To study corrosion and mechanical behavior of Friction Stir Processed AZ91 MG alloy

Ph.D. Synopsis

Submitted To

Gujarat Technological University

For The Degree

Of

Doctor of Philosophy

In

(Metallurgy Engineering)

By

Mrs. Minal Sanjay Dani

Enrolment No: 149997121004 (Metallurgy Engineering)

Supervisor:
Dr. Indravadan B Dave
Gujarat Technological University, India.
Professor (HEAD) Metallurgy Engineering
Govt. Engineering College, Gandhinagar

Index

1. Abstract:

On die cast AZ91Magnesium alloy Aluminum rich surface layer was successfully fabricated by Friction stir process(FSP) using very fine size pure Al powder. Corrosion resistance of die cast, friction stir processed and friction stir processed with Aluminum powder AZ91Magnesium (Mg) alloy were investigated by Salt spray in 5 % sodium chloride (NaCl) solution. Corrosion behavior was analyzed by Scanning electron microscopy for investigation of pits available after 48 hours in all specimens. The Scanning electron microscopy (SEM) investigation proved that Friction stir processed with Aluminum powder have lowest pit size compare to friction stir processed AZ91 Mg alloy and commercially available die cast AZ91 Mg alloy.

The electro Chemical behavior of the die cast AZ91 Mg alloy with and without Aluminum powder under different process parameters of FSPed AZ91 alloy specimens were investigated using Potentiostat in 5% NaCl solution. The electrochemical corrosion tests revealed least corrosion rate for FSP double pass(DP) with Aluminum powder compare to FSP single pass(SP) with aluminum , FSP DP and SP without Aluminum powder and die cast AZ91 Mg alloy which was confirmed by SEM and EDS study of corroded specimens. The improvement in corrosion resistance of FSP DP with Aluminum powder is because of more dissolutions of Al in α- Mg phase as well as more formation of β-phase($Mg_{17}Al_{12}$) which were confirmed by X-ray diffreactometer data(XRD).

Micro structural characterization of the materials revealed reasonably uniform distribution of aluminum powder and significant grain refinement observed in FSP DP with aluminum powder. Micro hardness studies revealed that double pass FSPed with aluminum powder in magnesium matrix led to a simultaneous increase in hardness. These is because of untreated die cast AZ91 Mg alloy dendritic structure having primary α-phase and intermetallic β-$Mg_{17}Al_{12}$ phase and eutectic(α+ β- phase($Mg_{17}Al_{12}$)) phases at the grain boundaries were homogenized and grain refinement were observed with increasing in β-$Mg_{17}Al_{12}$ phase developed during FSP double pass with Aluminum powder which were confirmed by SEM as well as XRD.

2. Brief description on the state of the art of the research topic(Introduction):

Magnesium alloys have low density, its high strength to weight ratio , high dimensional stability, good electromagnetic shielding characteristics, high damping characteristics, good machinability and is easily recycled makes it an ideal for automotive, aerospace, portable electronic and communication devices, sporting goods, structural materials, handheld tools, household equipment, and biodegradable implants[1]. The need for weight reduction, particularly in portable microelectronics, telecommunication, aerospace and automobile sector has stimulated engineers to be more adventurous in their choice of materials [3]. Mg alloys have density 1.8 gm/cc, which is 2/3 of Aluminum; 1/4 of steel and 1/5 that of copper and nickel alloys. Moreover the use of Mg alloys has also been restricted to a limited range, because of its poor workability at near room temperature due to its crystal structure (HCP). Magnesium alloys may be considered for aeronautical applications due their high mechanical properties if provided by a fine-grained structure [4].This is because high strength coupled with high ductility at room temperature is achieved by grain refinement. Furthermore, fine-grained magnesium based materials exhibit super plastic behavior at high strain rates ($\geq 10^{-1}\ s^{-1}$) or low temperatures (≤ 473 K)[5].

However the use of magnesium alloys is limited by their poor wear behavior and low corrosion resistance for many industrial applications. This has limited its use in the automotive and aerospace industries, where exposure to harsh service conditions is unavoidable. The simplest way to avoid corrosion and increasing wear resistance is to do surface modification of Magnesium alloys .Thus surface modification technologies applied to Mg –Al alloys for improvement in corrosion and wear resistance. The different techniques by which generally AZ91 Magnesium alloy surface modified include electrochemical plating, conversion coatings, anodizing, gas-phase deposition processes, thermo mechanical treatments, laser surface alloying / cladding and organic coatings, electro less Ni plating, thermal spray plasma deposition processes, Friction stir process.

The recently developed friction stir processing (FSP) technique has evolved as a promising technique, for achieving grain refinement, homogenization and removal of defects from the casting process [6,7]. In addition, the change in the microstructure and particularly the morphology of intermetallic phases in Mg alloys by FSP also influences the corrosion rate [8].
FSP is a solid state process known for its ability to modify microstructures and provide improved properties over conventional processing technologies [9-11]. FSP is the new emerging technology to make s/c composites. FSP is the process based on the principle of Friction Stir Welding (FSW). It started its journey from Al alloy and now extended it to most of all metals and their alloys. It is fact that the light alloys are more readily fabricated using this method. To produce S/c composite base metal either grooved or holed followed by filling of desired filler material [10].Filler/ reinforcing is material most probably ceramic .This grooved or holed surface stirred by high velocity of non-consumable tool and produces S/c composites [11]. This tool possesses a pin supported by shoulder. The new research is mainly based on the tool design; however it affects the metallurgy of the component. The rotating and linear motion of tool gives desired weld pool, i.e. s/c composite. [12,13]. From the literature it is evident that reinforcement element like Al_2O_3, SiC, Pure Al, C, TiC is possible for Mg and its alloys [14-18, 30-33]. In this work, on commercially available die cast AZ91Mg alloy Al-rich surface layer was successfully fabricated by FSP using very fine size pure Al powder. FSP were done with different rotational speeds (380 and 545 rpm), different passes(Single pass and double pass), with and without pure aluminum powder.

It has been reported by many researchers that, in FSPed magnesium alloys, the grain size could be decreased to a few micrometer and properties like strength, hardness, corrosion resistance, ductility and formability were significantly improved without affecting the bulk properties of the materials [10].Numerous studies have shown that when reinforcements have been added to base metal they help to improve the strength, wear performance, resistance to corrosion and hardness [11-12]. Adentula et al. reinforced Mg alloys with four different powders (i.e. Fly Ash, Palm Kernel Shell Ash, Ti-6Al-4V and 304 Stainless steel powders) to try to improve the acute corrosion resistance and also other mechanical properties such as hardness, tensile property and wear performance of the fabricated composites [13]. Furthermore, FSP has also been used to fabricate surface composites reinforced by intermetallic particles, Sic particles, SiO_2 particles, C60 molecules or fullerene on cast Mg alloy substrate. [14-16]. Chen et al., prepared, an Al-rich surface layer by adding aluminum powder in AZ91D alloy for improving their corrosion resistance properties using FSP method [17]. This improvement is mainly attributed to the increasing Al concentration in the α-Mg phase as well as increasing volume fraction of β-phase($Mg_{17}Al_{12}$) [17-19].Almost very negligible work has been done on FSP using pure Al powder as reinforcement material on magnesium AZ91 alloy.

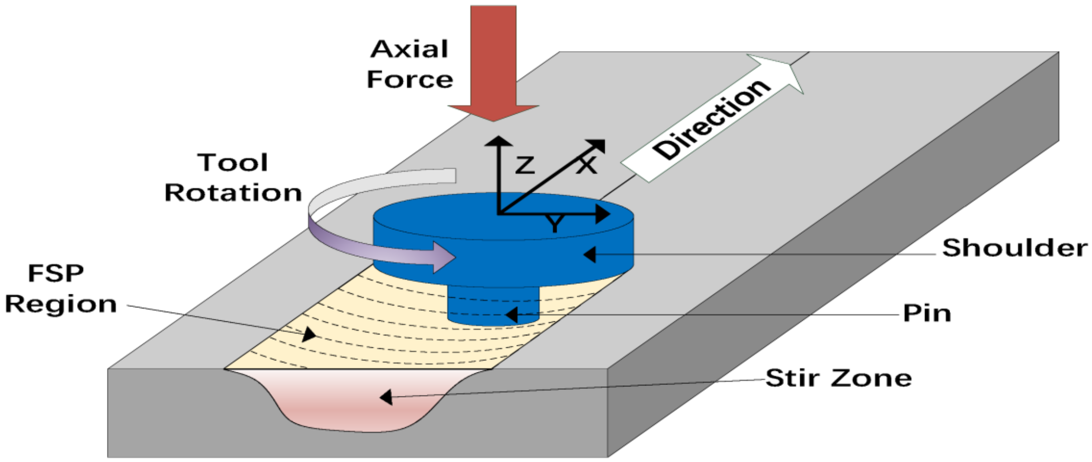


Fig: 1 Schematics of friction stir processing (FSP) [2].

