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High Performance Magnesium Composite Alloy by Employing Wasted High Purity SiO_2 Ingot

Katsuyoshi Kondoh, Ritsuko Tsuzuki, Wenbo Du and Tatsuhiko Aizawa[1]
RCAST, The University of Tokyo, 4-6-1, Komaba, Meguro, Tokyo, Japan
Fax: 81-(0)3-5452-5099, e-mail: kondoh@hpm.rcast.u-tokyo.ac.jp
Fax: 81-(0)3-5452-5085, e-mail: wenbodu@hpm.rcast.u-tokyo.ac.jp
Fax: 81-(0)3-5452-5085, e-mail: tsuzuki@hpm.rcast.u-tokyo.ac.jp
[1]CCR, The University of Tokyo, 4-6-1, Komaba, Meguro, Tokyo, Japan
Fax: 81-(0)3-5452-5185, e-mail: aizawa@hpm.rcast.u-tokyo.ac.jp

To realize the lightweight effects by materials technology, a new process for fabricating high-performance magnesium composites via a solid-state reaction by using high purity SiO_2 glass scraps has been established. From a viewpoint of the microstructures control of the composites, the core technologies to improve the physical and mechanical properties are; a solid-state synthesis of Mg_2Si and MgO particles by the deoxidization of SiO_2 glass by magnesium, and a refinement of both their dispersoids and the magnesium matrix grains by the RPW process. For example, when using the elemental Mg-Al-Zn-Ca-RE (rare earth) system alloy and 2mass% SiO_2 glass powder mixture as starting raw materials, the hot extruded composite via RPW shows 385MPa TS, 335MPa Y.S, and elongation of 10%. This process is quite safety and environmentally benign compared to the conventional re-melting process, because of utilizing course magnesium raw powder and no use of SF_6 toxic gas. It also shows a possibility to employ SiO_2 glass scraps as starting raw materials to fabricate magnesium alloys.
Key words: magnesium composite, SiO_2 glass, solid-state reaction, Mg_2Si, MgO

1. INTRODUCTION

Weight reduction is one of the key-technologies to create the safe and comfortable environment. For example, the lightweight effect of automotives reduces both the energy consumption and the air pollutions in traveling, such as CO_2, NO_x and SO_x. Magnesium is the lightest metals of the industrial alloys, and currently applied to the components or systems, such as housings of PDA, mobile phones and PCs. The mechanical properties, however, should be improved when applying the magnesium alloys to structural components or automotive parts. The previous works[1-4] indicated that comparing the conventional re-melting process, the solid-state process via hot extrusion or equal channel angular extrusion (ECAE) shows the following merits; the reduction of energy consumption, no need of SF_6 toxic gas used in melting, and the remarkably improved mechanical properties of due to the refined microstructures. The repeated plastic working (RPW) process [5] is effective on solid-state recycling chips, fragments or coarse powder of the light metal wastes. It also serves the improvement of mechanical properties by refining microstructures. On the other hand, magnesium composites with high-performance were developed, in using the elemental magnesium and silicon powder mixture as raw materials. The key technology is a solid-state synthesis of Mg_2Si compounds, which acted as reinforcements of the composites, because of their high hardness, high Young's modulus and superior corrosion resistance. In the present work, a new process for fabricating high-performance magnesium composites in solid-state was established by employing high purity SiO_2 glass scraps instead of silicon particles. In-situ reaction of magnesium and glass particles progresses to synthesize Mg_2Si and MgO, and distributed in the magnesium matrix. The effect of the glass content on the physical and mechanical properties of the magnesium composites is evaluated. From a viewpoint of the refinement of the Mg_2Si and MgO dispersoids, the RPW process is also applied to the magnesium alloy and SiO_2 glass powder mixture.

