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The potential of consolidated nano/sub-micron AZ31 magnesium alloy to become a new structural material

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Abstract Consolidated nano/sub-micron AZ31 Mg alloy is a new structural material that combines nano-scale grains with a size of up to 100 nm and sub-micron grains with a size of up to 300 nm. Inherently, this new material should have significantly improved strength, making it a potential candidate for special applications requiring increased specific strength.

The present paper evaluates the properties of nano/sub-micron AZ31 Mg alloy in terms of mechanical properties and corrosion resistance. The obtained properties are explained and associated with the micro-structure of the alloy. In addition, the nano/sub-micron structural alloy was compared to conventional extruded alloy with the same composition in order to distinguish the main differences between the two alloys.

Introduction

The growing demand for lighter structural materials with improved properties has led to the development of new magnesium alloys [1–5]. This was mainly motivated by the automotive industry in order to decrease fuel consumption and reduce harmful ecological effects [6]. Recently, the focus is on advanced new materials that introduce significant improved specific strength (strength to density ratio). Among those materials, one can consider consolidated magnesium alloys with nano/sub-micron structure as potential candidates for such requirements.

Nano-structured materials are characterized by an average grain size of up to 100 nm, while sub-micron materials have an average grain size between 100 and 300 nm. Hence, nano/sub-micron (NSM) structure relates to the case when the micro-structure is composed of a mixture of nano-scale and sub-micron scale grains. According to the Hall–Petch equation, reduced grain size generally results in improved strength. However, in consolidated nano-structures, when the grain size is below a critical value (around 20 nm), more than 50 vol.% of the atoms are associated with grain or interfacial boundaries. In this case, dislocation pile-ups cannot form and the Hall-Petch relationship for conventional coarse-grained material is no longer valid [7, 8]. In addition, if we add the environmental effect on the properties of consolidated nano/sub-micron structure, it is evident that the prediction of actual properties becomes a complex issue.

While research on nano-crystalline Mg for hydrogen storage has been given considerable attention, research into the development of nano-structured Mg alloy for structural applications is a relatively unexplored area. Lu et al. [9] carried out experiments on nano-structured Mg–Al–Nd base alloy and showed an increase in both strength and ductility due to grain refinement. Other works, specifically on the subject of nano-structured magnesium alloys for structural applications, are very scarce.

The aim of the present study was to evaluate the properties of consolidated nano/sub-micron structure in terms of mechanical properties and environmental behavior. The results obtained are explained and associated with micro-structure analysis.

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Experimental procedure

The production of nano-structured material was carried out by MBN Nanomaterialia using typical mechanical alloying synthesis technology such as introduced by Matteazzi et al. [10, 11]. In general, the consolidated nano/sub-micron material was initially produced in the form of nano-powder with a particle size of 30 nm. This was followed by a direct powder extrusion process that resulted in the production of bars 22 mm in diameter, designated as MBN-MechanoXT®. The selected material system for the present study was magnesium alloy MechanoXT®-E906, having a chemical composition compatible with AZ31 alloy.

The chemical composition of the tested E906 alloy, as well as the composition of conventional extruded AZ31 Magnesium alloy (produced by Alubin Ltd.), is shown in Table 1. This has revealed that the iron content in the NSM alloy was significantly higher, probably due to the ball milling process used during the mechanical alloying synthesis.

The mechanical properties of the nano-structured magnesium alloy and of the conventional alloy were tested in terms of tensile strength, hardness, and impact measurements (three samples each). The tensile strength was carried out on standard round specimens according to ASTM E8-95a Spec., while impact measurement was performed on un-notched rectangular specimens according to ASTM E23-94b Spec.

The environmental behavior of the tested alloys was evaluated by standard immersion tests (according to ASTM G31-72 Spec.) and by potentiodynamic polarization measurements. The selected corrosive solutions included 0.9% NaCl and 3.5% NaCl. The reduced amount of NaCl in the first solution was aimed at testing the alloys under moderate corrosion conditions in order to distinguish between small variations in the corrosion performance. The immersion tests were carried out using round specimens with 6 mm in diameter machined from the original bars. The cleaning of the corrosion products was conducted by dissolution in 20% CrO_3 solution at 80 °C for up to 1 min. The potentiodynamic polarization measurement evaluated the electrochemical behavior of the tested material. This was implemented using Autolab model potentiostat PGSTAT-30 with a scanning rate of 5 mV/s and within the potential range of –2 V and 0.4 V. The electrochemical tests were carried out, immediately after immersion of the tested alloy and again after corrosion potential stabilization obtained following an immersion period of 30 min. Measurements of the subsequent potentials were obtained relative to a standard calomel reference electrode [12].

