Surface Alloying of Mg Alloys After Surface Nanocrystallization

Ming-Xing Zhang1,∗, Yi-Nong Shi2, Haiqing Sun2, and Patrick M. Kelly1

1Division of Materials, School of Engineering, The University of Queensland, St. Lucia, QLD 4072, Australia
2Shenyang National Laboratory for Materials Science, Institute of Metal Research, Shenyang 110016, China

Surface nanocrystallization using a surface mechanical attrition treatment effectively activates the surface of magnesium alloys due to the increase in grain boundary diffusion channels. As a result, the temperature of subsequent surface alloying treatment of pure Mg and AZ91 alloy can be reduced from 430 °C to 380 °C. Thus, it is possible to combine the surface alloying process with the solution treatment for this type of alloy. After surface alloying, the hardness of the alloyed layer is 3 to 4 times higher than that of the substrate and this may significantly improve the wear resistance of magnesium alloys.

Keywords: Magnesium Alloys, Surface Nanocrystallization, Surface Alloying.

1. INTRODUCTION

As the lightest structural metallic material, magnesium alloys have considerable advantages for use in the automotive and aerospace industries to improve fuel efficiency. However, magnesium alloys suffer from low wear and corrosion resistance, which limits their applications. Surface treatment has been recognised as a major emerging technique to enhance the surface durability of magnesium alloys without significantly changing the mechanical properties of the substrate and increasing the density of the material.1 The currently available surface treatment techniques include coating, surface hardening and surface alloying. Surface hardening is only possible in some ferrous alloys. Surface coating is limited in improving wear resistance, due to the low bonding force between the coating layer and substrate. Surface alloying includes high-energy beam surface alloying (HEBSA) and diffusion coating. All HEBSA techniques involve melting of the surface layer using a high-energy beam, such as a plasma arc, laser, electron beam, ion beam, electrical discharge and their combinations, together with the addition of alloying elements.2,3 Their major disadvantage is the high cost and the poor surface finish. Thus, diffusion coating remains as the most efficient surface modification technique for light metals, because of the high binding forces, good surface finish and low cost. However, the major challenge for the diffusion coating of Mg alloys is to lower the treatment temperature, to at least below 413 °C, in order to avoid change of the microstructure and properties of the substrate. This also makes it possible to combine the surface alloying process with the solution treatment. In the last decade, the reported lowest surface alloying treatment temperatures for AZ91 alloy are 450 °C4 and 430 °C.5 At such high temperatures, not only does the microstructure and the properties of the Mg substrate change, but hot cracks are frequently observed within the alloyed layers.4 Hence, further lowering of the surface alloying temperature for Mg alloys will have technological and economic significance.

Surface nanocrystallization is a process that generates nanometer scale grains in the surface layer of conventional coarse grained materials. The large number of grain boundaries within the nanostructured layer act as diffusion channels. As a consequence, the atom diffusion kinetics may be significantly enhanced. Surface mechanical attrition treatment (SMAT), which was developed by Lu and co-workers,6–8 leads to severe plastic deformation of the surface layer of a bulk metals through the repeated, multi-directional impact of flying balls made of harder materials on the surface. It has been recognised as one of the most efficient techniques for surface nanocrystallization of metals. Previous work9 indicated that after SMAT, the nitriding temperature of pure iron can be made as low as 300 °C. Hence, surface nanocrystallization using SMAT may also provide a solution to lowering the surface alloying temperature for Mg alloys.

Recent work10 has shown that with SMAT, nanometer grains with average grain size of 30±5 nm can be generated within a 150 μm thick surface layer in AZ91 alloy.

∗Author to whom correspondence should be addressed.
The microhardness of the nanostructured surface is nearly twice of the substrate. The research has indicated that the mechanism of grain refinement from coarse grains to nanometer scaled grains involves twinning, dislocation cross-slip and dynamic recrystallization. The present work will investigate how the nanostructured layer affects the subsequent surface alloying process in pure Mg and an AZ91 alloy and how the hardness can be further improved.

