were chunky particles with a size $\leqslant 5$ mm to minimize the specific surface and, consequently, the oxygen content in the final powder. For this particular task of the planetary ball mill, the global parameters and the kinetic settings were examined to optimize the milling process.

For examination of the microstructural evolution of Mg_2Si, the following mill setting was chosen: 500 ml hardened steel vials with 100 milling balls having a diameter of 10 mm each; 10 g material with an addition of 80 g milling fluid (*n*-hexane) were processed for 8–30 h. All preparation steps were performed in an argon atmosphere.

The as-milled material was found to be a mixture of powder and bulk material. It was separated using a sieve (25 mesh) into the powder fraction and the remaining bulk. The powder was phase analysed by X-ray diffractometry (XRD). The microstructure was examined by transmission electron microscopy (TEM), scanning electron microscopy (SEM), and energy dispersive analysis of X-rays (EDX). The EDX results in the TEM were measured with a spatial resolution of ≈ 80 nm and were compared to the global composition of the powder measured by X-ray fluorescence analysis (XFA).

3. Results and discussion

3.1. Mill settings

A planetary ball mill can be characterized by two different types of parameters: the first set consists of global parameters describing the environment, and which are valid for each milling experiment, i.e. the material of the milling media, the size and amount of the milling balls, and the type and amount of the milling fluid. The second parameter set describes the kinetics inside the planetary ball mill. These are the

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system wheel's radius and angular velocity, R and Ω, respectively, and the planetary wheel's radius and angular velocity r and ω, respectively. These kinetic parameters will be summarized as the actual "mill setting".

3.1.1. Global milling parameters

When testing the milling media, i.e. vials and balls, of different materials, hardened steel was found to be the only suitable material. Stainless steel, agate (SiO_2), or tungsten carbide (WC) caused much stronger contamination of the powder than the usage of hardened steel. Stainless steel and agate were too tender in terms of abrasion, and in the case of WC, small particles were knocked out of the vial leading of its destruction and to WC contamination of the powder.

By varying the size of the milling balls, the best result was found to be obtained by balls with a diameter of 10 mm. Milling balls with a diameter of 20 mm led to a significant increase of iron contamination of the powder. When decreasing the diameter below 8 mm, the balls did not have enough kinetic energy to diminish and alloy the bulk material. In addition, the use of a mixture of different sizes did not improve the milling process. If there were great differences in the ball sizes, the smaller balls can even be destroyed by the larger ones. If the size distribution was too narrow, no additional effect could be observed compared to the milling condition with a single ball size.

Milling without milling fluid always led to strong agglomeration. Consequently, a milling fluid was employed. We used *n*-hexane (C_6H_{14}), which has the additional advantage to protect the material from oxidation. The occurrence of carbides and hydrides reported in the literature for titanium aluminium alloys [11, 12] was not observed in our experiments.

3.1.2. Kinetic parameters

The experiments showed that the absolute angular velocity of the system wheel should be 5 revolutions per second, which is the maximum speed of our mill, to achieve the most effective alloying progress. The resulting centrifugal acceleration is 10 g (gravitational acceleration), thus, the influence of gravity on the kinetics can be neglected. Indeed, the milling balls arrange themselves as a partial shell on the inside of the vial wall (Fig. 1a). The resulting peeling motion (Fig. 1b) could be confirmed by the occurrence of discrete horizontal grooves on the vial walls. The distance between such grooves in all experiments and in all vials had the same value and was very close to that of two-dimensionally close-packed spheres, as pointed out in Fig. 1a. This is an indication that the peeling movement of the milling balls occurs in discrete, stable layers.

If the angular velocity, Ω, was smaller than 5 revolutions per second, the kinetic energy of the milling balls was not high enough to diminish the chunky magnesium particles, even if the mass of the milling balls was raised to keep the product $m_B \Omega^2$ (m_B = mass of a milling ball) and thus the theoretical kinetic energy of the milling balls constant. The effect is due to the fact that such a change also alters the impact frequency and the flight paths: a decrease in the angular velocity, Ω, leads to a decrease of the centrifugal acceleration. Eventually, the influence of gravity is large enough to keep the milling balls on the bottom of the vial. This accumulation of the milling balls impedes their movement, and the milling process will proceed much slower.