2. FABRICATING PROCESS USING SIO_2 GLASS

Materials and process designs to fabricate magnesium composites with Mg_2Si dispersoids are available when using SiO_2 glass scraps as input raw materials instead of silicon. From a viewpoint of a free energy of oxides formation $\triangle G^0$, the Ellingham diagram[6] shows that $\triangle G^0$ of magnesium at 923K is quite lower than that of silicon. It means that silicon is easily formed after deoxidizing SiO_2 by magnesium at elevated temperature, and Mg_2Si synthesis occurs by a reaction of the silicon with magnesium as explained in Eq.1.

$$4Mg + SiO_2 \rightarrow Mg_2Si + 2MgO \quad (1)$$

Considering that the main ingredient of the glass products is SiO_2, the glass scraps, in particular with a high purity, also have a large possibility to be employed as input raw materials to form Mg_2Si and MgO by oxidization. Figure 1 schematically illustrates a new process of magnesium composite alloys including Mg_2Si and MgO fine dispersoids when using SiO_2 glass scraps with a high purity of 99.9~99.99%, such as sputtering target materials for electron devices and optical glass fiber. They are mechanically fractured into pieces by a milling process. After sieving them, SiO_2 glass powder is prepared as input raw materials. Concerning the magnesium alloys as another starting materials, from a viewpoint of the safety and its cost reduction, the coarse powder, having a mean particle size is 0.5~2mm, is employed. The elemental SiO_2 glass and magnesium powder mixture is consolidated at room temperature. The green compact, having a relative density of 85~90%, is heated in argon or nitrogen gas atmosphere. The heating temperature is an important parameter to synthesize Mg_2Si and MgO, and strongly depends on the particle size of input raw materials, the purity and content of SiO_2 glass powder, and relative density of the green compact. In the previous work, when employing the elemental Mg and crystalline SiO_2 powder mixture, the differential scanning calorimeter (DSC) thermogram of the compact revealed an exothermic peak due to the above reaction between raw materials [7]. That is, this remarkably exothermic heat causes the reaction to form Mg_2Si and MgO by a self-propagating high-temperature synthesis (SHS). Accordingly, an ignition temperature (T_i), which corresponds to the starting temperature of the exothermic peak of the DSC thermogram, is employed as a suitable heating temperature to synthesize them in this study. After heating the compact, it is immediately consolidated into a full density by the hot hot extrusion to fabricate the composites including in-situ formed Mg_2Si and MgO dispersoids. This process never requires any SF_6 toxic gas, that is, environmentally benign.

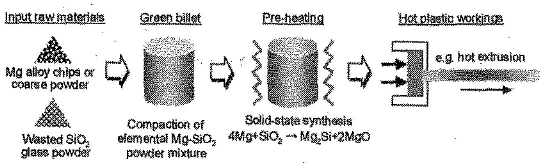

Figure 1. Schematic illustration of solid-state process to fabricate magnesium composite alloys from elemental SiO_2 glass scraps and magnesium powder mixture.

3. EXPERIMENTAL PROCEDURE

Figure 2 shows an appearance of in-house scraps of the wrought optical SiO_2 glass fiber with a purity of 99.99% (a), and their small blocks or fragments by a ball milling equipment (b), which are used as raw materials.

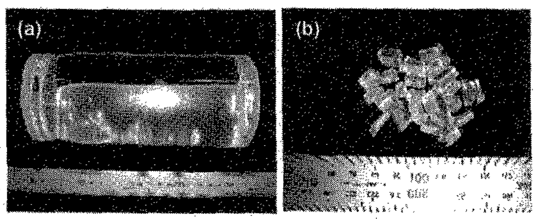

Figure 2. Appearance of wasted SiO_2 glass used for optical fiber (a) and refined blocks of SiO_2 glass wastes (b).

The glass blocks are grinded into fine powder, having a mean particle size of 16.8 μm. X-ray diffraction (XRD) of SiO_2 glass powder shows a broadened pattern due to their non-crystalline structure. Another ones come from the wasted magnesium alloy ingots; (1) AZ31 alloys and (2) Mg-0.5Zn-6Al-1Al-3Ca (mass%) alloys [8]. They are also in fragments with 0.5~2mm by tool cutting. When mixing both raw materials, the SiO_2 glass particle content of the powder mixture is 0, 2, 4, 6, and 8mass%. Each elemental powder mixture is consolidated to green compacts with a relative density of 86~88%. DSC thermal analysis on each green compact is carried out to examine T_i, when heating from 293K to 1000K in Ar gas. After heating each compact at T_i for 300s in nitrogen gas atmosphere, it is immediately consolidated into a full density by hot extrusion with an extruding ratio of 37. The structural evolution by XRD and optical microstructure observation, micro-hardness and ultimate tensile strength tests of the magnesium composite are carried out.