2. EXPERIMENTAL DETAILS

The materials used are industrial pure Mg (99.97% Mg) and a commercial AZ91 alloy with chemical composition of 8.47 wt% Al-0.69 wt% Zn-0.14 wt% Mn. 100 × 100 × 12 mm plate samples were cut from the as-received ingots and were then ground with silicon carbide paper to grade 1000 on both sides. Previous work shows that this surface finish is good enough for SMAT. The SMAT was carried out using a SNC-II (the stands for surface nanocrystallization type II) surface nanocrystallization treatment machine at room temperature. As optimized in previous work, the SMAT time for both the pure Mg and AZ91 alloy is 20 minutes, which leads to the finest grains with the deepest nanostructured layer on the surface. After SMAT, the grain size in the top surface layer was determined by X-ray diffraction (XRD), which was carried out in a Rigaku DMAX/2400 diffractometer with operating voltage of 40 kV and Cu-Kα radiation. The grain size was calculated using the Scherrer-Wilson equation. Subsequent to the SMAT, smaller 20 × 20 × 12 mm block samples were cut off from the plate samples. There are two routes for carrying out the surface alloying treatment on the side that has been undergone SMAT. The first route is to bury a small sample in a powder mixture of 70 wt% Al, 25 wt% Al₂O₃ and 5 wt% Zn in a crucible. The powder mixture occupied two-thirds of the crucible, which was then topped up with a mixture of foundry sand and coke to reduce oxidation of the underlying metallic powder and alloy. Al₂O₃ is used to prevent the metallic powder from consolidating in the subsequent heating process. The surface alloying process was undertaken at 450, 420, 400, 380 and 360 °C for 12 hours, respectively. The second route is to coat the SMAT treated surface with a paint-like mixture of pure Al powder and ethylene glycol. The painted samples were buried in dry foundry sand and then heat treated at 380 °C for 6 hours to promote the diffusion of Al into the substrate. After isothermal holding in both routes, the assembly was cooled to room temperature in air. Optical microscopy and a Philips XL30 SEM were used to examine the microstructure in the alloyed layer. Variation of hardness within the alloyed layer with distance from the treated surface was determined using a MVK-H300 Vickers hardness testing machine, with a load of 25 g and a loading time of 10 s. The hardness was measured on the cross section that is perpendicular to the treated surface.

3. RESULTS AND DISCUSSION

After SMAT of the AZ91 alloy, a TEM micrograph of the nanometer grained layer is shown in Figure 1. The average grain size is 60 nm, which was determined using X-ray diffraction and was further confirmed using TEM, as described in our previous work. If the grains are assumed to be spherical and to have equal size, when compared with the original grain size of 150 μm before SMAT, the total area of grain boundaries of the nanometer grains will have been increased 2500 times. The large number of grain boundaries will provide fast atomic diffusion channels, and therefore activate the surface.

3.1. AZ91 Alloy

Figure 2 shows the optical micrographs within the surface layer of the as cast AZ91 alloy after surface alloying treatment using the powder route at different temperatures. The temperatures do not change the morphology and the microstructure, but do affect the thickness of the alloyed layer. Figure 3 is the variation of the mean thickness of the alloyed layer with the temperatures. Treatment at 400 °C generates the thickest alloyed layer. A very thin and discontinuous alloyed layer was obtained after treatment at 450 °C and when temperatures are below 360 °C, no surface alloying occurs. These observations are considered to be the result of competition between recrystallization of the nanostructure and grain boundary diffusion. The surface nanocrystallization through SMAT occurs due to the server plastic deformation. The high strain energy stored in the surface layer provides the driving force for recrystallization. In addition, the inherent recrystallization temperature of Mg alloys is well below the surface alloying temperature, due to the low melting point. Hence, recrystallization can not be avoided. For surface alloying at higher temperature, such as 450 °C, recrystallization and grain growth takes place in a very short time.

Fig. 1. TEM micrograph showing the nanostructure in the surface layer of AZ91 alloy after SMAT.
This dramatically reduces the area of grain boundaries, on which the atomic diffusion relies on. Thus, lower temperature may lead to a thicker alloyed layer. However, atomic diffusion, of substitutional atoms in particular, requires higher temperatures to overcome the diffusion activation energy. From this viewpoint, the lower temperatures inhibit diffusion. The overall result is that the thickest alloyed layer is obtained at an intermediate temperature.