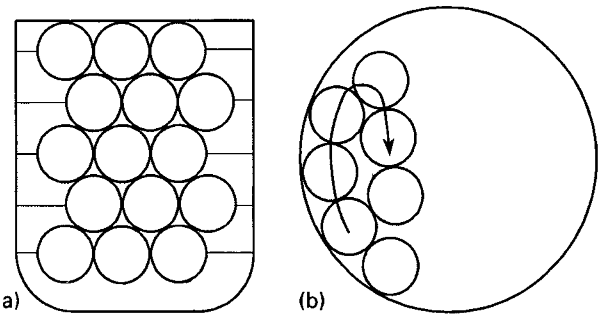

Figure 1 (a) Arrangement of the milling balls in the vial wall; thin lines indicate grooves (radial view from the centre of the vial). (b) Peeling motion of the milling balls in the vial view from above in a reference system that is fixed on the planetary wheel.

Therefore, the angular velocity was kept to 5 revolutions per second. The remaining free milling parameters are the ratio ω/Ω, and the size of the vial, and the mill settings are characterized in the following form: ω/Ω vial size (ml), e.g. $-3/250$. For a detailed comparison of the different mill settings, we chose the following: $-2/250$, $-3/250$, $-3/500$, each with an amount of 10 g powder, and $-3/500/20$ with an amount of 20 g powder. The minus sign in the ω/Ω ratio denotes opposite revolutions of the two discs.

3.1.3. Comparison of the mill settings

The mechanical alloying process can be described by the MA-degree, A, the impact factor, f_i, and the normalized alloying time, t_n [13]. The MA-degree is calculated from XRD measurements and for Mg_2Si defined as

$$A = \frac{a}{a + m + s} \tag{1}$$

with a the intensity of the (2 2 0) Mg_2Si peak in the XRD spectrum, m the intensity of the (1 0 1) Mg peak in the XRD spectrum, and s the intensity of the (1 1 1) Si peak in the XRD spectrum.

The impact factor is defined as the product of the ball-to-powder weight ratio (BPR) and the milling time, and is a measure for the energy input from the mill into the powder. If the plot of the MA-degree as a function of the impact factor is fitted by a curve in the form $A = 1 - e^{f_i/t_n}$ there will be only one free parameter, t_n, that can be determined by simple mathematics. This parameter is called normalized alloying time and it is the time constant of the alloying process. This means the smaller t_n, the more effective the mill.

The use of this description of the milling process requires only the determination of the MA-degree and the measurement of the BPR and the milling time. On the other hand, it avoid the use of collision velocity, collision energy, flight path of the milling balls, etc., that are all variables which can only be determined with an immense experimental expense. Consequently, our method allows a fast and easy experimental comparison of different mills or mill settings with ordinary experimental facilities.

Fig. 2 shows a plot of the MA-degree as a function of the impact factor for the different mill settings. For each setting a fitting curve in the form $A = 1 - e^{f_i/t_n}$ is calculated. It can be seen from the plots that the settings $-3/250$ and $-3/500$ lead to nearly the same behaviour. The setting $-2/250$ leads to one fitting curve lying below and the setting $-3/500/20$ to one lying above these two curves. This implies that the setting $-3/500/20$ is the most effective one. This behaviour can be quantitatively described by the normalized alloying time. For the settings $-3/250$ and $-3/500$ it is 142 and 137 h, respectively, i.e. nearly identical values. The setting $-2/250$ has a higher normalized alloying time of 195 h, whereas the one for the setting $-3/500/20$ is only 80 h. It is remarkable that all these calculated normalized alloying times are significantly smaller than that determined for the vibratory mill [13], thus showing that the planetary ball mill is much more effective than the vibratory type.

Theoretical calculations of the kinetics inside a planetary ball mill result in a larger kinetic energy of a milling ball for the setting $-3/500$ than for the setting $-3/250$ and consequently, a better efficiency [14] (kinetic effect). On the other hand, video observations proved the occurrence of a very large slip factor which is responsible for the peeling of the milling balls [15] (slip effect). These two effects are illustrated in Fig. 3. Employing a larger vial leads to a wider flight path and to a passing over from flight pass 2 to flight path 1. An increase of the slip factor narrows the flight path, i.e. a change from flight pass 2 to flight path 3. Our experimental results indicate that the second effect is the dominating one because the settings $-3/250$ and $-3/500$ led to the same energy input into the powder. This means that in both settings the slip factor is so large that peeling occurs and the movement is independent of the size of the vial. This assumption is confirmed by the occurrence of the grooves described above.