4. RESULTS AND DISCUSSION

4.1 In-Situ Formation of Mg_2Si/MgO by Using SiO_2 Glass Powder

As results of DSC analysis of the green compacts in using the AZ31 and SiO_2 glass powder mixture, each DCS curve except for 0% glass distinctly reveals an exothermic peak at about 730K. The exothermic heat gradually increases in proportion to the glass powder content. In general, non-crystalline SiO_2 glasses indicate an endothermic peak at 844K, corresponding to the glass transition temperature due to the phase transformation from α to β [9]. DSC curve of the compact including SiO_2 glass, however, shows no endothermic peak at 844K, and no SiO_2 powder remains in the green compact after heating over 844K. XRD analysis result on the green compacts annealed at 723K for 300s is show in Figure 3 (a). It detects the peaks of Mg_2Si and MgO, excepting 0% glass content. Fig.3 (b) shows that the relative peak intensity ratio of Mg(101) to Mg_2Si increases roughly in proportion to the glass content of the starting materials.

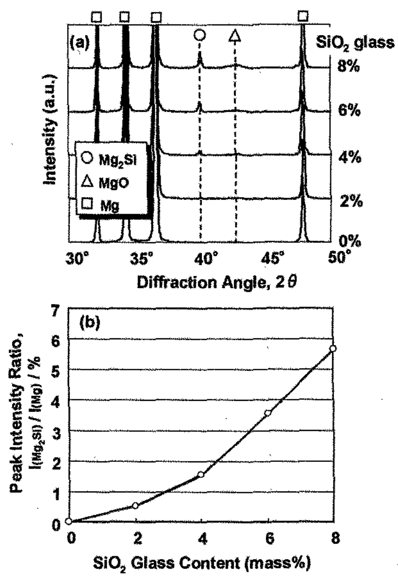

Figure 3. XRD patterns of green compacts after heating at 723K for 300s (a) and peak intensity ratio dependence on SiO_2 glass content based on XRD patterns (b).

Furthermore, the DSC curves of the green compacts heated at 723K show no exothermic peak. According to these results, it is considered that SiO_2 glass particles completely react with magnesium alloy powder, which is based on the SHS behavior, to form Mg_2Si and MgO during heating over T_i.

4.2 Magnesium Composites with Mg_2Si in Using High

purity SiO_2 Glass Scraps and Wasted Magnesium Ingots

Figure 4 shows the optical microstructures of the hot extruded AZ31 alloys with Mg_2Si and MgO dispersoids via the above solid-state reaction, when using the elemental AZ31 and 2mass% SiO_2 glass powder mixture. There is no pore in the AZ31 matrix, and its relative density is 99.8%. Most of the particles are uniformly distributed in the matrix, however, some ones locally gathered at the primary particle boundaries. This is due to a quite difference of the particle size of AZ31 and glass powder. The matrix grain size of the composite alloys is 10-15 μ m, and significantly small compared to the input AZ31 raw powder with a mean particle size of 120 μ m. The refined texture is due to the dynamic re-crystallization during hot extrusion.

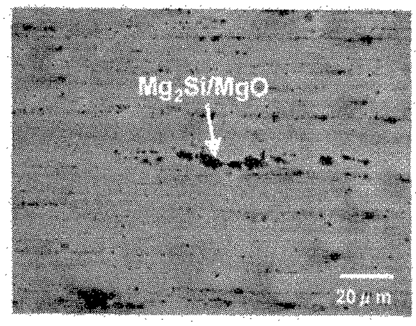

Figure 4. Optical microstructure of hot extruded AZ31-2mass%SiO_2 composite alloy on root of solid-state synthesis process.

Figure 5 shows the micro-hardness dependence of the composites on the SiO_2 glass content. It proportionally increases with increase in its content, because the hardness of Mg_2Si and MgO are 600~700Hv and 280~450Hv, respectively, and much harder than that of the AZ31 matrix alloy.

