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NanoMag® High Strength/Density Mg Alloy Sheet

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Abstract

High strength/density (strength-to-density-ratio) Mg alloy sheet has been developed by a Thixomolding® plus Thermal Mechanical Processing (TTMP) means. Its key mechanism is the starting fine grain (5-10μm), isotropic, homogeneous microstructure that is inherent in rapidly solidified Thixomolded sheet bar. The subsequent TMP step consists of pre-heating and rolling in heated flat rolls. Thereby in some recent trials, grain size was observed to have been refined by continuous dynamic recrystallization during the rolling to less than 1 μm. At the same time, coarse intermetallic phases were refined in-situ to nanometer dispersions. Detrimental twinning and shear banding are thus minimized, while slip mechanisms are favored.

Introduction

Light weight Mg sheet would be in high demand in the automobile, aerospace, truck / trailer, battery, military and electronic/communication markets were it not for two factors, 1) high cost, and 2) poor formability. If cost could be reduced and if formability could be enhanced, the aforementioned markets could enjoy the benefits of lightweight Mg on fuel economy and reduction of pollutants.

Inherent Deformation Problems of State-of-The-Art Commercial Practice –

Despite significant efforts and the ever increasing need for light weight magnesium wrought products, limited commercial application of forming processes for magnesium alloys has been realized. This can be attributed to: (1) limited operative slip systems at room temperature in the hcp crystal structure [Hart1968, Ree1960, Kel1968, Bart1980, Kim2003, Bar(2007a, 2007b, 2004), Koi(2005a,2005b), Agn(2001,2003,2004,2005, 2006), Jai(2007,2008)], where for Mg the CRSS for basal slip has been shown to be significantly less than for prismatic or pyramidal slip, as reviewed by Koike [Koi2003b]; (2) the tendency to form strong textures during deformation as described in recent years by Agnew and others [Agn(2001,2003,2004,2005,2006), Jai(2007,2008), Kim2003]; (3) the highly anisotropic deformation behavior of textured microstructures that lead to macroscopically anisotropic mechanical properties [Kel1968, Agn2006, Kle2004, Koi2005a]; and (4) the prevalence of significant twinning during deformation that can lead to premature fracture, as described by Barnett [Bar2007a, 2007b,2007c), Jai(2007,2008)]. For these reasons, metal forming, which involves complex deformation paths to produce a component, is virtually impossible for ordinary grain size Mg alloys at ambient temperatures and at strain rates that are commercially viable. Microscopically, it has been shown that twinning becomes more prevalent as grain size increases, temperature decreases and strain rate increases [Yan2006, Jai2008) Mey2001] and it can cause fracture at low strains. An example of this is illustrated from the work of Barnett [Bar2007c]. Figure 1 shows crack formation associated with $\{10\bar{1}1\}$ double twins in room temperature deformation of rolled and annealed sheet derived from DC (direct cast) billet. Double twins are more favorably oriented for slip of <a> type dislocations than the parent grains from which they form, and large strains in the twins can lead to incompatibility stress and fracture [Hart1968, Ree1960, Bar2004, Yoo1981, Jai2008]. It has also been shown that activation of <c + a> slip rather than <a> slip on non basal planes is responsible in limiting ductility. Obara [Oba1973] has reasoned that this is because the <c + a> dislocations quickly dissociate into glissile <a> and sessile <c> segments greatly increasing work hardening and leading rapidly to fracture.

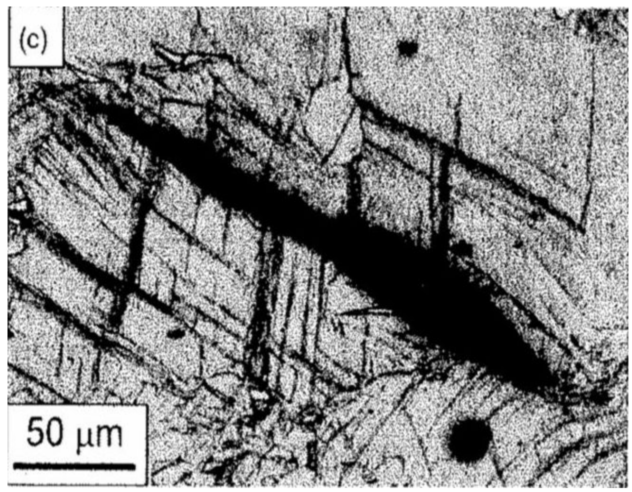


Figure 1. Crack initiation and voids in coarse grained commercial AZ31 sheet (Bar 2007c).