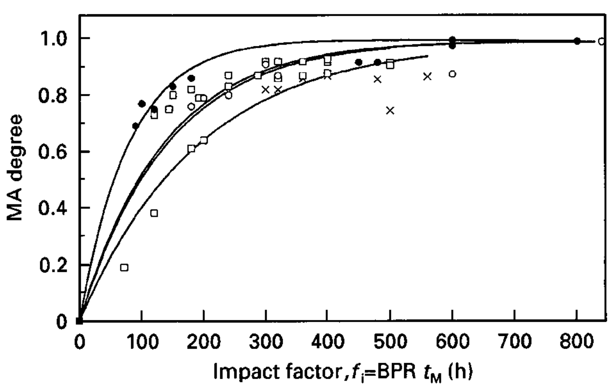

Figure 2 MA-degree as a function of impact factor for the different mill settings. (×) $-2/250$, (□) $-3/250$, (○) $-3/500$, (●) $-3/500/20$.

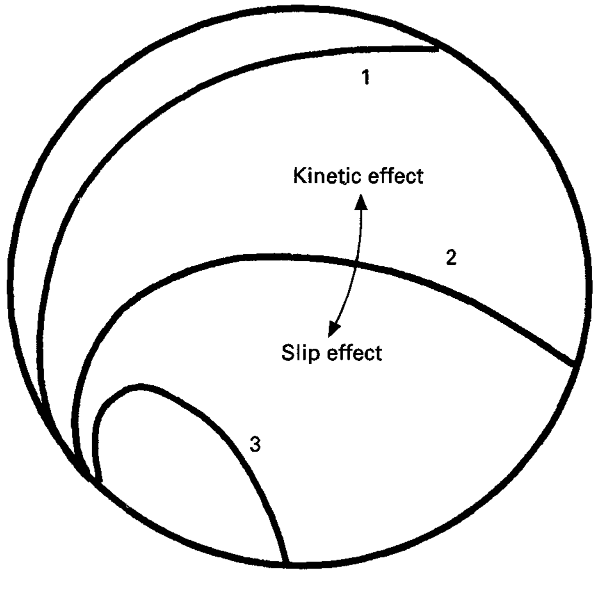

Figure 3 Influence of the slip effect and the kinetic effect on the flight path of a milling ball.

As the angular velocity of the system wheel, Ω, is held constant, the angular velocity of the planetary wheel is smaller for the setting $-2/250$ than for the other ones. In this way the energy resulting from friction between the milling balls and the vial wall is smaller for this setting, thus explaining the smaller efficiency.

The improvement of the efficiency for the setting $-3/500/20$ shows that an increase of the load leads to a better performance of the planetary ball mill. Experiments with the mill settings $-3/500/40$ and $-3/500/50$ showed that a further increase of the load is indeed possible, but this further increase is accompanied by an increase of the iron contamination of the powder resulting from the milling media.

3.2. Microstructural evolution of alloy formation

The evolution of the material's microstructure was examined by taking samples from the series with the mill setting $-3/500$ and a BPR of 40 : 1. The milling times were 8–30 h

In the intermediate state of ball milling, i.e. at milling times shorter than 25 h at the chosen mill setting, the vial load consisted of loose powder and of the larger bulk remaining after separation from the powder by sieving at 25 mesh. After 25 h milling, all the remaining bulk had completely disappeared, and the whole load had a particle size less than 25 mesh.

Fig. 4 shows XRD signals from the powders which were milled for 8 h (intermediate milling stage, with presence of remaining bulk) and 25 h (completely diminished load). The first powder consists of pure silicon and the desired Mg_2Si compound. No elemental magnesium could be detected in the powder, thus concluding that all the still available elemental magnesium was in the bulky pieces.

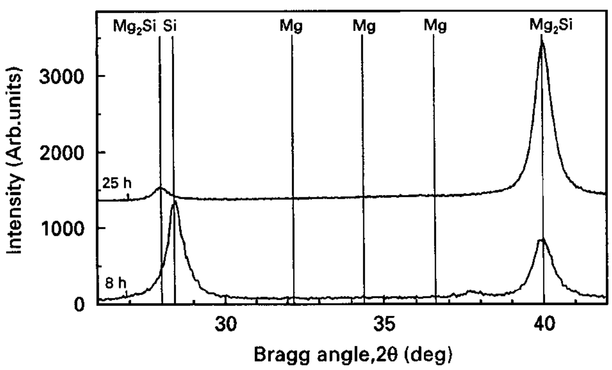

Figure 4 XRD spectra for the powder fraction after a milling time of 8 and 30 h at a BPR of 40:1; mill setting: − 3/500.