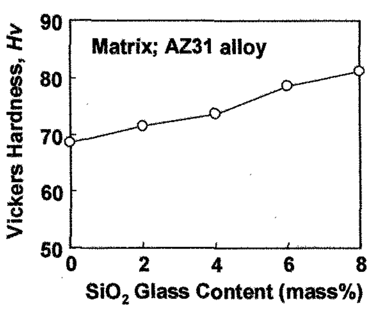

Figure 5. Hardening effect of magnesium composite alloys with various content of Mg_2Si/MgO.

4.3 Microstructure Control by Repeated Plastic Working

The utilization of fine glass particles has a possibility to improve the mechanical properties of the magnesium composites with Mg_2Si and MgO dispersoids. When employing ultra-fine additives, however the partial gathering of them in the matrix causes the extreme decrease of the properties. In this study, the cyclically repeated plastic working process is applied as a microstructure control method to distribute the fine particles uniformly in the matrix. In the RPW process, the two upper punches go down into the die alternatively. The punch I and II, for the compaction of raw powder mixture and the backward extrusion of the compact, respectively, are automatically controlled by PC. The impact energy into the compact via the upper punch II is much effective on the fragmentation and refinement of raw materials. The relative density control of the compact by the punch I is also important to refine them effectively. At the same time, the backward extrusion promotes a mixing effect of the two kinds of the starting raw materials. Refined glass powder are embedded in the magnesium matrix during plastic working, that is, the partial gathering of them at the primary magnesium raw particle boundaries is completely obstructed. From a viewpoint of the high-speed compaction with large impact energy, the 1000kN screw-driven press machine (ENOMOTO 100AF-AB type) is used in this study. According to the increase with the number of cycles of the plastic working, the uniform distribution of refined SiO_2 particles in the AZ31 matrix occurs drastically. After a suitable cycle number (e.g., 100~200 cycles), it outputs the columnar AZ31 green compact dispersed with the refined glass particles, and served to the next pre-heating process to synthesize Mg_2Si/MgO. Figure 6 shows the DSC curves of the compacts on the root of the RPW process, compared to that by the conventionally cold press. The elemental AZ31 and 4mass% SiO_2 glass powder mixture are used. The RPWed compact indicates the extremely lower ignition temperature of 643K than that in using the conventional one, not via RPW process. When the number of cycles is 200, the difference of T_i between both green compacts is about 70K.

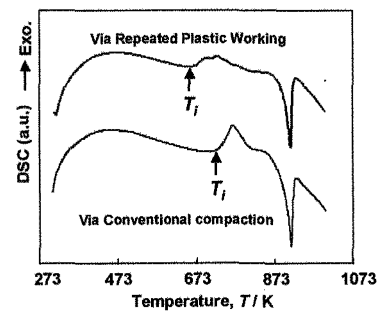

Figure 6. DSC thermograms of AZ31-4mass%SiO_2 glass compact on root of RPW process, compared to conventionally cold press.

It means that the reaction for the synthesis of Mg_2Si and MgO occurs at lower temperature by the RPW process. The reasons of the remarkable decrease of T_i on the root of the RPW process are considered as follows;

(1) Increase of the contacting area between SiO_2 and AZ31 powder because of the increase of the specific surface area of refined glass particles.

(2) Formation of the fresh surface area of AZ31 powder after mechanical breakage of its surface oxide films by the RPW process.

(3) Increase of the defect density of magnesium matrix and the internal energy by a lot of plastic deformation.

(4) Progress on diffusion between SiO_2 and magnesium by the refinement of the matrix grains.

The lower pre-heating temperature is effective on the microstructure control, because the matrix grain growth and the coarsening of the synthesized compounds are obstructed under the small thermal history. That is, the refined matrix grains and fine dispersoids in the matrix cause the strengthening effect of the magnesium composite alloys. Figure 7 shows optical microstructure of the hot extruded AZ31-2mass% SiO_2 glass alloys via the RPW process with 200 cycles. The pre-heating temperature of the green compact is 653K for 240s in nitrogen gas atmosphere. There is no pore of the composite, and the extrusion is available for the densification of the green compact. The XRD analysis results reveal that glass particles are completely reacted with AZ31 magnesium alloys to form Mg_2Si and MgO dispersoids. They are distributed even more uniformly in the matrix, compared to the microstructures by the conventional compaction shown in Fig.4. The mean particle size of the dispersoids, measured by the image analysis, is 3.4 μ m in a diameter. It means that the input raw SiO_2 glass powder, having a mean particle size of 16.8 μ m, is effectively refined by the RPW process. The matrix grain size with about 3~8 μ m is also significantly smaller than that of the hot extruded composite via the conventionally cold press.

