Key Engineering Materials Vol. 313 (2006) pp. 77-82
online at http://www.scientific.net

AZ61 Mg with nano SiO_2 particles prepared by spray forming plus extrusion

Y.P. Hung[1], K.J. Wu[2], Chi Y.A. Tsao[2], J.C. Huang[1], P.L. Hsieh[1], J.S.C Jang[3]

[1] Inst. Materials Science and Engineering; Center for Nanoscience and Nanotechnology,
National Sun Yat-Sen University, Kaohsiung, Taiwan, ROC

[2] Dept. Materials Science and Engineering, National Cheng Kung University, Tainan, Taiwan, ROC

[3] Dept. Materials Science and Engineering, I-Shou University, Kaohsiung, Taiwan, ROC

Corresponding e-mail jacobc@mail.nsysu.edu.tw

Keywords: Mg alloy, nano particles, spray forming, extrusion, composites

Abstract. The current study applies the inclusion of thermally stable ceramic nano powders into the light weight AZ61 Mg base alloys via spray forming plus extrusion. The combination of spray forming and severe extrusion provides a new processing route for fabricating nano composites, with uniform distribution of the nano fillers. Parallel tries using the PM route followed by the same severe extrusion can also yield sound composites but the dispersion of the nano SiO_2 appears to be less uniform. The processed composites are characterized in terms of microstructure examination, thermal analysis, phase identification, and mechanical testing.

Introduction

The success in fabricating various nano-sized powders, wires or tubes has provided the new possibility in modifying the existing commercial materials in terms of their functional or structural characteristics. Inorganic nano oxide, nitride, refractory or highly electrically conductive metallic powders may be inserted in polymers, ceramics, metals, or semiconductors by various sorts of simple or sophisticated means. Except for few reports, the majority of achievements were focused on the polymer matrix modified by ceramic nano particles so as to significantly improve its mechanical or physical properties. The addition of nano powders in metallic alloys has been relatively much less addressed [1].

However, dispersion of the nano reinforcements in a uniform manner is a critical and difficult task. Due to the high surface area ratio, nano powders tend to cluster together, sometimes forming micro-sized aggregates. The performance of the modified alloys would be degraded rather than upgraded. A secondary severe deformation processing might be one of the promising routes. In this study, the new scheme of spray forming (SF) followed by severe extrusion (EX) is tried. A parallel effort using the powder metallurgy (PM) method plus severe extrusion is made for comparison. Spray forming is recently considered to be a potential tool to produce advanced materials. It applies inert gas atomization of the liquid stream into variously sized droplets which are then propelled away form the region of atomization by fast flowing atomizing gas [2-6], as depicted in Fig. 1. Droplets are subsequently deposited and collected by a substrate on which solidification takes place. Finally a coherent and near fully dense preform is produced.

Experimental methods

The AZ61 (Mg-5.88wt%Al-0.74wt%Zn) alloy, purchased from the CDN Company, Deltabc, Canada, was fabricated through semi-continuous casting. Amorphous SiO_2 powders measuring ~20 nm (Fig. 2), with a density of 2.65 Mg/m^3, are introduced into AZ61 Mg alloys via spray forming and powder metallurgy routes, all followed by extrusion.

Spray forming was conducted with the SiO_2 nano particles pre-mixed in the AZ61 billet. Then the billet with nano particle was spray formed under special control. Short heating time before spray forming was to reduce the condensation of the nano particles during melting of the Mg alloys. Subsequent extrusion was conducted using a 350 ton hot extrutor at 300 or 400°C to an extrusion ratio of 100:1 (acting as server deformation) to refine the microstructure.

The PM route applies the AZ61 Mg powders measuring around 10-200 μm prepared by spray forming, as shown in Fig. 3, with the substrate being placed further lower so as to gather more oversprayed AZ61 Mg powders. The powders were then screened by several meshes to render a smaller size distribution within 20-50 μm. After a self-designed wet mixing technique, the AZ61 Mg and SiO_2 powders were hot pressed in vacuum at 430°C under a pressure of 100 MPa.