The present results also indicate that surface nanocrystallization plays a key role in the reduction of the subsequent surface alloying treatment temperature. The lowest surface alloying temperature for diffusion coating of AZ91 alloy is 430 °C without surface nanocrystallization. The SMAT can reduce this temperature to 380 °C, as shown in Figures 2 and 3. Although the temperature reduction is not as large as that in nitriding of pure iron, where the nitriding temperature is reduced from 500 °C to 300 °C, surface alloying at 400 °C makes it possible to combine the process with the solution treatment of this Mg alloy (normally 413 °C). The reason for limited effectiveness is the slow diffusion of substitutional elements (Al and Zn atoms) in AZ91 alloy, compared with interstitial diffusion in the nitriding of pure iron.

Figure 4 is a SEM back scattered electron micrograph taken from the alloyed layer in AZ91 alloy after surface alloying treatment at 400 °C. EDS analysis shows that the
Surface alloying treatment dramatically hardens the surface of AZ91 alloys. Figure 5 shows the variation of microhardness in the surface alloyed layer with the depth below the specimen surface. The outer single \( \gamma \) phase layer has a hardness that is four times greater than the matrix, but the hardness of the lamellar structure is about three times higher than the matrix. The lower hardness of the lamellar structure is due to the low precipitation hardening response of the \( \gamma \) phase, since it precipitates on the \( (0001)_{\text{Mg}} \) slip plane.\(^{13,14}\) Hence, in order to further improve the hardness after surface alloying of AZ91 alloy, either the single \( \gamma \) phase regions should be enlarged, or less Al powder should be used to avoid the formation of the \( \gamma \) phase.\(^{15}\)

Surface alloying of AZ91 alloy after SMAT can also be achieved through the second route described above. Figure 6 shows the optical and SEM micrographs of the alloyed layer formed at 380 °C. EDS analysis indicates that the chemical compositions of regions A and B are 55.5 at% Mg-44.5 at% Al, which is within the composition range of the \( \gamma \) phase. Region C is a solid solution of Mg, since it only contains 10.5 at% Al. Because of the large amount of \( \gamma \) phase, the overall microhardness of the alloyed layer is 1.8 GPa, which is three times higher than the matrix. It should be emphasised that Zhu and Song\(^{12}\) reported a similar method for surface alloying of AZ91 alloys, but the minimum treatment temperature is 420 °C. The present result shows that SMAT can reduce the subsequent surface alloying temperature by about 40 °C.
3.2. Pure Mg

Surface alloying of pure Mg through diffusion coating is much harder to achieve than in AZ91 alloy. To date no success has been reported either through route 1 or route 2. However, surface nanocrystallization effectively activates the surface of pure Mg and an alloyed layer can be obtained at 400 °C using route 1. Figure 7 is a typical optical micrograph of the alloyed layer in pure Mg. EDS analysis confirms that the lamellar structure is close to the eutectic composition of Mg and \( \gamma \) phase, in which some Al atoms may be substituted by Zn atoms. The microhardness of the alloyed layer is 2.4 GPa, which is four times higher than the pure Mg matrix, due to the large amount of finer \( \gamma \) phase formed.

One may argue that as pure Mg is actually not used in industry as a structural material, the practical significance of the surface modification of pure Mg is questionable. However, the results confirm the efficiency of surface nanocrystallization in enhancing subsequent surface alloying and atomic diffusion in AZ91. Pure Mg also offers an ideal metal to study of the mechanism of diffusion of substitutional atoms in nanostructured materials.

4. CONCLUSIONS

(1) Surface nanocrystallization by surface mechanical attrition treatment effectively activates the surface of magnesium alloys and therefore enhances the atomic diffusion due to the increase in areas of grain boundaries that can act as diffusion channels. After SMAT, the subsequent surface alloying temperature for AZ91 alloy is reduced from 430 °C to 380 °C. Hence, it is possible to combine the surface alloying process with the solution treatment of this alloy. In addition, surface alloying treatment of pure Mg can only be undertaken after surface nanocrystallization.

(2) After surface alloying, the microhardness of both the AZ91 alloy and the pure Mg can be significantly increased, and therefore it is possible to improve the wear resistance of the metal.

(3) Recrystallization can not be avoided during surface alloying process. Any techniques that can increase the recrystallization temperature or can suppress the growth of grains may further reduce the surface alloying temperature.

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References and Notes


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