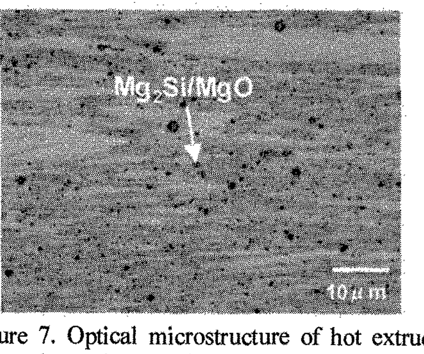

Figure 7. Optical microstructure of hot extruded composite with Mg_2Si/MgO dispersoids via RPW process in using AZ31-2mass%SiO_2 powder.

Concerning the mechanical properties of the hot extruded AZ31-2mass% SiO_2 glass alloys on root of the RPW process, the ultimate tensile strength is 363MPa, and much higher than that of the composite via the conventional compaction. Furthermore, in allying RPW process to Mg-0.5Zn-6Al-1Ca-3RE heat resistance alloys, tensile strengthening dependence on the number of cycles in RPW is shown in Fig.8.

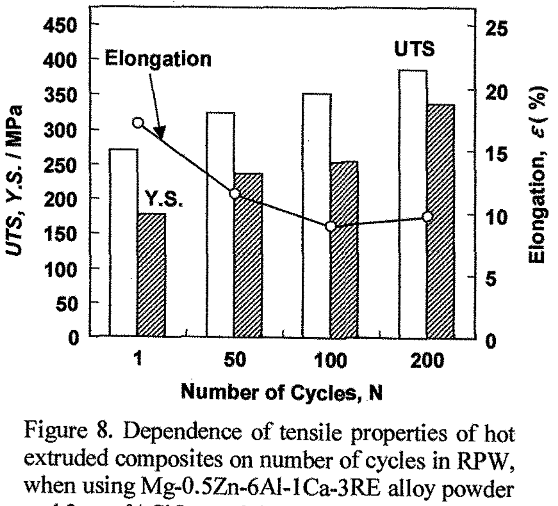

Figure 8. Dependence of tensile properties of hot extruded composites on number of cycles in RPW, when using Mg-0.5Zn-6Al-1Ca-3RE alloy powder and 2mass% SiO_2 particles.

The UTS and Y.S of this alloy via die-casting process are 200MPa and 170MPa, respectively. The same alloy via hot extruded and RPW (N=200) shows 373MPa UTS, 303MPa Y.S and elongation of 15%. By adding 2%SiO_2 glass powder, the increase of Y.S of 30MPa occurs. In both composites, the remarkably improved strength of the magnesium alloys is due to the refined matrix grain, the uniform distribution of fine Mg_2Si and MgO particles by the RPW process, and the obstruction of microstructure coarsening by the low temperature heating. Accordingly, the high purity SiO_2 glass scraps can be employed as useful raw materials to fabricate the magnesium alloys with superior physical and mechanical properties, when using the solid-state synthesis of Mg_2Si and the refining effect by the repeated plastic working.

5. CONCLUSIONS

New process of high-performance magnesium matrix composite via a solid-state reaction has been established, in using high purity SiO_2 glass scraps. This is quite safety and environmentally benign compared to the conventional re-melting process, because of utilizing course magnesium raw powder and no use of SF_6 toxic gas. From a viewpoint of the microstructures control of the composites, the core technologies to improve the properties are; a solid-state synthesis of Mg_2Si and MgO particles by deoxidizing glasses by magnesium, and the refinement of both their dispersoids and the magnesium matrix grains by the RPW process. For example, when using the elemental Mg-Al-Zn-Ca-RE alloy and 2mass% SiO_2 glass powder mixture as starting raw materials, the hot extruded composite shows 385MPa of UTS and 335MPa of Y.S, respectively.

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