The processed specimens were characterized by optical, scanning electron, and transmission electron microscopy (OM, SEM, and TEM), as well as X-ray diffraction (XRD), differential scanning calorimetry (DSC), hardness, and tensile tests.

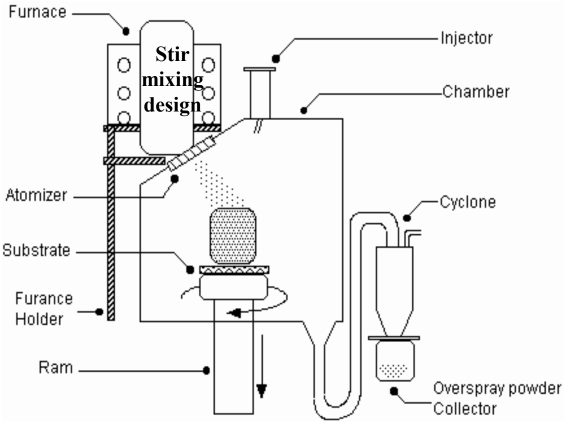


Fig. 1 Schematic illustration of the spray forming facility, with stir mixing design in the furnace.

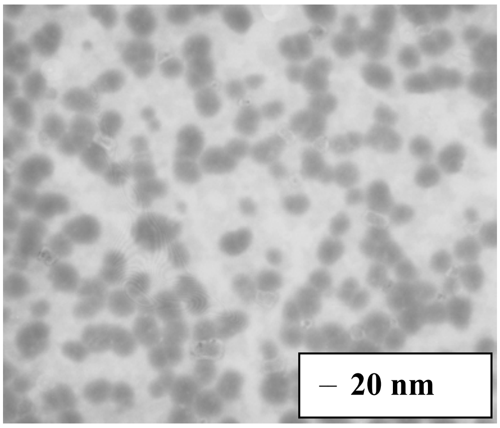


Fig. 2 TEM micrograph of the nearly spherical nano SiO_2 particles, measuring ~20 nm.

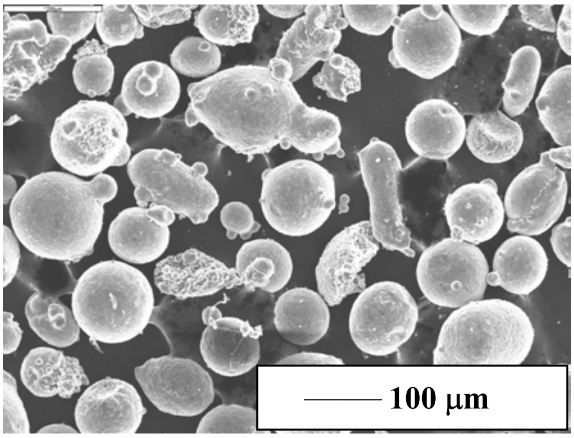


Fig. 3 SEM micrograph showing nearly spherical AZ61 Mg powders prepared by spray forming.

Fig. 4 Photograph of a successful spray formed Mg/SiO_2 composite billet.

Results and Discussion

The fabrication of spray formed AZ61/nano-SiO_2 composite encountered numerous difficulties. Inappropriate spray form parameters would result in small billets with abundant Mg powders sprayed all over the chamber. The byproduct of AZ61 Mg powders measuring around 10-100 μm in size can also be utilized in fabricating nanocompoistes via the powder metallurgy method. An example of the successful products with 0.2 vol% SiO_2 is shown in Fig. 4, measuring 180 mm in diameter, 280 mm in length, 11.7 kg in weight, and with around 7% porosity. The spray formed composite specimens were machined into cylinders 65 mm in diameter, and then extruded at 300-400^{o}C to an extrusion ratio of 100:1, resulting in long bar of 6.5 mm in diameter. Full 100% density was achieved at this stage.