It can be expected that an aluminum-rich surface on Mg alloy can be prepared by FSP so that corrosion resistance can be improved. Corrosion behavior of specimens i.e., as-received die-cast AZ91 Mg alloy, FSPed Mg alloy and FSPed with pure Al powder AZ91 Mg alloy, was investigated by salt spray test and immersion test according to ASTM B 117-11 practice and G31–71 practice. No work has been done with pits behavior in terms of calculating pit size after definite hour of test (48 h), and thus, objective of the research is to investigate behavior of pits generated during salt spray test by scanning electron microscopy and compare weight loss in immersion test.

In this work, our main focus is to improve the corrosion resistance of AZ91 Mg alloy using Aluminum powder under various rotation speeds and passes by FSP. An attempt has been made to study the corrosion behavior in 5 wt. % NaCl solution of the die cast AZ91 Mg alloy along with FSP treated AZ91 Magnesium alloy, with and without Al powder by electro chemical test on Potetiostat. Mechanical behavior of same processed specimens were investigated with respect to micro structural analysis by optical as well as SEM with EDS , micro hardness and grain size measurements were compared with die cast AZ91 Mg alloy.

3. Definition of the Problem:

The problem title is “To study corrosion and mechanical behavior of Friction stir processed AZ91 Mg alloy”. Based on Literature survey, Mg alloys are lighter in weight, have high strength to weight ratio, high vibration damping capacity, full recyclability will make them in good demand as replacement with Aluminum alloys. Only Mg alloys have poor corrosion and wear resistance. here are so many developments and research work have carried out in surface treatment of Magnesium alloys for improvement in corrosion resistance, but very less work are done in modification of Magnesium alloys. Main objective is to modify Mg alloy and improve corrosion resistance and mechanical properties with lighter weight, good strength to weight ratio, good recyclability, cost effective.

Almost negligible work were done with friction stir processing with aluminum powder with single pass as well as double pass with different rotational speeds. Due to addition of Aluminum more β-phase ($Mg_{17}Al_{12}$) as well as more aluminum in α – Mg phase are developed which were main reason for improvement in corrosion resistance of FSPed with aluminum specimens.

4. Objective and Scope of the work:

- Main objective is modification of surface of conventional die cast AZ91 Mg alloy by friction stir processing for betterment in corrosion and mechanical properties so that it can be used in structural applications of aerospace , automobile, electronics industries**.**
- Modification of AZ91 Mg alloy by Friction stir processing with different process parameters, singe pass and double pass with and without pure aluminum powder for grain refinement and improvement in hardness which also improves corrosion resistance.
- Corrosion behavior can be analyzed by salt spray test, immersion test and by potetiodynamic techniques by Potetiostat.
- Mechanical behavior can be measured by grain size measurement; micro hardness and detailed microstructure analysis by optical and scanning electron microscopy as well as for study of morphology of phases XRD were performed.
- By gaining properties of aluminum alloys, these alloys can be easily replaced in place of aluminum alloys with lighter weight and compactable corrosion and mechanical properties.

5. Original contribution by the thesis:

5.1 Friction stir process of AZ91 Mg alloy :

The conventional plate of die-cast AZ91 was cut to the required size for FSP work. Commercially available pure aluminum powder with average particle size of 19 µ was filled in groove at center on AZ91 Mg alloy plate for FSP with aluminum powder. Two H 13 grade non-consumable steel tools were used ,one without pin for counter pass to cover top of groove after implanting aluminum powder into groove in order to prevent the particles to be scattered during FSP work and second tool used for FSP work. With rotational speed 380 rpm and 545 rpm with same transverse speed 31.5 mm/min with 3^0 tool tilt angle FSP were done with SP as well as DP with and without aluminum powder so eight different specimens were prepared which were compared with die cast AZ91 Mg alloy for all investigations. Fig : 1 shows specimen's preparation with different parameters.

SR No	Specimen no	Specimens condition
1	0/1	Commercial available die cast AZ91 Mg alloy
2	1	AZ91 FSP 545 Double Pass with Al
3	2	AZ91 FSP 545 Double Pass without Al
4	3	AZ91 FSP 545 Single Pass with Al
5	4	AZ91 FSP 545 Single Pass without Al
6	5	AZ91 FSP 380 Single Pass with Al
7	6	AZ91 FSP 380 Single Pass without Al
8	7	AZ91 FSP 380 Double Pass with Al
9	8	AZ91 FSP 380 Double Pass without Al

Table 1: show all specimens conditions

5.2 Corrosion Test:

5.2.1 Salt spray and immersion tests:

They were done for die cast AZ91 Mg alloy, FSP with Al powder and FSP without Al powder according to ASTM B 117-11 standard. The first visible pit observed by naked eye under salt spray test was indication of breakdown of surface of specimen. Here we had observed pit generation in all three conditions samples and made comparison of pits formation in each specimen by measuring size of pit by scanning electron microscopy. Immersion test was carried out according to ASTM G31-71. Prior to the tests, specimens were measured and weighed. Once the test was finished after 48 h of immersion time, weighed again. Stereoscopic as well as SEM with EDS was carried out to study corroded samples surface for pit behavior in specimens of all three conditions after salt spray test.

5.2.2Electro chemical measurements:

The electrochemical measurements were performed on commercially available die cast AZ91Mg alloy and FSP treated under various rotational speeds during single and double pass with and without aluminum powder specimens by Gamry make Reference 600 Potetiostat. The corrosion rate as well as potetiodynamic polarization measurements were carried out which give corrosion behavior of all specimens.

5.3 . Characterization of Specimens:

Microstructures were observed by optical microscopy as well as by Scanning Electron Microscopy (SEM) in order to study the morphology and evolution of corrosion products formed on the material surface for corroded samples. Microstructure analysis can be done for all processed specimens by optical as well as SEM with EDS to know elemental analysis .XRD were performed on all specimens as well as die cast AZ91 Mg alloy to understand morphology of phases present in specimens.

5.4 . Mechanical tests:

The micro-hardness was measured using a micro- Vickers hardness tester. Grain size measurements were carried out for all specimens according to ASTM E 112 practice. The as-received and FSP with and without Aluminum powder specimens were analyzed by X-ray diffractometer (XRD) and energy-dispersive spectrometer(EDS) in order to verify the status of the Al powder.

6. Methodology of Research, Results / Comparisons:

6.1 Friction Stir Processing: FSP was successfully done with and without pure Al powder at 380 and 545 rpm rotational speed and 31.5 mm/min transverse speed with non consumable H13 grade steel tool .(tilt angle of tool 3^0) .

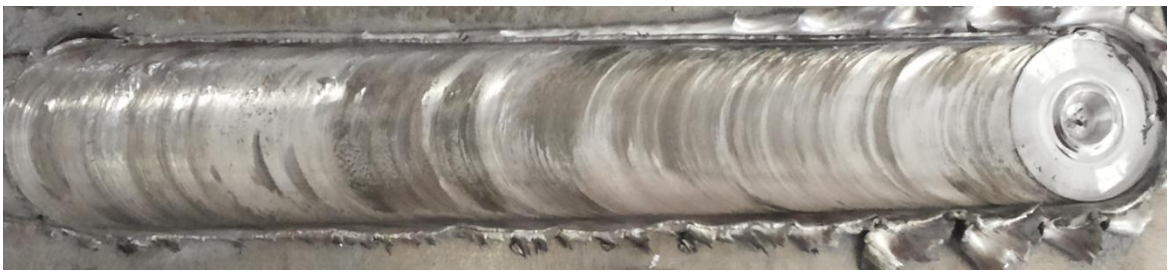
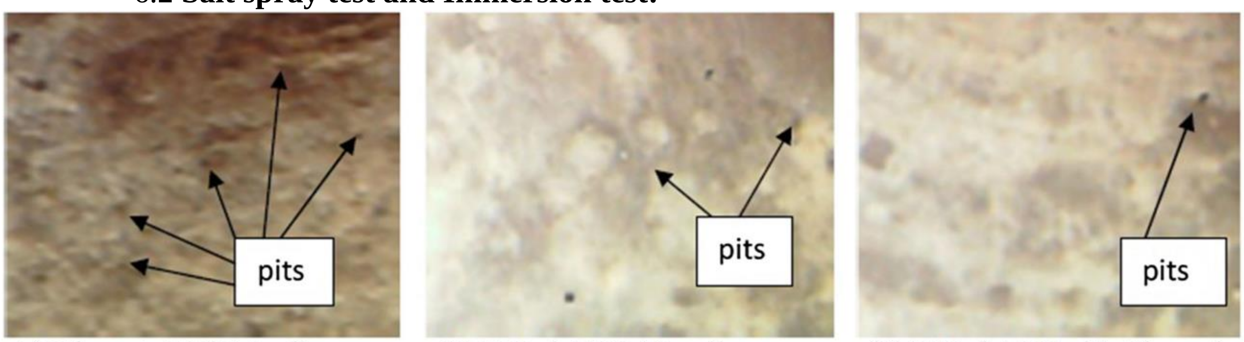