General micro-structure analysis was obtained by using optical microscopy and scanning electron microscopy with an energy dispersive spectroscope (JEOL JSM-5600). High-resolution SEM (HRSEM) and high-resolution TEM (HRTEM) were used to evaluate the micro-structure of the nano-structured material. The specimens for the HRTEM were prepared by an electro-polishing technique using the following process parameters: Nitric acid solution at –25 °C, voltage of 45 V, and current of 200 mA. The HRSEM was carried out on fractured specimens. X-ray diffraction analysis was obtained using Rigaku X-ray diffractometer type D/max 2100. The diffraction parameters included Cu Kα radiation, angular range 5–15°, scanning range of 2°/min, voltage of 40 V, and a current of 30 mA.

Results and discussion

The micro-structure of the nano/sub-micron (NSM) alloy MechanoXT®-E906 shown by optical microscopy in as received condition is shown in Figure 1. This revealed the presence of stringers which appear in the direction of the extrusion. The length of the stringers ranges from a few hundred microns up to 2 mm. The width of these stringers was up to 50 μm, the average distance between these stringers was about 300 μm.

The typical micro-structure of NSM-structured alloy obtained by scanning electron microscopy (SEM) is shown in Fig. 2. This revealed the presence of α phase solid solution matrix, iron, Mn, and pure Mg inclusions, as well as relatively high porosity. It is believed that the high porosity is attributable to the compact limitations of the direct powder extrusion process. The stringers revealed during optical microscopy were found using SEM-EDS to be pure Mg inclusions. Apparently the presence of the pure Mg stringers comes from the mechano-synthesis process. Probably these Mg stringers were generated from pure Magnesium powder residues that were not synthesized during the mechanical alloying process.

In order to evaluate the grain size of the NSM alloy, micro-structure analysis was carried out using high-resolution SEM (HRSEM) as shown in Fig. 3. This revealed

Table 1 Chemical composition of MechanoXT®-E906 and of conventional extruded AZ31 alloy (three points tested)

Content (wt%)	Al	Zn	Mn	Fe	Others	Mg
MechanoXT®-E906	2.63 ± 0.18	1.27 ± 0.56	0.4 ± 0.19	<1.0	<0.001	Bal.
Conventional extruded AZ31	2.74 ± 0.2	0.76 ± 0.04	0.47 ± 0.065	<0.015	<0.001	Bal.

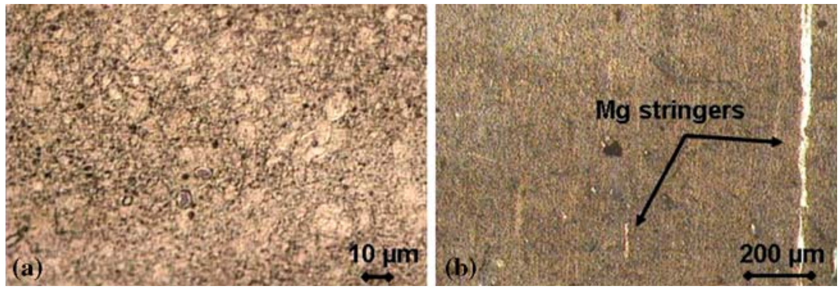

Fig. 1 Micro-structure at (**a**) transverse and (**b**) longitudinal cross section of NSM alloy obtained by optical microscopy

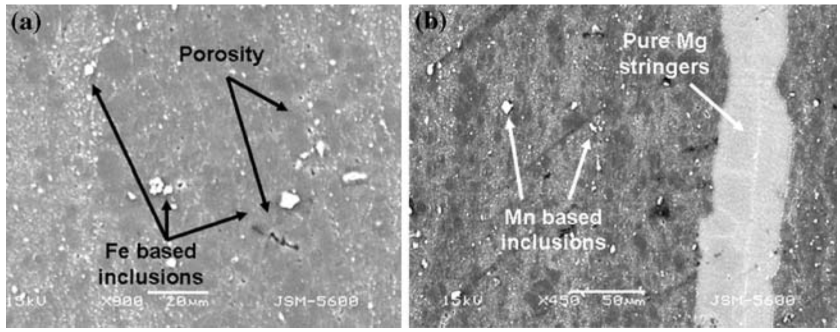

Fig. 2 Micro-structure of NSM alloy obtained by scanning electron microscopy showing Fe inclusions (**a**) and Pure Mg stringers in (**b**)