The OM micrographs of the as-received AZ61 billet and the as-SFed composite are shown in Fig. 5, showing the average grain sizes of 75 μm and 25 μm, respectively. The much refined grain size in the SFed composite is due to fast cooling and solidification rates during SF and the restriction from grain growth by the embedded tiny ceramic particles. After high ratio extrusion, the grain size was further refined to 2-10 μm, as shown in Fig. 6, dependent on the materials and extrusion temperature, as listed in Table 1. The grain sizes of the cast and PM AZ61 composites with 0.2% or 1vol% nano-SiO_2 are also included in Table 1 for comparison. Also listed are the hardness data which are consistent with the grain size.

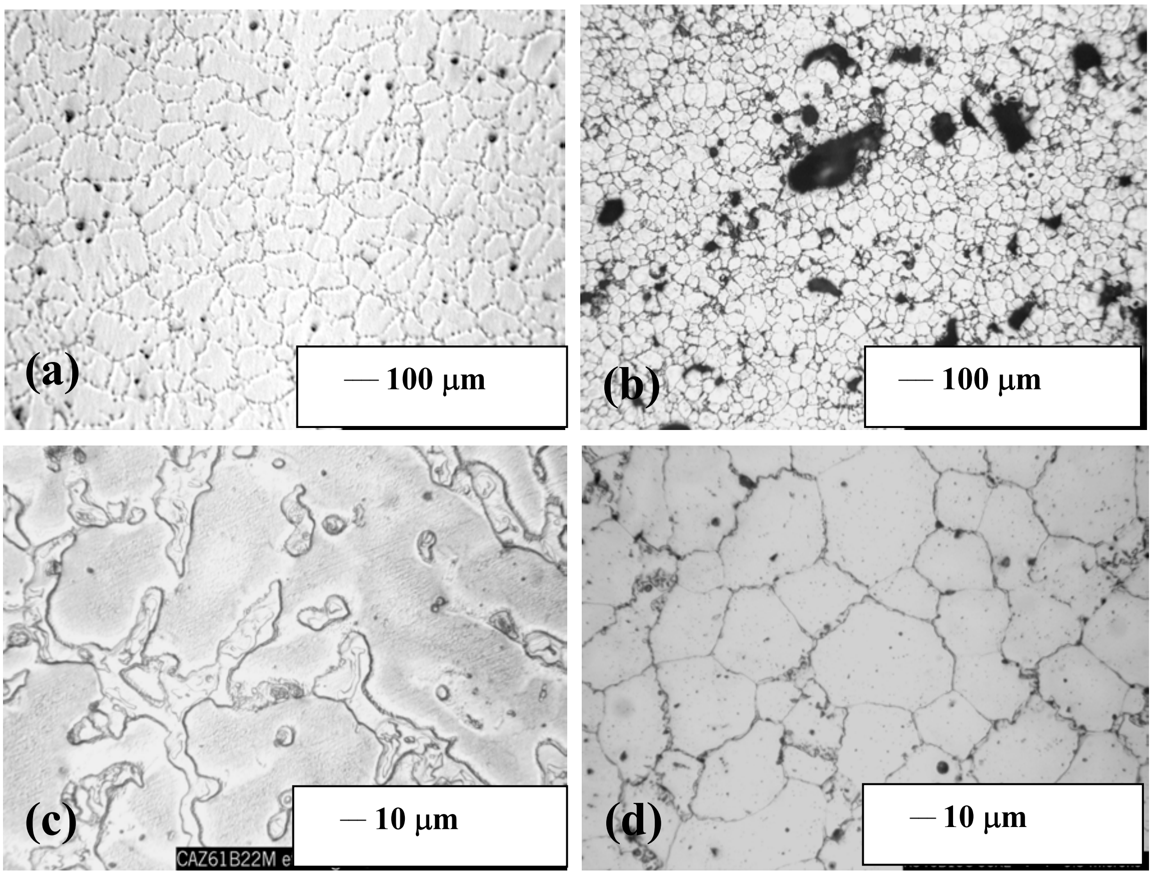


Fig. 5 OM micrographs showing the grain structures in the (a) as-received AZ61 billet and (b) spray formed AZ61/nano-SiO_2 composite billet, as well as the grain boundary second phases at a higher magnification in the (c) as-received AZ61 billet and (d) spray formed AZ61/SiO_2 composite billet.