Fig : 2 Surface appearance of the FSPed specimen

6.2 **Salt spray test and Immersion test:**



(a) Die cast AZ91 Mg alloy (as received) **(b)** FSPed AZ91 Mg alloy **(c)** FSPed AZ91with Al powder

Fig: 3Stereoscope results of specimens of all three conditions after salt spray test

(a) Die cast AZ91 Mg alloy (b) FSPed Az91 Mg alloy (c) FSPed AZ91 with Al powder

Fig: 4 Corroded specimens after 48 h of immersion test

Sample ID	Initial Weight (gms)	Final Weight (gms)	Total Weight loss(gms)
As received AZ91 Mg alloy	6.3790	5.8442	0.5348
FSPed AZ91	1.4028	1.1276	0.2752
FSPed AZ91 with Al powder	1.4245	1.2271	0.1974

Table2: show weight loss by Immersion of all three conditions specimens

6.3 **Salt spray test SEM**:

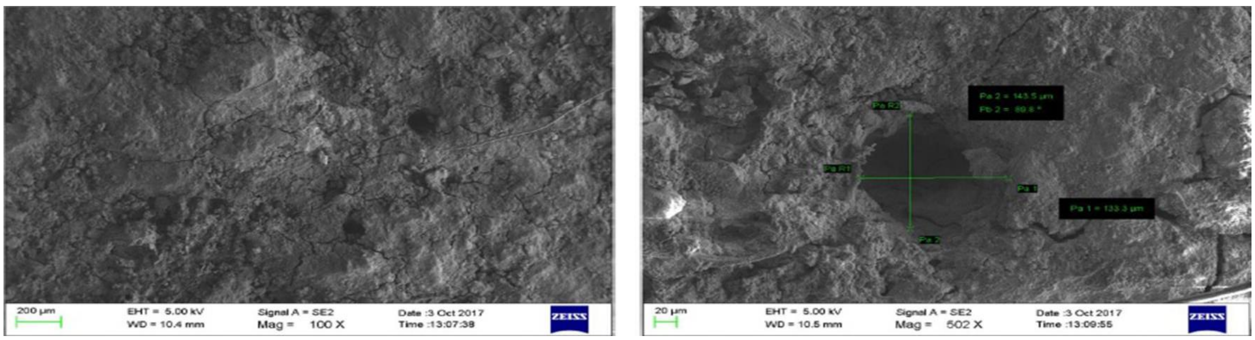


Fig: 5 SEM micrograph of die-cast (as received) AZ91 Mg alloy

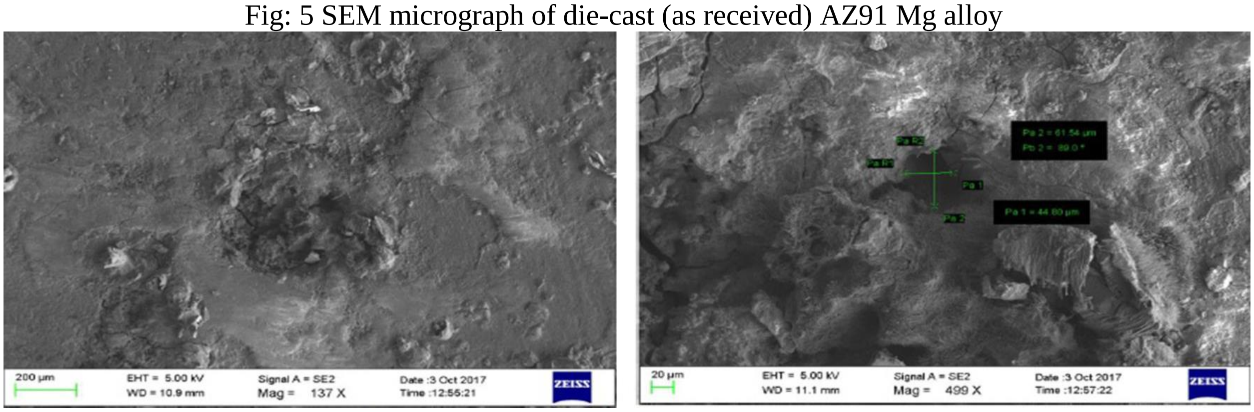


Fig : 6 SEM micrograph of FSPed AZ91 Mg alloy

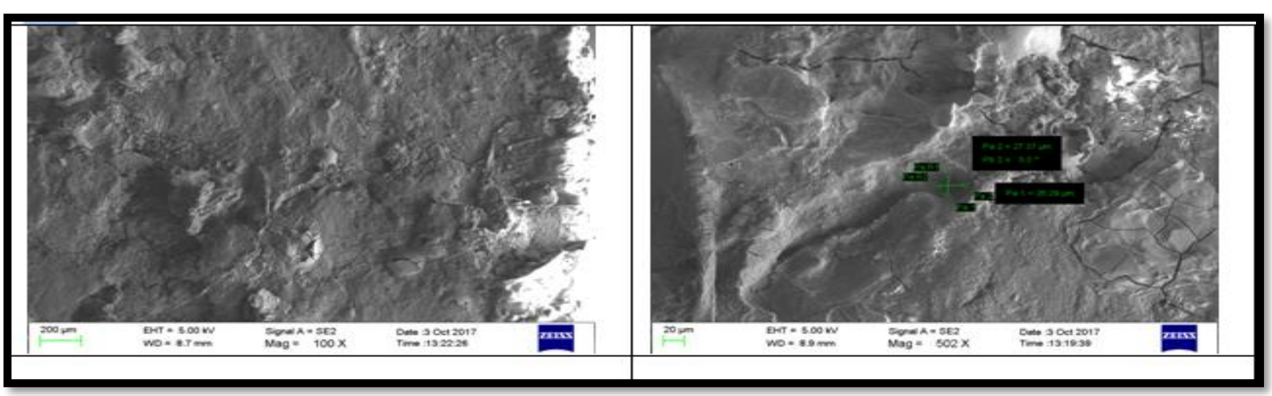


Fig: 7 SEM micrograph of FSPed AZ91 Mg alloy with Al powder

Fig: 5shows SEM micrographs of die-cast AZ91 Mg alloy shows surface was covered with thick and uneven film of salt solutions. Fig: 6shows SEM micrographs of FSPed AZ91Mg alloy show less numbers of pits in FSPed AZ91 Mg alloy compared to as-received diecastAZ91 Mg alloy. Specimen surface was covered with thin layer of salts and very less and small corrosion pits were observed. Fig: 7shows the SEM micrographs of FSPed AZ91 Mg alloy with Al powder. Specimens show rarely pits available in this specimen compared to both previous conditions.

Sr No	Specimens	Sample 1 Pit size μm		Sample 2 Pit size μm		Sample 3 Pit size μm		Average Size Pit size μm	
		Pa 1	Pa 2	Pa 1	Pa 2	Pa 1	Pa 2	Pa 1	Pa 2
1	Die cast AZ91 Mg alloy	134.10	141.10	133.20	143.3	132.6	144.2	133.3	143.8
2	FSPed AZ91 Mg Alloy without Al powder	44.61	61.32	44.72	62.10	45.10	62.52	44.81	61.94
3	FSPed AZ91with Al powder	26.20	26.80	26.92	27.32	26.84	27.84	26.65	27.32