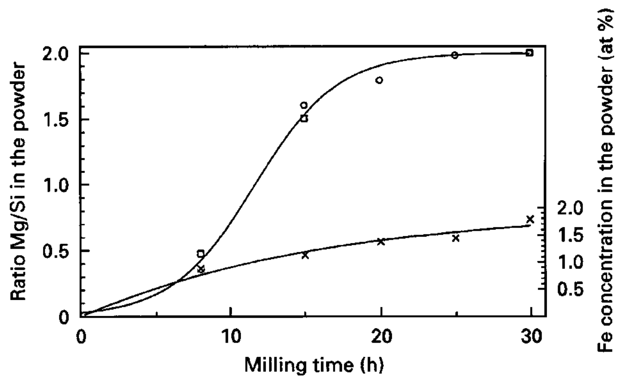

Figure 5 Ratio of magnesium to silicon and iron concentration in the powder fraction. (□) Mg/Si (EDX measurements at TEM), (○) Mg/Si (X-ray fluorescence analysis), (×) Iron concentration (XFA).

EDX measurements on the bulk verified that it consisted of a core of pure magnesium which is covered by a thin layer (thickness $\approx 20\,\mu m$) having the same composition as that of the loose powder. Thus the powder acts as an emery agent leading to a diminution in the size of the remaining bulk. During this abrasion, silicon particles of the powder come into direct contact with the surface of the magnesium core. This contact, which is induced by the impact of the milling balls is accompanied by a high local pressure and the formation of defects. These effects favour diffusion processes. As Chu *et al.* [16] have shown, magnesium is the moving species. It diffuses into the silicon leading to a diffusion profile similar to that observed in the brittle–brittle silicon–germanium system [17]. As no elemental magnesium can be detected in the powder, all the abraded magnesium diffuses into the silicon and directly forms the Mg_2Si. When all the remaining bulk has vanished, i.e. after a milling time of 25 h, the powder consists of the pure intermetallic compound.

The global powder composition was quantitatively analysed by means of XFA. The local compositions of single powder particles were measured by means of EDX in a TEM. From these measurements, the atomic ratio of magnesium to silicon was calculated and its time-dependent development approximated by a logistic growth function. The measured values and the fitting curve are plotted in Fig. 5. Both, local and global measurements led to nearly the same atomic ratio of magnesium to silicon which is initially small and increases with time, finally reaching the stoichiometric composition. The local and the global magnesium concentrations never exceed the value of 68 at %, thus confirming that the powder only consists of the intermetallic compound and elemental silicon.

The high homogeneity of the mechanically alloyed powder, even in an early milling state, can be seen from the evaluation of the measurements in the TEM of the powder milled for 8 h. The EDX spot has a resolution of 80 nm, and in this small area the magnesium concentration only varies from 24–51 at % with an average value of 33 at %. After 25 h milling, the magnesium concentration varies from 65–68 at % in the EDX measurements. This means that, within the accuracy of the measurement, the powder appears to be homogeneous having the stoichiometric composition.

The contamination of the powder with iron from the milling media, determined by XFA measurements, did not exceed 2 at %. The time-dependent development of the impurity concentration is summarized in Fig. 5. It can be seen that most of the contamination is induced in the early milling stages, when a lot of hard elemental silicon is available. In the later milling states, the silicon has reacted to form the softer intermetallic compound and the abrasion of iron slows down.

4. Conclusion

The synthesis of Mg_2Si from elemental bulk material in a planetary ball mill is feasible. The mechanical alloying process is caused by abrasion and attrition in the examined mill settings. The calculation of the quantities describing the milling process showed that mechanical alloying in a planetary ball mill is much more effective than in a vibratory mill. A further improvement of the mill setting could be attained by changing the ratio ω/Ω from − 3 to, for example, − 4, thus increasing the speed of the planetary wheel. This will lead to a separation of the milling balls from the vial wall and to a higher energy transfer into the powder.

All the beginning of the milling process the silicon particles are diminished and act as an emery powder for the magnesium chunks. The alloying occurs instantly during this abrasion on the surface of the magnesium. Finally, all the magnesium bulks vanish and at the same time the powder is completely alloyed to Mg_2Si.

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