The dispersion of SiO_2 in the SFed composite was examined under FEG-SEM. There are a certain level of dispersoids in distinct white contrast in the BEI micrographs, measuring around 1-3 μm, in both the AZ61 alloy and composite (Fig. 7a). These were identified to be the Mn bearing particles (basically Al_4Mn). The BEI contrasts for Si and Mg are weak due to the small difference in atomic number. In the background of the SEM BEI micrographs, after image enhancement through image software, the nano particles can be traced by the faint whiter contrast (Fig. 7b). The particles are seen to be within 50-1000 nm in size, which are larger than the mean size of 20 nm for the SiO_2 particles. Local clustering is still inevitable, but the distribution overall is reasonably uniform.

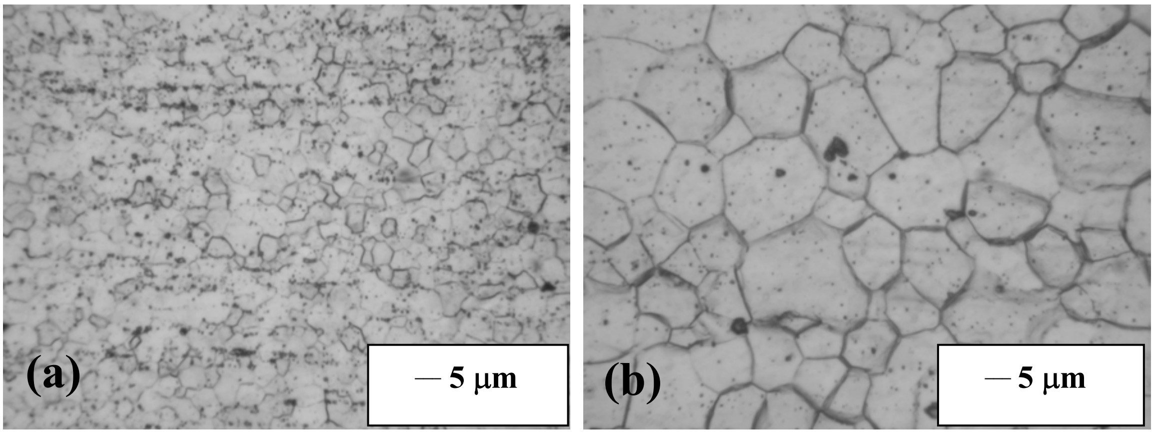


Fig. 6 OM micrographs showing the grain structures in the spray formed AZ61/ nano-SiO_2 composites after severe extruded to 100:1 at (a) 300 and (b) 400°C.

Table 1 Summary of the grain size and Hv hardness of the AZ61 composites under various material and processing conditions

Material	Processing condition	Grain size [μm]	Hv hardness
AZ61 alloy	As-received billet	75	60
SF AZ61/0.2%SiO_2	As-SFed (with porosity)	25	56
SF AZ61/0.2%SiO_2	Extruded at 400°C	9.6	67
SF AZ61/0.2%SiO_2	Extruded at 300°C	3.5	73
PM AZ61/0.2%SiO_2	Extruded at 400°C	6.0	74
PM AZ61/1%SiO_2	Extruded at 300°C	2.8	100

It is well known that the major second phase in the AZ61 Mg alloy is the β phase ($Mg_{17}Al_{12}$). With the minor elements of Zn, Mn, Si, Cu, etc, the calculated phases to be induced, based on the available information on the phase diagrams stored in the commercial software Thermocalc, include Mg_2Si, Al_8Mn_5, $Al_{11}Mn_4$, Al_4Mn, $MgZn_2$, $Al_7Cu_2Mg_6$, AlCuMgZn, AlMgZn, etc, as shown in Fig. 8. However, only the $Mg_{17}Al_{12}$ and Mn bearing phases would occupy sufficient amounts. The Mn bearing phases are referred to $Al_{11}Mn_4$ and Al_4Mn at temperatures above and below 350°C, respectively. The $Al_{11}Mn_4$ phase formed at higher temperature would transform into Al_4Mn during cooling. Thus, the notable observed second phases in the SFed AZ61/nano-SiO_2 composite should be $Mg_{17}Al_{12}$, Al_4Mn, and SiO_2. Provided that the nano SiO_2 would undergo phase transformation when reacting with Mg, some minor MgO and Mg_2Si phases might also be induced at the interface.

