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Nanocrystallized magnesium alloy – uniform dispersion of C_{60} molecules

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C_{60} was successfully dispersed in a magnesium alloy (AZ31) using friction stir processing (FSP). The grain size of the AZ31 was reduced by the uniform distribution of the C_{60} molecules. The stir zone of the FSPed AZ31 with the C_{60} consisted of very small grains, sized less than 100 nm. The maximum microhardness of the C_{60}/AZ31 nanocomposite reached ~126 Hv, which is almost three times higher than that of the AZ31 substrate.

Keywords: C_{60}; Nanocomposite; Magnesium alloys; Grain refining; Hardness

Much attention has recently been paid to C_{60} because it has many unique structural, chemical, and physical properties [1–3]. However, most reports are related to its functional applications such as a superconductive material [4–6]. There are few reported applications of the C_{60} as a structural material based on its nanostructure (diameter: about 1 nm) and its excellent mechanical properties due to its strong covalent bonds [7,8]. Though the hardness of a C_{60} crystal is very low (about 150 MPa at room temperature), each C_{60} molecule has extremely high hardness (about 310 GPa) [9,10]. If the C_{60} could be used as the molecule, the C_{60} might be the best candidate as reinforcement for metal matrices.

A new surface modification technique, called friction stir processing (FSP), has been developed in order to decrease any casting defects and abnormal structure in metals [11–14]. FSP is a solid-state processing technique to obtain a fine-grained microstructure. This is carried out using the same approach as friction stir welding, in which a rotating tool is inserted into a substrate and produces a highly plastically deformed zone (stir zone). It is well known that the stir zone consists of fine and equiaxed grains produced by a dynamic recrystallization [15]. Recently, the authors revealed effective grain refinements of a magnesium alloy by FSP with multi-walled carbon nanotubes or SiC particles from the point of view of their pinning effect [16,17]. The grain refinement technique is very important because mechanical properties of metals, such as strength and hardness, are increased on the basis of the Hall–Petch relation.

In this study, the C_{60} was dispersed in a magnesium alloy (AZ31), which is one of the best structural materials used to decrease the weight of various vehicles. The AZ31 was modified by FSP with and without C_{60}, and metallographic examinations and hardness tests were carried out.

Commercially available C_{60} (MER corporation, 99.9% pure) and an AZ31 rolled plate (thickness: 6 mm) were used in this study. The C_{60} molecules are typically agglomerated by van der Waal's bonds and form an face-centered cubic-packed structure. Some C_{60} crystals which have cleavage planes could be observed in Figure 1.

The C_{60} powders were poured into a groove (1×2 mm) before the FSP was initiated, as shown in Figure 2. The FSP tool made of SKD61 has a columnar shape (ϕ12 mm) with a probe (ϕ4 mm, length: 1.8 mm). The probe was inserted into the groove filled with the C_{60}. A constant tool rotating rate of 1500 rpm was adopted and the travel speed was 50 mm/min. A tool tilt angle of 3° was used. Transverse sections of the as-received AZ31 and the FSPed samples were mounted, and then mechanically polished. The distribution of the C_{60} and the grain sizes of the etched samples were observed by scanning electron microscopy (SEM, JEOL

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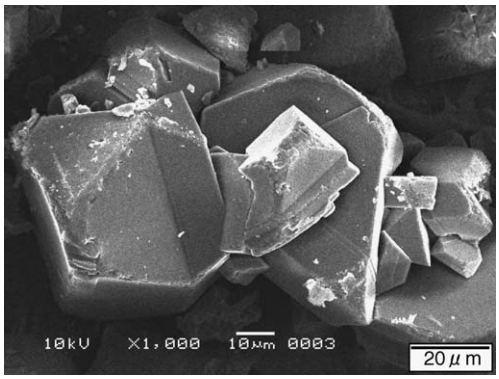

Figure 1. SEM image of the as-received C_{60}.

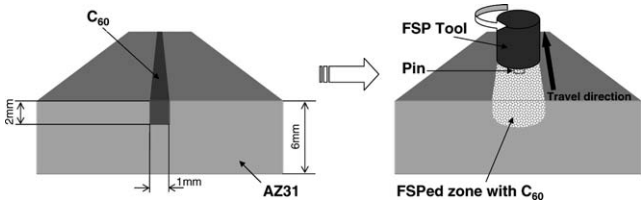

Figure 2. Schematic of the friction stir processing.

JSM-6460LA). The elemental analysis was carried out using energy dispersive X-ray spectroscopy (EDX, JEOL EX-23000BU). The microstructures of the FSPed samples were observed by transmission electron microscopy (TEM, JEOL JEM-1200EX). The microhardness was measured using a micro-Vickers hardness tester (Akashi HM-124) with a load of 200 g.