Table 3 : Pit size observation of all three condition specimens

6.4 **Microstructure analysis:**

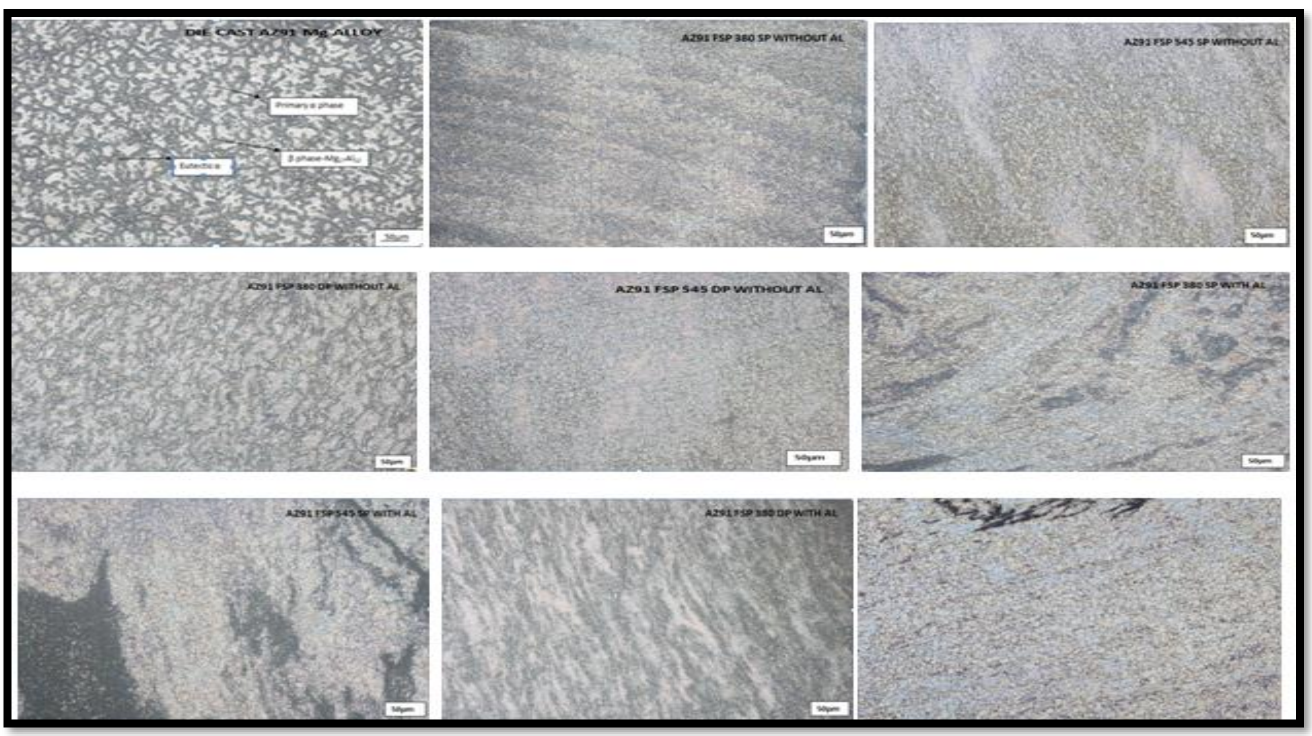


Fig: 8 show optical microscopy of all specimens

An optical image of the microstructure of the commercially available die-cast AZ91 alloy is observed in Fig. 9a. The alloy in as cast condition showed a dendritic structure of Al in α –matrix having α-grains and intermetallic phases in different forms at the grain boundariesβ-Mg17Al12 phase and Eutectic α + β-Mg17Al12 phase combined with α-phase are produced during the solidification and they can be observed at the grain boundaries. The β-Mg17Al12 phase was seen to be precipitated discontinuously in lamellar form after slow cooling below the solvus temperature at the grain boundaries and also within the α-grains, as observed in Fig. 9a and 9b

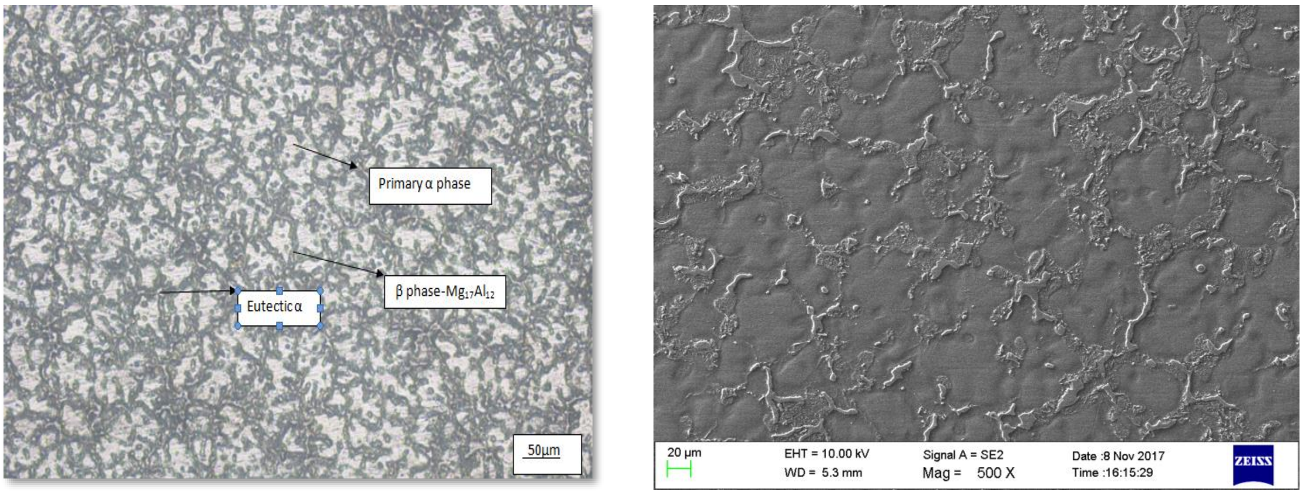
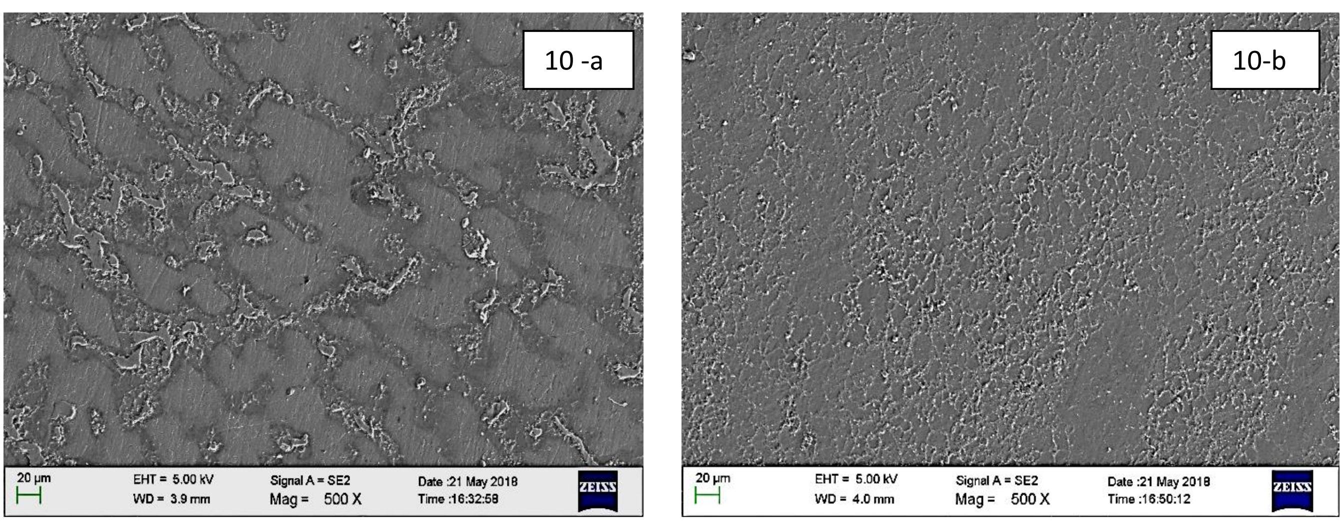


Fig: 9 As received die cast AZ91 Mg alloy a) Optical micrograph b) SEM image in BSE mode

After single pass, FSPed AZ91samples at 380 and 545 rpm are shown in Fig. 10a, b, c and d respectively. It is seen that the α-and β-phases were not homogenously distributed in a and b. When the friction stir processing was done with double passes at 380 and 545 rpm rotation speeds the micrographs shown in Fig. 10 c and d, respectively exhibit a homogeneous distribution of both phases together with grain refinement. This is because the eutectic or βphase is relatively hard and difficult to deform while the α- phase is soft and easy to deform [32].