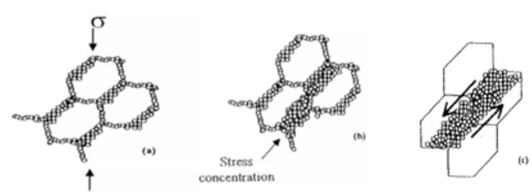


Figure 2. Twin induced heterogeneous recrystallization leading to shear banding and hot cracking in coarse-grained commercial Mg alloys (Ion1982).

Attempts to produce finer-grained stock from commercially cast alloys as a means to avoid twin-induced fracture are fundamentally limited by the microstructure and deformation behavior described above. In particular, warm deformation of coarse grained material can, through both basal slip and twinning, cause local dynamic recrystallization to form fine grains favorably oriented for deformation while at the same time leaving large grains between these soft regions where shear bands form and cause catastrophic cracking [Ion1982, del(2003, 2005b, 2008)], as illustrated from Ion's work in Figure 2. To avoid this inherent propensity, many small reductions and reheats are required to gradually coax the original coarse-grained cast material down to sheet. These small increments of reduction of large grained stock limit the ability to refine grain size and to refine eutectic intermetallic size. Such wrought commercial stock retains a grain size of 15 to 90 µm, strong texture and brittle behavior well above ambient temperature. Hence formability and mechanical properties suffer.

Therefore, an NSF STTR was undertaken to commercialize new technology in Mg processing that promised to overcome the cost and formability obstacles. In the STTR, the technical approach was to generate fine grain size uniformly to improve strength, ductility and formability in a process of few steps, compared to the costly 27 step procedure now required in commercial Direct Cast (DC) Mg sheet production. At the same time, the uniform fine grain structure was also postulated to overcome the large grain size and segregation problems associated with the relatively new developmental Twin Roll Cast (TRC) process. The project targets were yield strength of 250 MPa and elongation of 10%.

Experimental Procedures

As the starting stock, Thixomolded® sheet bar was selected for its isotropic and fine grain structure, with minimum segregation and minimum porosity [Dec2008]. Alloy content was varied in the Thixomolder by Thixoblending® [Nan2007] to attain compositions with increasing strength. TMP (Thermal-Mechanical Processing) by heated rolling generated continuous dynamic recrystallization.

The starting Thixomolded sheet bar was in the form of 100 mm x 150 mm panels of 1, 3 or 6 mm thickness. These panels were molded on Thixomat's 280 ton commercial machine in AM60 (6 wt% Al, 0% Zn), AZ6Al/1.5Zn and AZ6Al/1.8Zn Mg alloys. Thixomolding is an environmentally friendly and worker safe process, yielding stock that solidifies and cools at rates faster than 80°C/second – thus producing isotropic grain size < 10 µm with less segregation and much smaller grain size than Direct Cast and Twin Roll Cast starting stock.

The Thixomolding operating parameters included (1) screw RPM of 158 to 170, (2) graphite die spray, (3) cycle time of 30 seconds, (4) shot pressure of 1541 to 2000 psi, (5) nozzle temperature of 500ºC to 530ºC, (6) peak barrel temperature of 615ºC to 640ºC, (7) die temperature of 230ºC and (8) shot time of 50 msec.
Thixoblending enabled the agile variation of alloy content of the sheet bar product. Granules of AM60 and ZK60 were pre-blended at room temperature before adding to the hopper; in various ratios in order to vary the Zn contents over the range of 0 to 1.8 %.