Figure 3(a) is an SEM photograph obtained from the FSPed sample with C_{60}. The microstructure was clearly different between the AZ31 substrate and the stir zone. The grain size in the stir zone was too small to confirm by SEM observations. The distribution of the C_{60} in this zone, however, could be confirmed as the distribution of the carbon element in Figure 3(b). The SEM image of the "nanocomposite" layer and the carbon element mapping show good agreement. SEM photographs of the microstructures in areas A and B are shown in Figure 4(a) and (b), respectively. The grain size of the AZ31 was drastically changed from micro to nanometer order.

The TEM photograph of the boundary between the AZ31 substrate and the nanocomposite layer and a selected area diffraction (SAD) pattern are shown in Figure 5. The SAD pattern was taken from the nanocomposite region using an aperture with a diameter of 2.0 μm at a magnification of ×100,000. The observation area for the diffraction pattern on the nanocomposite was selected at about ϕ250 nm under this condition. The SAD pattern showed multiple rings, which were identified by the d-spacing that originated from the Mg fine grains. Additionally, the spots attributed to the C_{60} crystal did not appear. This result implies that the C_{60} molecules were uniformly dispersed in the AZ31 matrix without forming any crystals.

The ultra-fine grain structure of the AZ31 could be confirmed in Figure 6. The very tiny gray spots (diameter: ~3 nm) should be C_{60}. The grain size of the AZ31 is ~100 nm, which corresponds with the SAD pattern shown in Figure 5. The grain refinement by FSP has been focused on and reported with regard to the dynamic recrystallization process. However, the micro-

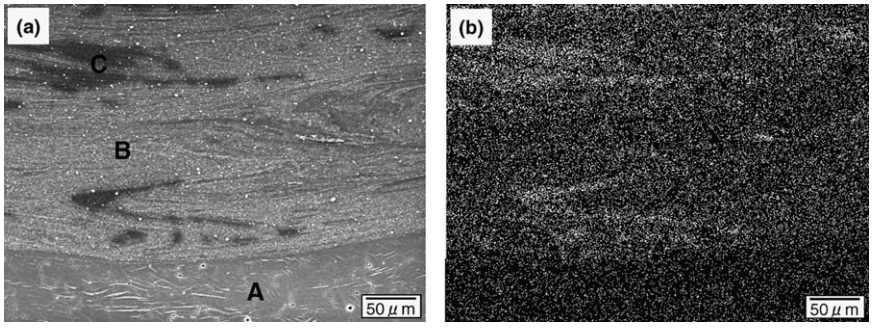

Figure 3. SEM image of (a) C_{60}/AZ31 nanocomposite and (b) distribution of carbon element.

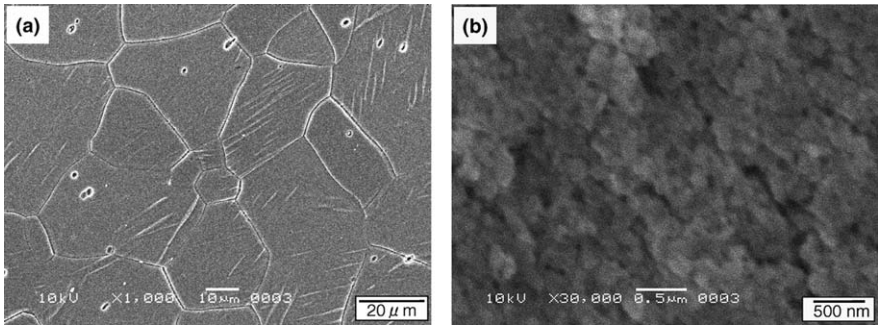

Figure 4. SEM images of the grain structure for (a) AZ31 substrate and (b) C_{60}/AZ31 nanocomposite.

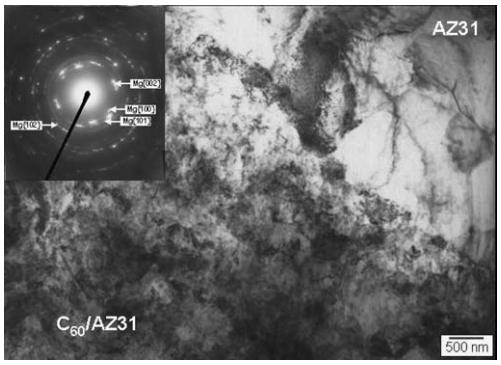

Figure 5. TEM microstructure and corresponding SAD pattern of the C_{60}/AZ31 nanocomposite.