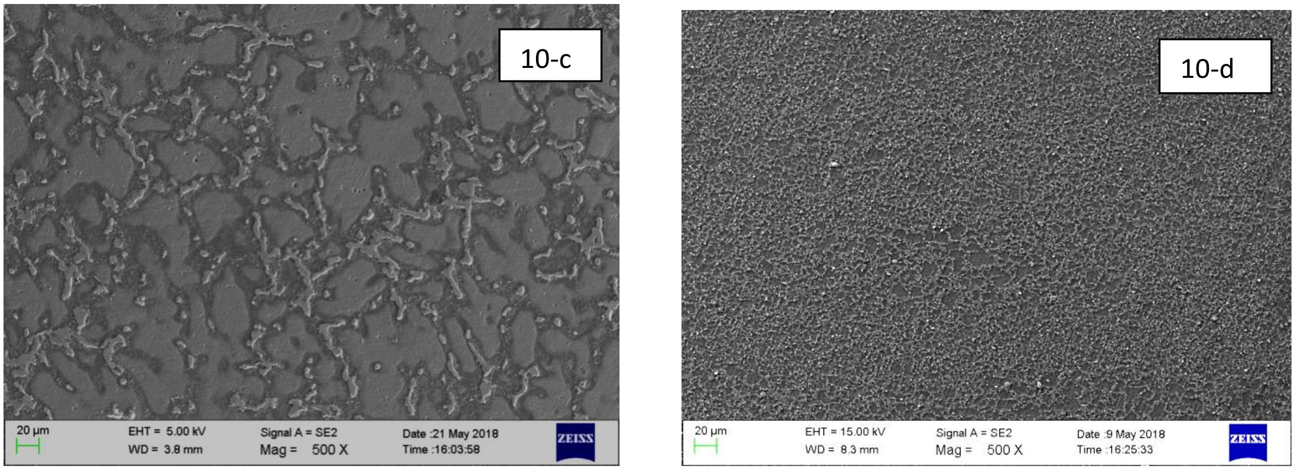
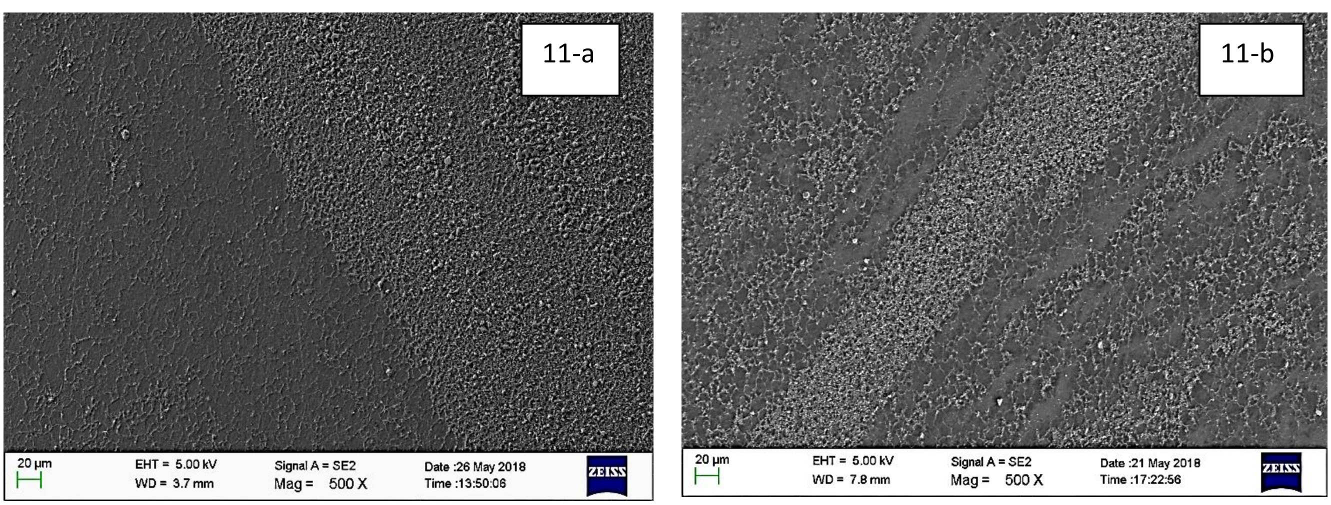


Fig: 10:SEM images of AZ91 Mg alloy friction stir processed at a) 380 rpm with single pass b) 545 rpm with single pass c) 380 rpm with double pass d) 545 rpm with double pass

Figure: 11 shows the microstructure of AZ91 alloy after friction stir processing by reinforcement with aluminum powder during both single and dual passes. During the single passes the aluminum powder is found to be distributed along the friction stir direction in the friction stirred zone. At higher rotation speeds the aluminum particles are found to occupy the spaces in the α-grains. As a result a cloudy appearance is observed when friction stirred at 545 rpm (Fig. 11b). The results from EDS show that these white particles are Al-rich phase. During the double pass, the aluminum powder is found to be agglomerated and is seen as long streaked lines made of white particles. This indicates that large number of white particles are distributed along the material flow lines (Fig. 4c). However, at higher rotational speeds a cloudy appearance was observed as seen earlier for single pass.



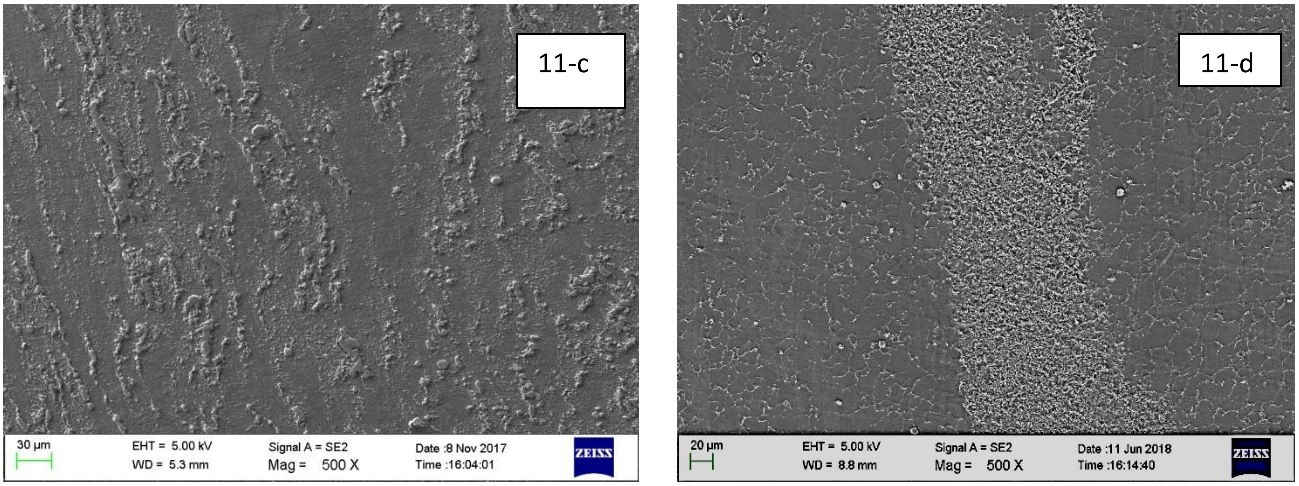


Fig: 11: SEM images of AZ91 Mg alloy friction stir processed with aluminum powder at a) 380 rpm with single pass b) 545 rpm with single pass d) 380 rpm with double pass e) 545 rpm with double pass

6.5 XRD analysis:

The XRD patterns for untreated AZ91 and FSPed without aluminum powder reinforcement magnesium alloys are shown in Fig. 12. It was found that the peaks corresponding to the diamond and circle represented α-Mg and β-Mg17Al12, respectively. Both bare and frictions stir processed samples showed both these phases. Moreover the intensity of α-Mg and β-Mg17Al12 peaks increased after friction stir processing. A strong refinement of grains is attributed to the increased intensities of these processed samples in comparison to the as-cast condition. Comparing the processing conditions of the processed samples, it was observed that the samples processed at 545 rpm with both single and double passes showed higher amount of α-Mg phases compared to that processed at 380 rpm. This is because there was higher grain refinement at higher rotation speeds

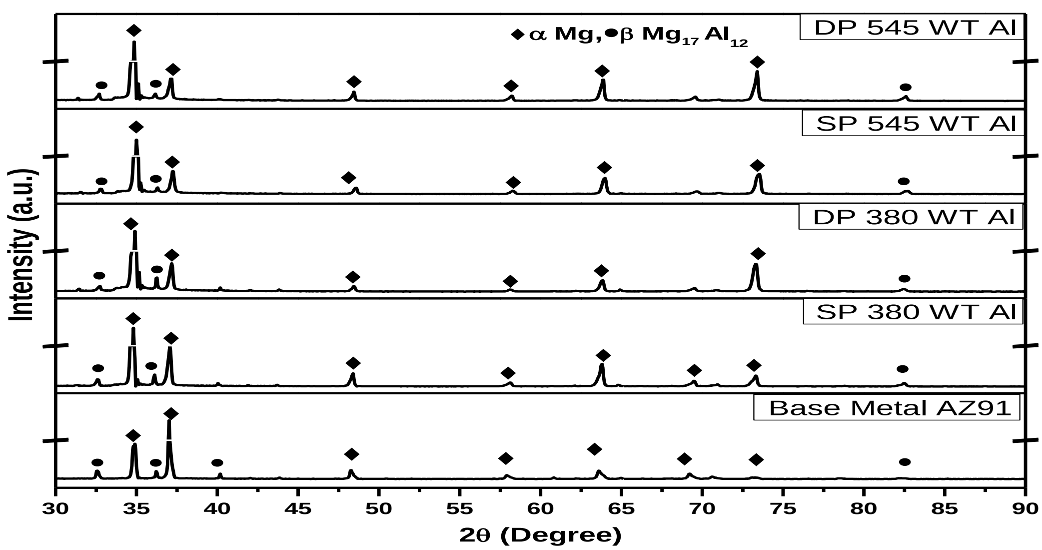


Fig: 12 comparison of XRD pattern of FSPed without aluminum powder with die cast AZ91 Mg alloy.