The XRD and DSC results in Fig. 9 of the processed AZ61 alloy and composites (with 0.2-1vol% SiO_2) contain predominantly HCP Mg, with minor trace of $Mg_{17}Al_{12}$. The textures of all samples resemble to each other, indicating that different processing routes may not affect the texture after extrusion. The DSC heating rate was set as 10°C/min till 650°C. All samples experienced consistent thermal histories, indicating that no significant phase transformation took place with increasing temperature till melting. It also suggests that there have been minimum $Mg_{17}Al_{12}$ and Mg_2Si phases. And the ceramic SiO_2 and MgO would maintain stable up to 650°C.

Figure 10 is an example of the TEM observations, showing a PM 1% composite after extrusion. The diffraction pattern reveals both crystalline and amorphous phases, indicating that both amorphous SiO_2 particles and AZ61 alloy were diffracted. No significant agglomeration of the nano SiO_2 particles was observed.

The tensile results are summarized in Table 2. The ultimate tensile stress (UTS) data of the processed composites show strengthening and/or toughening with the addition of nano reinforcements. The PM composite with 1% SiO_2 possesses the highest UTS, due to the additional

MgO oxides formed on the surface of AZ61 Mg powders during SF. The tensile elongation of the SFed composites is higher than the AZ61 billet and composites made by other routes, suggesting more uniform particle distribution.

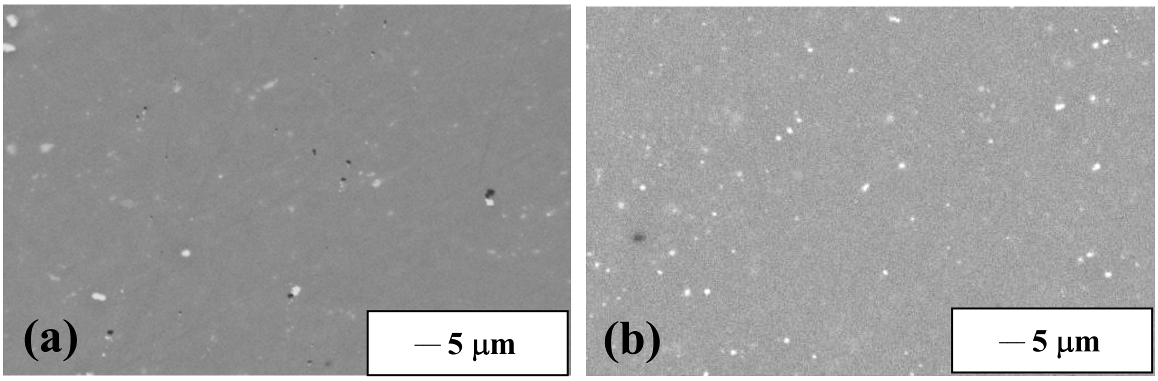


Fig. 7 SEM-BEI micrographs showing the white contrast from (a) Al_4Mn, ~1-2 μm in the as-received AZ61 billet, and (b) the distribution of nano SiO_2 (~50-1000 nm) in the SFed composites.