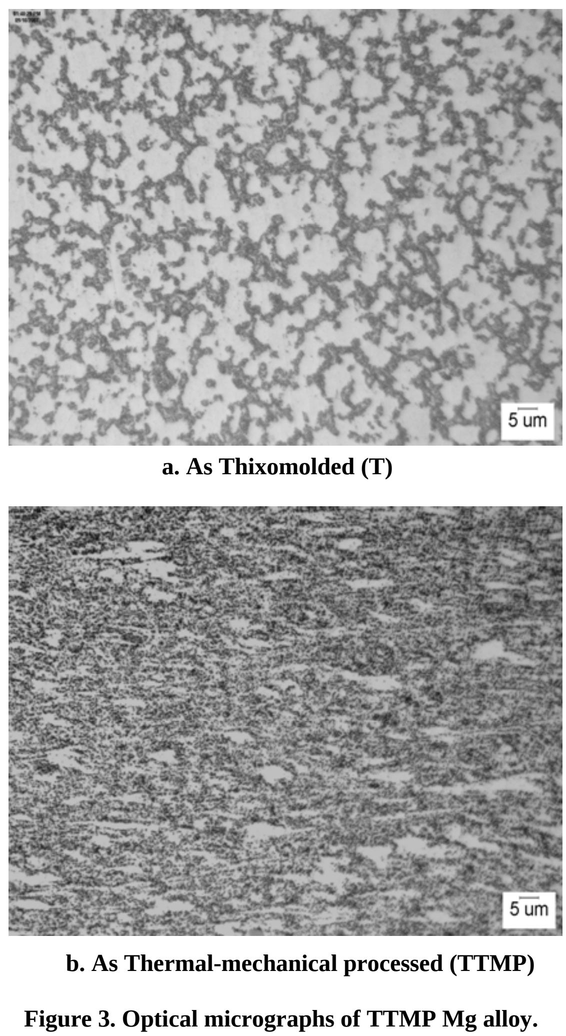
In the early TMP experiments, direct rolling was performed on 8 inch unheated rolls on a Fenn rolling mill at Convergent Technologies Corporation (CTC). Samples were rolled – first with co-heated steel plates, then without plates, then with moderate heating of the rolls to about 100°C to 130°C by ceramic blankets. Plates were preheated for 15 minutes to reach 252°C to 350°C in an air atmosphere in an electric-resistance furnace. In the 2nd campaign of rolling, much improved rolling was done on a 6 inch rolling mill with rolls heated to 260°C at International Rolling Mills. Bare sheet bar was heated 5 minutes on an electric-resistance powered "hot plate" at 287°C to 290°C. Sheets as large as 100 x 600 mm were produced. Reductions of 50 to 85% were imparted in one pass.

Room temperature tensile tests were run at a strain rate of 0.5in/in/sec. Tensile elongation was measured between gauge marks on the samples.

Metallographic specimens were mounted, fine ground and mechanically polished and were later etched with an acetic- picral solution - containing 4.2 g picric acid, 70 ml ethanol, 10 ml acetic acid and 10 ml distilled water. Cross sections of the processed and tested materials were examined by optical and scanning electron microscopes.

Results

The microstructure as Thixomolded is presented in Figure 3.a. The dendrite arm spacing and grain size are about 5-7 µm. Solid α phase from the Thixomolding machine was kept below 5%. Porosity was <1.0%. The phases in Figure 1.a. are proeutectic α (white), surrounded by dark divorced eutectic β phase ($Mg_{17}Al_{12}$). The latter intermetallic reports in a coarse array of up to 15 µm length, surrounding the proeutectic α. The texture is random and there is little macro-segregation throughout the sheet bar.



a. As Thixomolded (T)

b. As Thermal-mechanical processed (TTMP)

Figure 3. Optical micrographs of TTMP Mg alloy.

The effect of TMP is revealed in Figure 3.b. The β phase is refined to nanometer dimensions by subdivision and/or by solution-reprecipitation. The minor porosity, as Thixomolded, is

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healed. The proeutectic α has experienced continuous dynamic recrystallization to finer grain size of <1 to 2 µm. An electron micrograph, Figure 4, revealed grain size of 800 nanometers. Some of these intermetallics appeared to pin grain boundaries of the α phase.

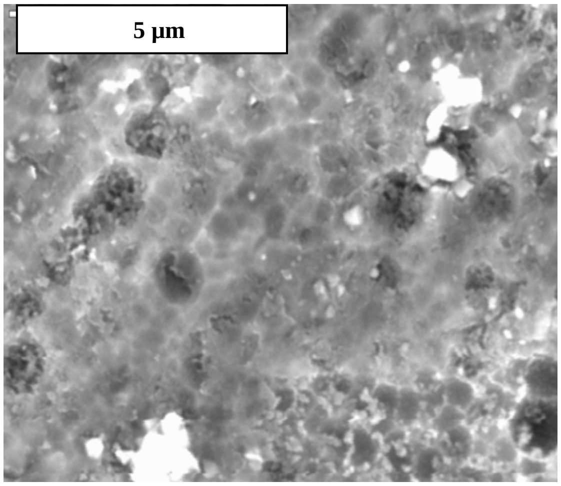

Figure 4. Electron micrograph of TTMP Mg alloy, with 300 to 600 nm lineal grain dimension.