The XRD patterns for untreated AZ91 and FSPed magnesium alloy reinforced with aluminum powder are shown in Fig. 13. Friction stir processed samples with aluminum powder showed both α-Mg, β-Mg17Al12and aluminum phases. Moreover the intensity of α-Mg and β-Mg17Al12 peaks increased after friction stir processing also when reinforced with aluminum. Comparing the processing conditions of the processed samples, it was observed that the samples processed at 380 rpm with both single and double passes showed higher amount of β-$Mg_{17}Al_{12}$ phases compared to that processed at 545 rpm. However, separate peaks of aluminum were observed in the case of samples processed by double passes. This is also confirmed from the SEM images as shown in Fig. 11c. As the rotational speed increased, very few peaks of β-$Mg_{17}Al_{12}$ phases and no separate aluminum peaks were visible.

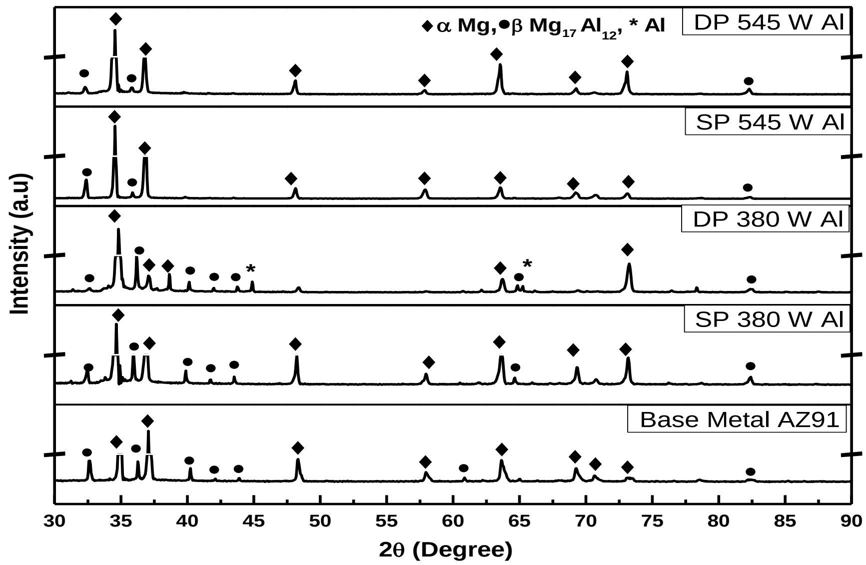


Fig: 13 comparison of XRD pattern of FSPed with aluminum powder with die cast AZ91 Mg alloy.

6.5 Electro chemical behaviour study:

6.5.1 Comparison of potetiodynamic curves and corrosion rate measurement in mpy of FSPed AZ91 without aluminium powder single pass and double pass with 380 and 545 rpm were done with untreated die cast AZ91 Mg alloy at 5 wt% NaCl solution.

Table: 4 show corrosion rate derived by the Tafel extrapolation with different corrosion parameters i.e. Corrosion potential (E_{corr}), corrosion current density (I_{corr})

Sr. No	Sample ID	E_{corr} (V)	I_{corr} (Amp)	Corrosion Rate (mpy)
1	Die cast untreated AZ91 Mg alloy	- 1.360 V	670.00 µA	1.537 X 10^3
2	AZ91 FSP 380 SP without Al	-1.400 V	146.00 µA	3.787 X 10^2
3	AZ91 FSP 380 DP without Al	-1.380 V	165.00 µA	3.362 X 10^2
4	AZ91 FSP 545 SP without Al	-1.560 V	364.00 µA	8.348 X 10^2
5	AZ91 FSP 545 DP without Al	-1.310 V	46.00 µA	1.055 X 10^2

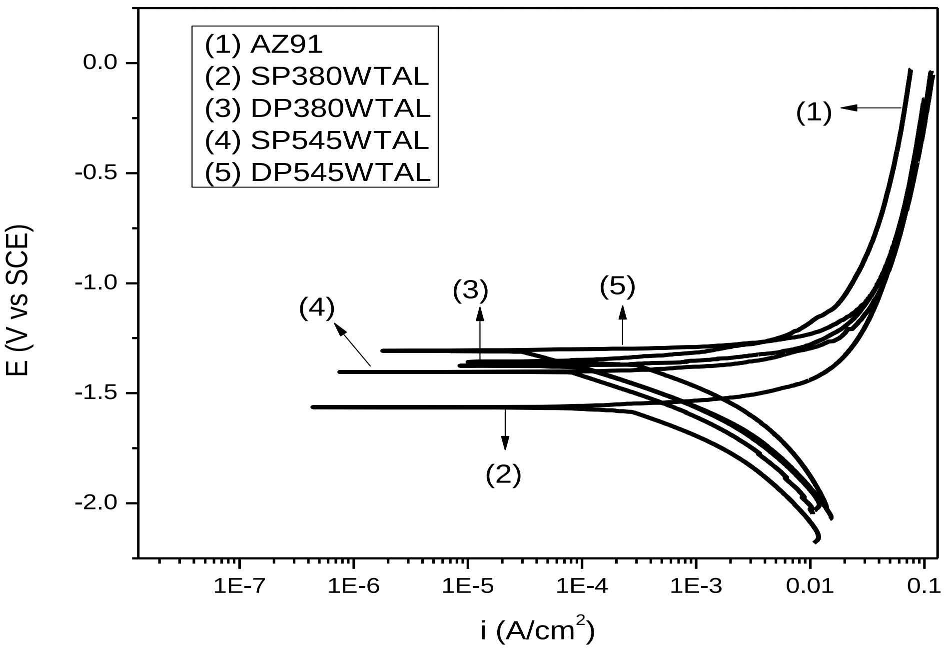


Fig: 14 Comparison of potetiodynamic curves of friction stir processed AZ91 without aluminum powder single pass and double pass with 380 and 545 rpm were done with untreated die cast AZ91 Mg alloy.

As shown in fig: 14, potetiodynamic curves, Specimens in as-cast had lowest corrosion rate (shown in curve 1), SP FSP condition had a one order less corrosion rate (shown in curve 2 and 4) , while DP FSP showed the lowest corrosion rate(shown in curve 3 and 5).Improved Corrosion resistance of FSP DP 545 rpm was because of FSP more grain refinement and α-grains were smaller in size with increase in β-phase. The precipitation of β phase reduces average Al content in α –matrix and hence reduce the area rich in Al and further increase low Al area where corrosion were likely to initiated as shown in die cast AZ91 Mg alloy. The fine β-phase size and its homogeneous distribution in the matrix, obtained after DP FSP improved the corrosion resistance.