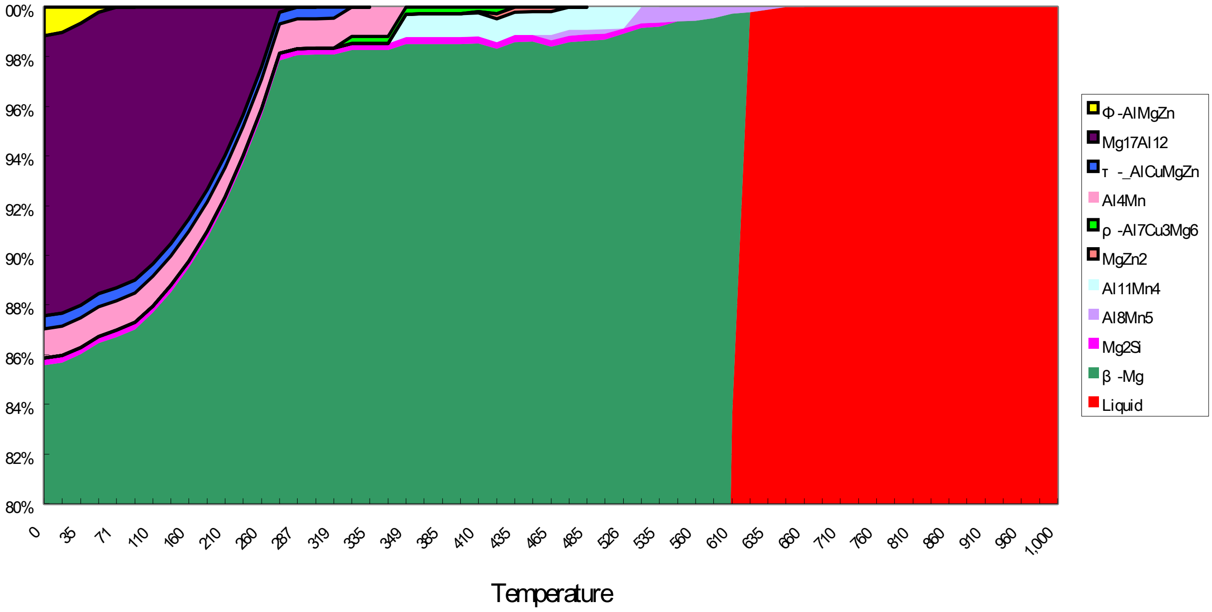
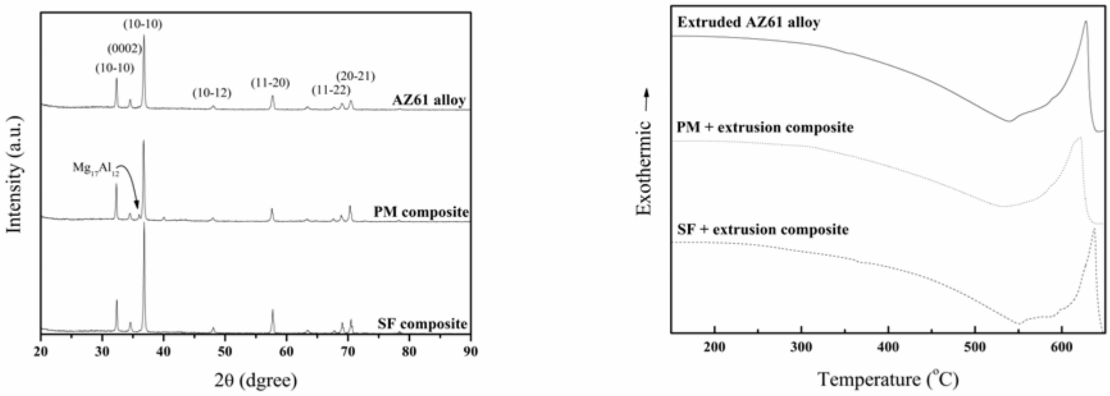


Fig. 8 The theoretically predicted equilibrium mass fractions of the phases to be induced in the AZ61 Mg alloy, simulated by the commercial software Thermocalc.



(a) (b)

Fig. 9 (a) XRD and (b) DSC results of the AZ61 alloy, and the SF and PM AZ61/SiO_2 composites after 100:1 extrusion.