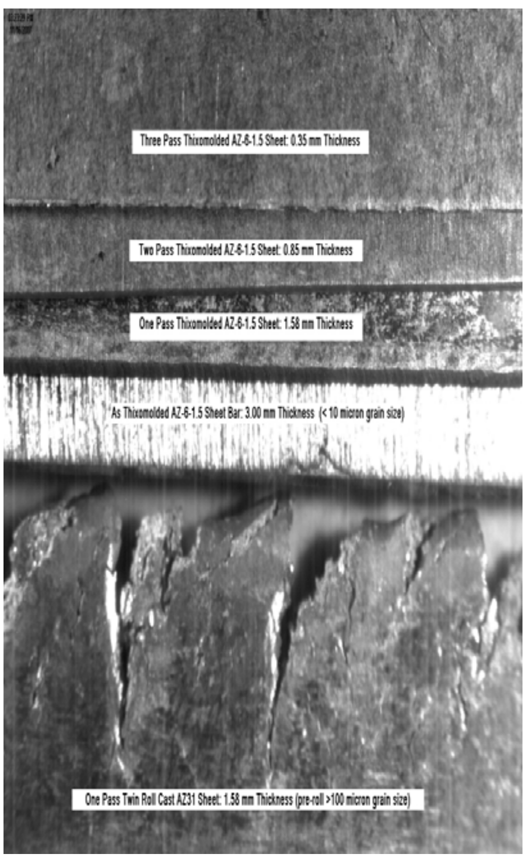

Figure 5. Comparison of Edge Cracking of Twin Roll Cast AZ31 and Thixomolded AZ6/1.5 Sheet, as TMP on 260°C Rolls.

Table I. Comparison of Properties of Twin Roll Cast AZ31 and Thixomolded AZ6/1.5 Sheet, as Direct Rolled on 260°C Rolls

Alloy	Process	Red, %	YS, MPa	El, %	Edge Cracking
AZ31	ASTM Spec	H24	200	6	--
AZ31	Twin Roll Cast	44	187	10	Severe
AZ31	Twin Roll Cast	73	199	9	Severe
AZ6/1.5	Thixomolded	47	232	9	None
AZ6/1.5	Thixomolded	76	303	10	None

Table II. Effect of Direct Rolling and Stack Bonding on Tensile Properties of Thixomolded AM60, Rolled on Cold Rolls between Steel Plates Heated to 350°C.

No. of Sheet Bars Bonded	No. of Passes	Red, %	YS, MPa	UTS, MPa	El., %
As Molded	---	---	140-145	210-230	6-11
1	1	42	194	279	14
1	1	48	222	318	20
1	1	58	191	298	14
3	1	62	210	298	13
3	1	70	225	312	24
3	1	81	203	300	16
3	1	81	237	327	17
5	1	85	189-219	295-317	11-18
3	2*	86	196	306	18

*Cross Rolled – Tested in transverse direction to 1st pass

Edge cracking during TMP was also markedly reduced with the fine grain of the Thixomolded stock compared to the 67 to 87 µm grain size of the TRC stock (see Figure 5). The edge cracking of the TRC stock took on the 45º aspect of shear banding. Twinning was evident in the TRC material; but not in the TTMP material.

Yield strength of TTMP AZ61.5 was superior to that of warm rolled TRC AZ31 and the ASTM specifications for AZ31 in the H24 condition (see Table I). Table II reveals tensile data on AM60 rolled 42 to 58 % in one pass, resulting in yield strengths of 191 to 222 MPa along with 14 to 20 % elongation.

As a means to amplify the sheet area attainable from a given sheet bar size, sheet bar of AM60 was stacked and roll bonded. A further purpose was to open the possibility of generating gradient alloy compositions through the sheet thickness. Tensile results from this stack rolling are provided in Table II as well. Stacks of 3 and 5 sheet bars were successfully bonded in one pass of 62 to 85 % reduction. Yield strength ranged from 189 to 237 MPa, with elongations of 11 to 24 %, was observed. A 3 sheet bar stack was cross rolled in 2 passes to a total reduction of 86 %, resulting in comparable strength and elongation in the transverse direction. An optical micrograph of stack rolled TTMP showed excellent metallurgical bonding between layers (see Figure 6). Again, twinning was not evident in optical micrographs of the fine grained TTMP samples.