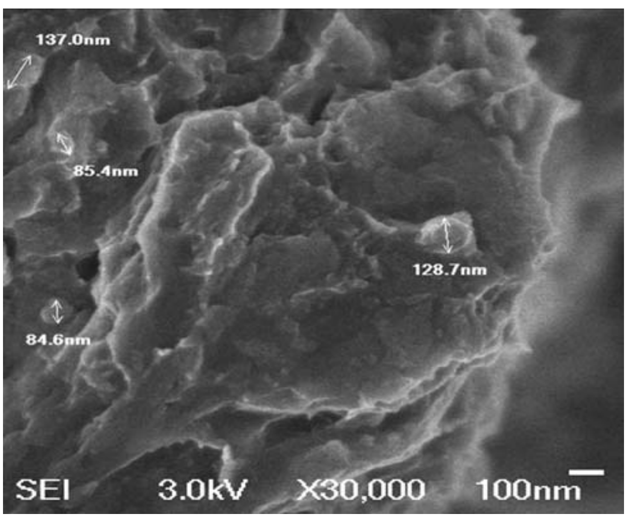

Fig. 3 Micro-structure obtained by HRSEM for NSM alloy showing a mixture of nano-scale and sub-micron scale grains

that the micro-structure of the NSM alloy was a mixture of nano-scale grains with typical grain size of up to approximately 100 nm and sub-micron grains with grain size of approximately 100–300 nm. It is believed that the relatively large sub-micron scale grains probably evolved during the consolidation phase of the synthesized nano-powder. Similar results were obtained by Lu et al. [9] after sintering of nano-scale powder based on a Mg–Al–Nd alloy.

The HRSEM results were also supported by TEM analysis. An individual sub-micron grain and its selected area diffraction pattern that gives an indication of its orientation are shown in Fig. 4. Attempts were also made to obtain Cyclic Pattern Diffraction from a larger area which can be indicative of pure nano-scale structure as indicated by Karnthaler et al. [13]. However, due to the fact that the actual structure was made from a mixture of nano-scale and sub-micron-scale grains, only Spot pattern diffraction could be obtained. In addition, the presence of magnesium oxides was detected in the TEM analysis. This can explain the lack of ductility in the NSM alloy, but it is more likely that the presence of magnesium oxides is a result of the TEM sample preparation method.

The average mechanical properties of the NSM structured alloy and of the conventional extruded AZ31 alloy are shown in Table 2 (impact results for the conventional extruded AZ31 are not available due to its high ductility). It is clearly evident that the tensile strength (along the extrusion direction) and hardness of the NSM alloy was significantly higher compared to the conventional extruded alloy. This was accompanied with a considerable decrease in the elongation performance of the NSM alloy. The significant difference in the ductility of NSM alloy compared to the conventional extruded alloy was also supported by fractography analysis as shown in Fig. 5.

This revealed a relatively ductile fracture in the conventional extruded alloy compared to a brittle fracture of the NSM structured alloy. In terms of fracture mechanisms, it is believed that the brittle fracture is related to the presence of inherent porosity which is probably a result of the powder extrusion process.

The reason for the significant increase in strength and considerable loss of ductility can be derived from the

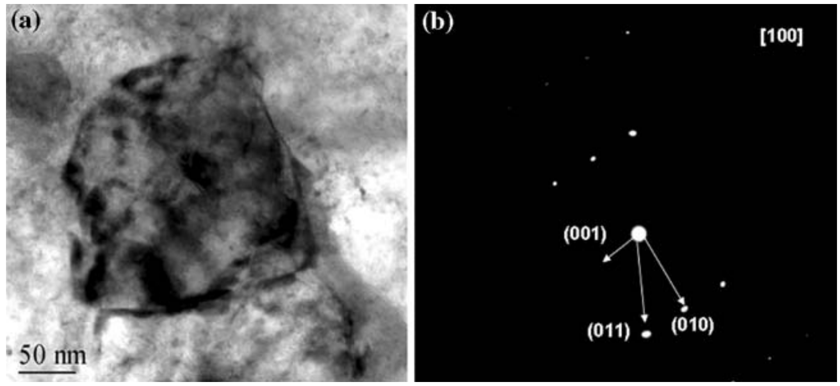

Fig. 4 Micro-structure of an individual grain in NSM alloy (**a**) and its selected area diffraction pattern (**b**)

Table 2 Average mechanical properties of MechanoXT®-E906 and of conventional extruded AZ31 alloy