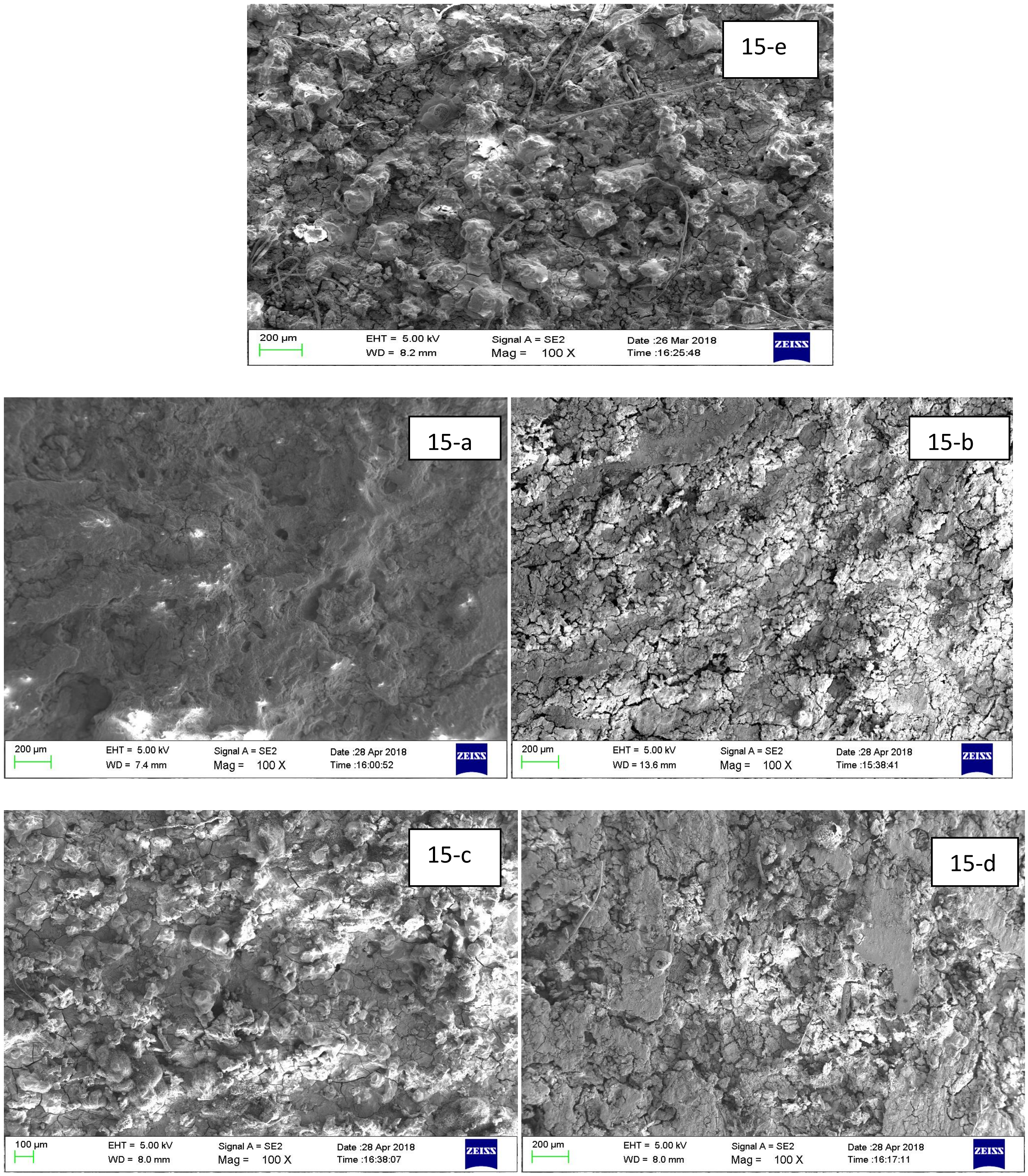


Fig: 15 Comparison of SEM images of friction stir processed AZ91 without aluminium powder single pass and double pass with 380 and 545 rpm were done with untreated die cast AZ91 Mg alloy. (15-a FSP 380 SP without aluminium, 15-b FSP 545 SP without aluminium, 15-c FSP 380 DP without aluminium, 15-d FSP 545 DP without aluminium, 15-e die cast AZ91 Mg alloy)

6.5.2 Comparison of potetiodynamic curves and corrosion rate measurements in mpy of FSPed AZ91 with aluminium powder single pass and double pass with 380 and 545 rpm were done with untreated die cast AZ91 Mg alloy at 5 wt% NaCl solution.

Table: 5 show corrosion rate derived by the Tafel extrapolation with different corrosion parameters i.e. Corrosion potential (E_{corr}), corrosion current density (I_{corr})

Sr No	Sample ID	E corr in V	I Corr in Amp	Corrosion Rate in mpy
1	Die cast untreated AZ91 Mg alloy	- 1.360 V	670.00 µA	1.537 X 10^3
2	AZ91 FSP 380 SP with Al	-1.370 V	102.00 µA	2.346 X 10^2
3	AZ91 FSP 380 DP with Al	-1.360 V	48.60 µA	1.10 X 10^2
4	AZ91 FSP 545 SP with Al	-1.530 V	236.010^{2}0 µA	5.423 X 10^2
5	AZ91 FSP 545 DP with Al	-0.746 V	26.30 µA	0.6031 X 10^2

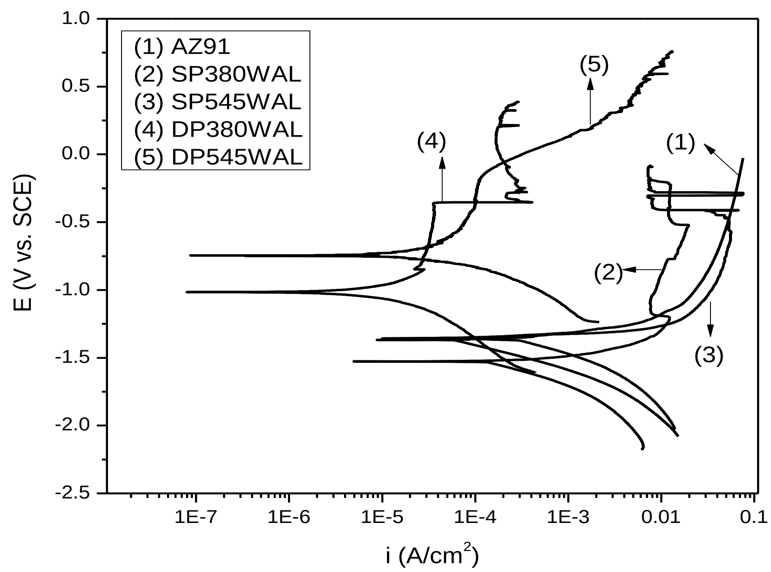


Fig: 16Comparison of potetiodynamic curves of friction stir processed AZ91 without aluminum powder single pass and double pass with 380 and 545 rpm were done with untreated die cast AZ91 Mg alloy.

As shown in fig: 16**,** Curve 4 and 5(with FSP double pass with Al powder) shows better corrosion resistance than curve 3, 2 and 1. Passivation observed in double pass 380 and 545 rpm with aluminum powder FSP specimens. In addition, grain refinement might also have played a role in enhancing the stability of the passive film. Thus would suggest that FSP of AZ91 alloy with aluminum powder, double pass (545 rpm and 380 rpm rotational speed) could be highly beneficial in homogenizing the surface microstructure and hence enhancing the corrosion resistance. These would also prove by checking SEM images in which very less pits were observed in FSP DP with aluminum.