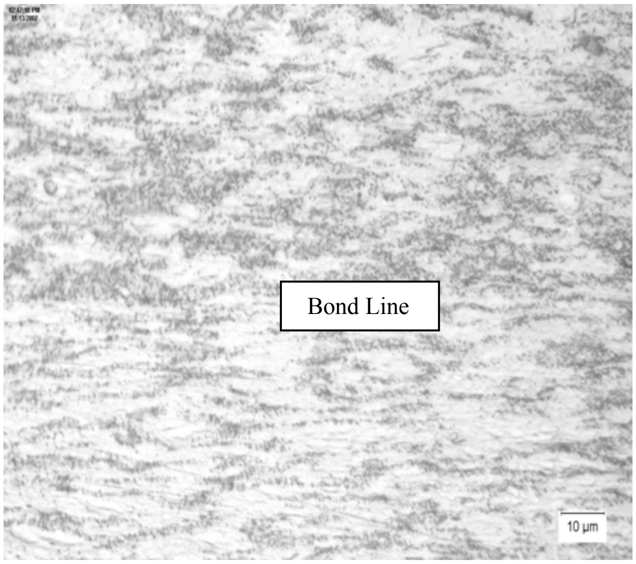

Figure 6. Bond line in TTMP stack rolled AZ6/1.8 on 260ºC rolls.

Discussion

Many of the shortcomings of DC and TRC Mg sheet have been attributable to their proclivity to shear banding during hot working and to twinning - and to the limitations in slip systems. A fall out of these mechanisms is generation of strong textures, anisotropic properties, cracking during hot working and poor room temperature formability. This study confirmed the hot cracking at 45° during hot working and associated twinning in large grained TRC AZ31.

The technical hypothesis of this project was that initial fine grained, isotropic, homogeneous molded sheet bar would alleviate the above-mentioned deformation problems and, rather, would favor more uniform slip deformation. This study confirmed that this is the case since twinning and shear banding were minimized in the TTMP process.

The TMP studies confirmed that the high strain rates of direct rolling at relatively modest temperatures could impose continuous dynamic recrystallization upon the sheet bar; thus refining grain sizes further to micron and finer dimensions. At the same time, intermetallic eutectic phases can be refined to nano sizes. Both strength and ductility were enhanced by TTMP. It is our belief that such response can be a result of grain refinement, intermetallic refinement and increase of residual dislocation content. The morphology of β particles as Thixomolded and after TMP indicated that some elongated eutectic β particles were subdivided by TMP into smaller, more equiaxed particles. In addition, some β particles were dissolved and reprecipitated as nano particles by TMP. Some of these fine β particles reported to grain boundaries, thus possibly retarding grain growth.

AM 60 was successfully fortified by Thixoblending® to add Zn; purposely designed to take advantage of the TTMP process and to increase strength. The scope for further alloy development is promising – both for optimizing the Zn/Al ratio and for experimenting with additional alloying elements by means of Thixoblending. In Thixoblending, chips of different alloy compositions and master alloys are premixed before feeding to the machine. These differing compositions then melt together and homogenize under the heat of the barrel and the mechanical action of the screw. Previous studies [Nan2007] showed that these blended alloys follow the rule of mixtures, rendering the same mechanical properties as an alloy of the same average composition. A further aspect of Thixoblending is manufacturing agility, wherein purposely designed alloys can be ordered and delivered upon short notice. This degree of agility is undoubtedly not open to large scale DC and TRC plants. Thixoblending is likened to ordering from the “paint store”.

The successful bonding experiments auger well for development of new Mg matrix composites. One variety might be gradient alloy sheet varying from surface to center – to enhance corrosion resistance and/or surface hardness.

The TTMP process is a safe and low cost route to nanostructures. Such micro/nano-structure is generated in situ in the bulk by inexpensive processing, and fine nanopowders need not be handled – obviating safety concerns. The adoption of Thixomolded sheet stock on heated rolls affords fast and inexpensive commercial production - with few steps - on extant commercial equipment.

Conclusions

1. Thixomolded Mg alloy stock is an attractive starting stock for thermal-mechanical processing of Mg alloy sheet. The advantages of this starting material derive from the rapid freezing that results in fine as-molded grain size, low porosity, low texture and homogeneous microstructure throughout the molding.

2. Warm thermal-mechanical processing serves to refine the grain size by continuous dynamic recrystallization with minimum crystallographic twinning. Furthermore, coarse intermetallics are refined to nanometer dimensions by subdivision or dissolution/reprecipitation. The refined intermetallic particles thus serve to retard grain growth by their presence in grain boundaries.

3. In concert, strength and ductility can be improved by the Thixomolding Thermal-Mechanical Process (TTMP).

4. The TTMP process is a very efficient and cost effective manufacturing means and should render Mg wrought products more commercially viable in the future.

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