Alloy type	Tensile strength (MPa)	Hardness (HRB)	Impact energy (kJ)	Elongation (%)
MechanoXT®- E906	439 ± 2.1	67.6 ± 0.8	5 ± 0.8	<1%
Conventional extruded AZ31	240 ± 7	44 ± 0.5	-	20%

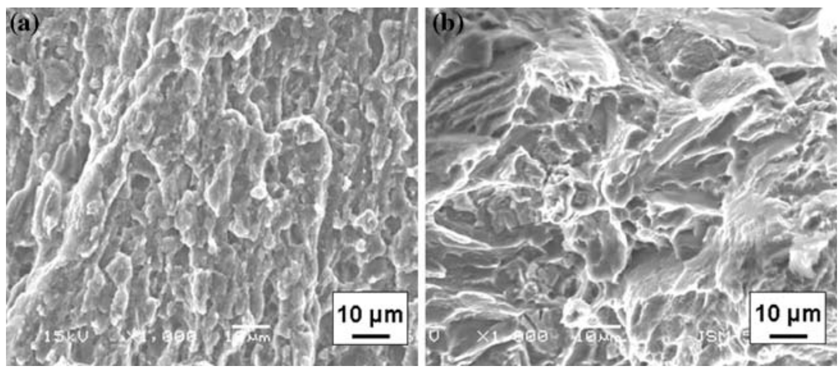

Fig. 5 Fractography analysis images on longitudinal cross-section (**a**) NSM structured alloy (**b**) conventional extruded alloy

inherent micro-structure of the NSM alloy. According to Tjong and Chen [10], this type of variation in mechanical properties can be explained by the differences in the plastic deformation mechanism. While the plastic deformation of coarse-grained structure is dominated by dislocation flow and interaction, the deformation in nano-crystalline structure is considered to be associated with grain boundary sliding assisted by grain boundary diffusion or rotation. In addition, it is believed that the presence of high porosity within the NSM alloy has a detrimental effect on the ductility of the alloy. Nevertheless, it should be pointed out that structural material having less than 1% elongation, as obtained with the NSM alloy, cannot be used for practical engineering applications. For example, typical components in the automotive industry that are made from magnesium alloys require elongation greater than 3%, and usually the actual demand is for elongations greater than 5%.

X-ray diffraction analysis of the NSM alloy and conventional AZ31 alloy on transverse cross section was similar as shown in Fig. 6. This has revealed that both alloys were made from the same structural phases.

In order to evaluate the general corrosion behavior of NSM structural alloy compared to conventional extruded AZ31 alloy, immersion tests were performed in 0.9% sodium chloride solution. The results obtained are shown in Table 3, indicating that the corrosion resistance of the NSM alloy was dramatically lower than conventional extruded AZ31 alloy. This result was also supported by electrochemical analysis in the form of potentiodynamic polarization tests shown in Fig. 7. The electrochemical test revealed a difference of one order of magnitude in the corrosion current density in both 0.9% and 3.5% sodium chloride solutions, demonstrating again the relatively inferior and unacceptable corrosion resistance of the NSM alloy.

The accelerated corrosion of the NSM alloy, compared to conventional extruded AZ31 alloy, can be explained due to the differences in micro-structure. A schematic diagram illustrating the mechanism of corrosion in the NSM alloy is shown in Fig. 8. According to this mechanism, the accelerated corrosion of NSM alloy is attributed to the presence of pure Mg stringers that act as preferred anodes. In par-

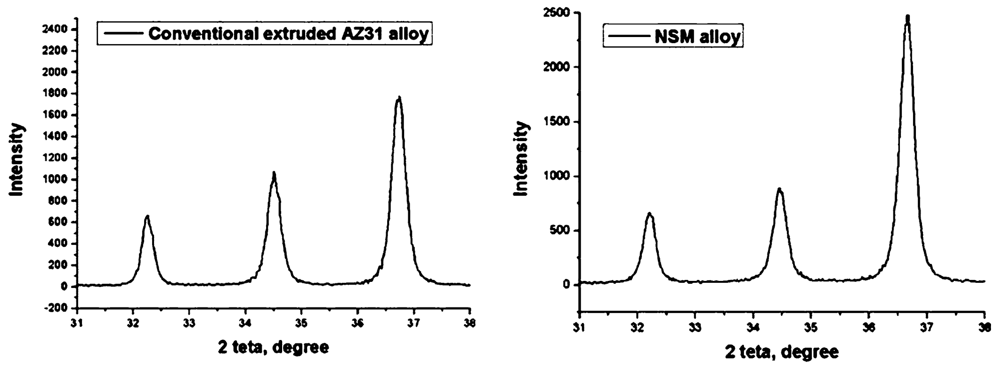

Fig. 6 X-ray diffraction analysis of NSM alloy and conventional extruded AZ31 alloy on transverse cross-section