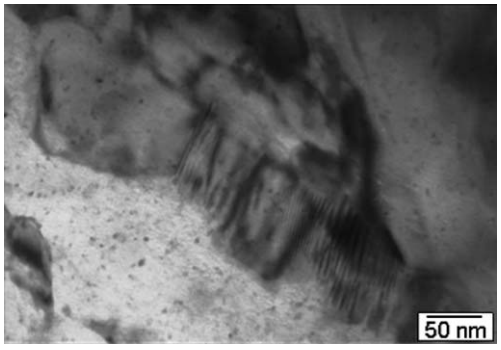

Figure 6. TEM micrograph showing the microstructure of the C_{60}/AZ31 nanocomposite.

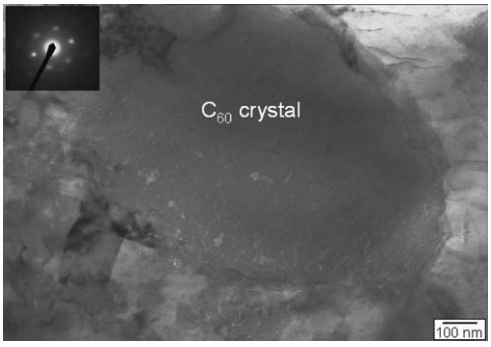

Figure 7. TEM microstructure and corresponding SAD pattern of the C_{60} crystal in the C_{60}/AZ31 nanocomposite.

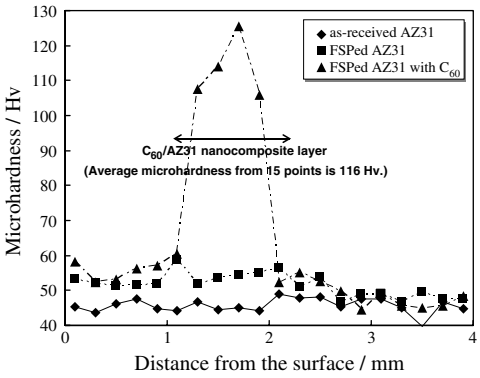

Figure 9. Microhardness profile of the cross section in the as-received AZ31, the FSPed AZ31, and the FSPed AZ31 with the C_{60}.

structure of the nanocomposite layer is surprisingly fine compared to the ordinary FSPed structures.

The C_{60} crystal, as shown in Figure 7, was rarely observed in area C of Figure 3(a). However, it is considered that the C_{60} crystal could disappear by repetition of the FSP [18]. The C_{60} seems unreactive to the AZ31 matrix due to the low process temperature and the short process time. It has also been reported that the C_{60} crystal/AZ91 composite could be fabricated by a powder metallurgy route without the reaction between C_{60} and AZ91 matrix [19].

Figure 8 shows the indentation prints marked by the microhardness test under a 200 g load. The optical micrographs were obtained at the same magnification to compare the size of the indentation prints. The indentation print for the nanocomposite layer was obviously smaller than that of the as-received AZ31. The value of 126 Hv was measured as the maximum microhardness for the nanocomposite, as shown in Figure 9. This value is almost three times higher than that of the AZ31 substrate. It is considered that the grain refinement and the uniform dispersion of the C_{60}, which has an extremely high hardness, resulted in an increase in the microhardness for the C_{60}/AZ31 nanocomposite fabricated by FSP.

The C_{60}/AZ31 nanocomposite was successfully fabricated by FSP. The microstructure and microhardness were evaluated by evaluating the grain size and the dispersion of the C_{60}. The results can be summarized as follows:

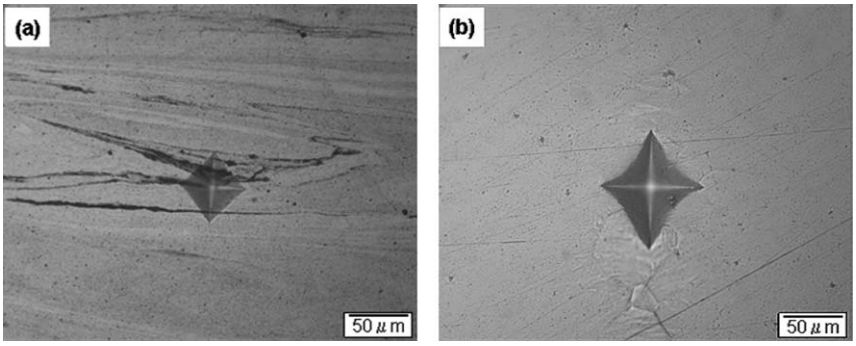

Figure 8. The representative indentation prints for (a) C_{60}/AZ31 nanocomposite and (b) as-received AZ31.

(1) The C_{60} molecule could be uniformly dispersed in the AZ31 substrate using FSP.
(2) FSP with the C_{60} drastically increased the microhardness of the AZ31 substrate. The value of 126 Hv is almost three times higher than that of the AZ31 substrate.
(3) FSP with the C_{60} produced an AZ31 ultra-fine grain structure. The grain size is less than 100 nm.

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