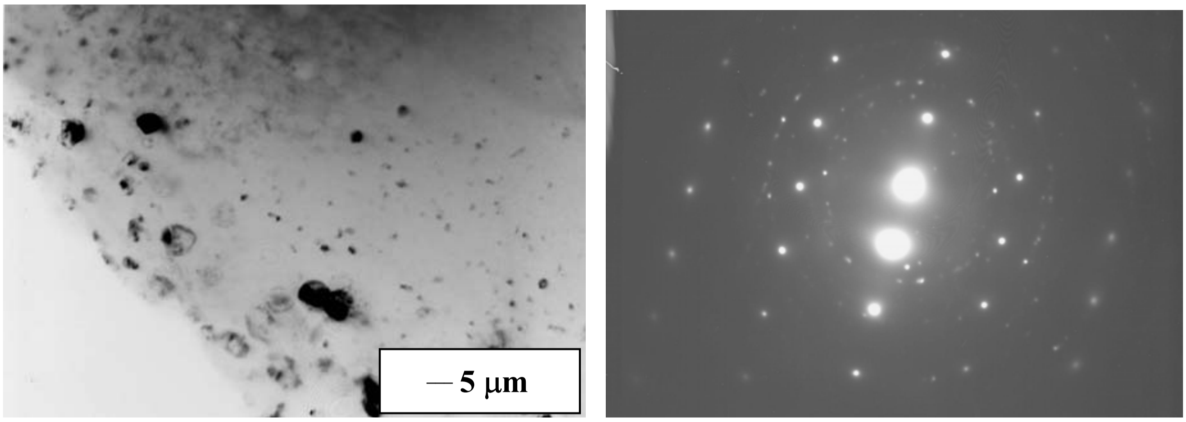


Fig. 10 TEM micrograph and the associated diffraction pattern of the PM composite, showing the presence of crystalline MgO and Mg_2Si in addition to the amorphous SiO_2.

Table 2 Summary of the room temperature tensile properties of the AZ61 alloy and composites under various material and processing conditions

Material	Processing condition	UTS [MPa]	Elongation
AZ61 alloy	As-received billet	250	15%
SF AZ61/0.2%SiO_2	As-SFed (with porosity)	--	--
SF AZ61/0.2%SiO_2	Extruded at 400^{o}C	316	35%
SF AZ61/0.2%SiO_2	Extruded at 300^{o}C	340	32%
PM AZ61/0.2%SiO_2	Extruded at 400^{o}C	351	27%
PM AZ61/1%SiO_2	Extruded at 300^{o}C	375	12%

Summary

Spray forming process can refine the grain size and most grains become equiaxed. Nearly no eutectic phase $Mg_{17}Al_{12}$ would form at grain boundaries due to the high cooling rate. Extrusion can disperse uniformly the nano particles and further refine the grain structure, with the pinning effect by the SiO_2 nano particles. The combination of spray forming and severe extrusion provides a new processing route for fabricating nano composites. Parallel tries using the PM route plus severe extrusion can also yield sound composites but the dispersion of the nano SiO_2 appears to be less uniform.

Acknowledgement

The authors gratefully acknowledge the sponsorship by National Science Council of Taiwan, ROC, under the projects NSC 92-2216-E-110-017 and NSC 92-2216-E-006-037.

References

[1] T.D.Wang and J.C.Huang: Mater. Trans. JIM. Vol. 42 (2001), p. 1781.
[2] A.R.E.Siger: Met. Mater. Vol. 4 (1970), p. 246.
[3] B.Williams: Met. Powder Rep. Vol. 35 (1980), p. 464.
[4] S.Spangel, E.M.Schulz, A.Schulz, H.Vetters, P. Mayr: Mater. Sci. Eng. Vol. A326 (2002), p. 26.
[5] C.Y.Chen, ChiY.A.Tsao: Mater. Sci. Eng. Vol. A383 (2004), p. 21.
[6] Y.H.Frank Su, Y.C.Chen, ChiY.A. Tsao: Mater. Sci. Eng. Vol. A364 (2004), p. 296.