Table 3 Corrosion rates calculated from immersion experiment in 0.9% NaCl solution

Material	Corrosion rate (mpy)
MechanoXT®-E906	443
Conventional AZ31	6

allel, the iron-based inclusions and the Mg–Al solid solution matrix act as cathodes. Hence, the micro-galvanic cell that is produced results in accelerated dissolution of the pure Mg stringers creating a significant enlargement of the surface area which is further enlarged by the inherent porosity. The overall result in terms of corrosion degradation has a synergistic characteristic which can explain the abnormal corrosion deterioration of the NSM alloy. Evaluation of corrosion performance in terms of Fe/Mn ratio could be only implemented in the conventional extruded alloy. In this case, the Fe/Mn ratio was 0.0319, according to the composition given in Table 1. This ratio is lower than the required ratio of 0.032 which is indicative of adequate corrosion resistance. However, due to the large quantity of iron in the NSM-structured alloy, the Fe/Mn ratio was significantly higher than the standard 0.032, which is also an indication to inadequate corrosion resistance.

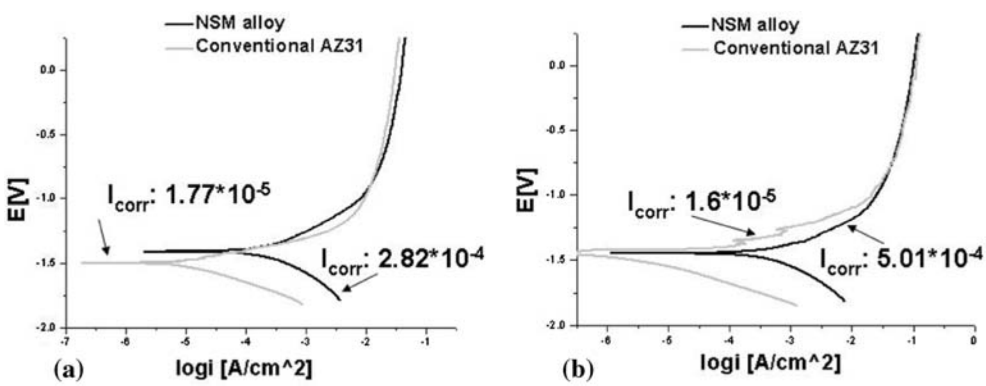

Fig. 7 Potentiodynamic polarization results for NSM structural alloy and conventional extruded AZ31 alloy in (**a**) 0.9% NaCl and (**b**) 3.5% NaCl solutions

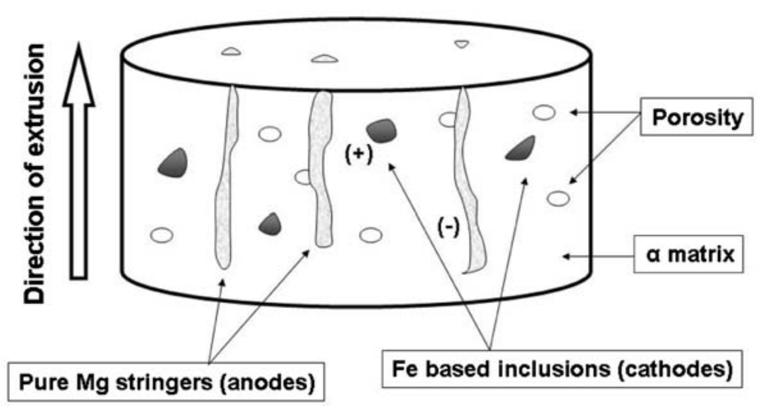

Fig. 8 Schematic diagram illustrating the mechanism of accelerated corrosion in NSM alloy

Conclusions

The result of the present study clearly demonstrates that although consolidated nano/sub-micron AZ31 Mg alloy has significantly higher strength compared to conventional extruded alloy with the same composition, its ductility and corrosion resistance are unacceptable. Hence, in order that the consolidated nano/sub-micron Mg alloy can be considered as a potential new structural material for practical engineering applications, its process technology should be modified and upgraded to address the current limitations of its micro-structure.

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