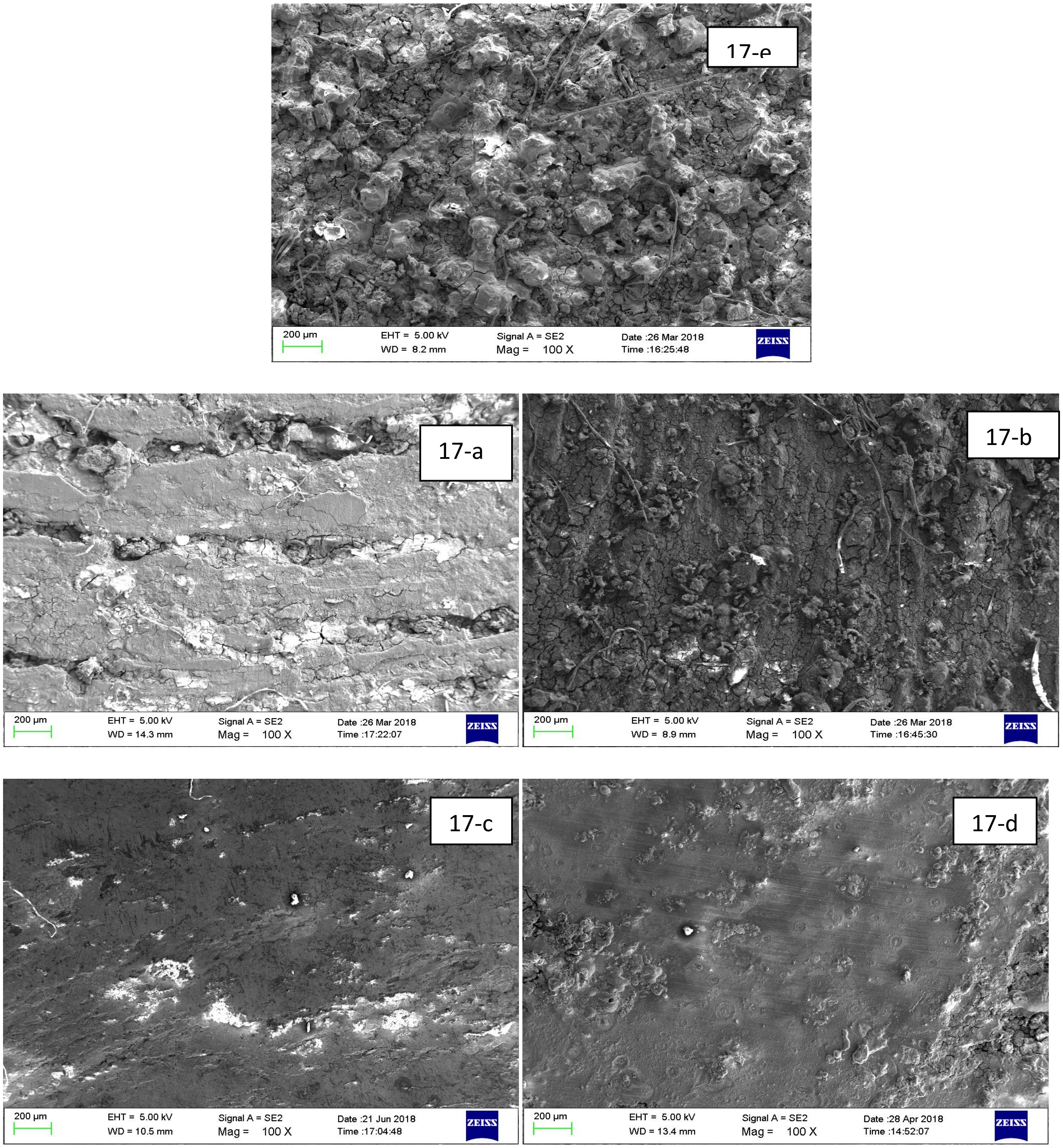


Fig: 17 Comparison of SEM images of friction stir processed AZ91 with aluminium powder single pass and double pass with 380 and 545 rpm were done with untreated die cast AZ91 Mg alloy.(17-a FSP 380 SP with aluminium, 17-b FSP 545 SP with aluminium, 17-c FSP 380 DP with aluminium, 17-d FSP 545 DP with aluminium, 17-e die cast AZ91 Mg alloy)

6.6 Micro hardness and grain size measurement Test:

Micro hardness test method adopted was ASTM E 384 – 11 & IS 1501, ASTM B 578 with given load 200 GMS, D well time: 10Sec and Grain size measurements were done according to ASTM E 112-12 .(table : 6)

SR No	Specimen condition	Specimen 1	Specimen 2	Specimen 3	Ave Hardness Vickers HV	ASTM grain size No
1	Die Cast AZ91 Mg alloy	84.64	84.83	84.50	84.66	6.5-7.0
2	AZ91 FSP 380 SP without Al	91.50	93.65	90.20	91.78	9.0-9.5
3	AZ91 FSP 545 SP without Al	93.90	91.73	96.69	94.10	8.5 – 9.0
4	AZ91 FSP 380 DP without Al	105.90	104.76	99.22	103.29	10.5-11.0
5	AZ91 FSP 545 DP without Al	102.05	101.57	105.52	103.05	11.0-12.0
6	AZ91 FSP 380 SP with Al	108.00	103.02	107.00	106.00	9.5-10.5
7	AZ91 FSP 545 SP with Al	103.52	106.29	108.10	105.97	9.5-10.5
8	AZ91 FSP 380 DP with Al	114.13	115.80	117.50	115.81	11.0-12.0
9	AZ91 FSP 545 DP with Al	114.99	119.44	115.01	116.48	12.0-13.0

Table: 6 Micro hardness and grain size no. for all specimens

The average hardness of the base metal was 84 HV. Maximum Grain refinement in case of FSP with aluminum powder double pass may be attributed to the presence of reasonably uniformly distributed aluminum particles which act as nuclei and also restricted grain growth during solidification. In all FSPed specimens micro hardness increase compare to base metal AZ91 alloy in stir zone was because of a) a severe grain refinement during dynamic recrystallization and b) aluminum powder distributed uniformly will increase volume fraction of β-phase($Mg_{17}Al_{12}$)[13].

The eutectic β- phase($Mg_{17}Al_{12}$) in die cast AZ91 Mg alloy was disappeared after FSP because stir zone temperature exceed the dissolution temperature of β- phase($Mg_{17}Al_{12}$) in Mg matrix[10], the refinement of grain size are affected by the FSP parameters like rotational speed, transverse speed etc. and slightly affected by addition of aluminum powder. It seems that grain refinement was caused due to dynamic recrystallization during FSP double pass with aluminum powder.

7. Achievements with respect to objectives:

The main objective of research was to develop FSPed specimens with and without pure aluminum powder for enhancement of corrosion resistance and improvement in mechanical properties.

1. FSP were successfully done on AZ91 Mg alloys with 380 and 545 rpm rotational speed for single pass as well as double pass with and without aluminum powder.
2. Best Corrosion resistance observed in FSPed DP with Aluminum powder which was also confirmed by pit size measurement of salt spray test specimens, potetiodynamic measurements and corrosion rate measurements in mpy of all processed specimens and by weight loss methods of Immersion test specimens.
3. Passivation was observed in FSP DP with aluminum powder in potetiodynamic curves.
4. Microstructure analysis proved that, best grain refinement was obtained in FSP DP which improved micro hardness too.

8. Conclusions :

1. Friction stir processing was applied for modification of surface of AZ91 Mg alloy successfully with and without pure aluminum powder.
2. Friction stir-processed AZ91 Mg alloy surface was giving better corrosion performance compared to base metal which was proved by comparing pit size and weight loss in immersion test.
3. Friction stir-processed with pure Al powder AZ91 Mg alloy surface shows the best improvement in corrosion performance compared to friction stir-processed AZ91 Mg alloy and die-cast AZ91 Mg alloy as size of pits developed was almost five times smaller than that of AZ91 alloy and two times smaller than that of friction stir-processed AZ91 Mg alloy. In immersion test, minimum weight loss was achieved in this condition. Thus, by addition of pure Al powder in friction stir processing, high Al content in a-phase and high volume fraction of b-phase act as anodic barrier to inhibit overall corrosion.
4. By microstructure analysis, it was proved that by FSP grain refinement and homogeneity of surface were achieved by dissolution of β -phase ($Mg_{17}Al_{12}$). Thus, minimizing localized galvanic α- and β phase interaction would drastically minimize corrosion effect.
5. Micro hardness show best hardness with FSP DP with Al powder in both 380 and 545 rpm .Very fine Grain size were obtained in FSP DP with Al powder.
6. Corrosion resistance were compare by potetiodynamic curves in which Friction stir process double pass with Aluminum powder have best corrosion resistance compare to FSP single pass and untreated die cast AZ91 Mg alloy in 5 wt% NaCl solution.

9. Copies of papers published and a list of all publications arising from the thesis:

Sr.No.	Title of Paper Proceeding	Details of Journal / Conference	ISSN / ISBN No.	Month & Year of Publication
1	A Review on Corrosion behavior of Mn added Magnesium and its alloys	International Advanced Research Journal in Science, Engineering and Technology	ISSN (Online) 2393-8021 ISSN (Print) 2394-1588	Vol. 2, Issue 12, December 2015
2	A review on surface modification of az91 magnesium alloy for improvement in corrosion and wear resistance	International journal od advance technology in Engineering and Science	ISSN- 2348-7550	Vol – 5, Issue no.01, January 2017
3	Corrosion Behavior of Die-Cast and Friction Stir-Processed AZ91 Magnesium Alloys in 5% NaCl	Springer (Journal of The Institution of Engineers (India): Series D, Metallurgical & Materials and Mining)	Engineering, ISSN 2250-2122 DOI :10.1007/s40033-019-00173-6	4 march 2019
4	Effect of Process Parameters on microstructure, grain size and Micro-hardness of Friction stir processed AZ91 magnesium alloy	Materials	Latest Developments in the Field of Magnesium Alloys and their Applications	To be submit in May 2091
5	Corrosion behavior of Friction stir processed AZ91 Mg alloy Improved corrosion resistance of Friction stir processed AZ91 Mg alloy	Materials and corrosion	Wiley	To be submit June 2019

10. References:

[1] E. F. Emley, *Principle of Magnesium Technology*, Pergamon Press, London, UK, 1966.

[2]Kan Li,Xuemei Liu * andYi Zhao,"*Review*Research Status and Prospect of Friction Stir Processing Technology,"coatings 2019,https://doi.org/10.3390/coatings9020129

[3] RajanAmbat*, NaingNaingAung, W. Zhou," Evaluation of microstructural e€ects on corrosion behaviour of AZ91D magnesium alloy, Corrosion Science 42 (2000) 1433±1455

[4] K. Kubota, M. Mabuchi, and K. Higashi, "Processing and mechanical properties of fine-grained magnesium alloys," Journal of Materials Science, vol. 34, no. 10, pp. 2255–2262, 1999.

[5] M. H. Abdelaziz, M. Paradis, A. M. Samuel, H. W. Doty, and F. H. Samuel,"Effect of Aluminum Addition on the Microstructure, Tensile Properties, and Fractography of Cast Mg-Based Alloys", Advances in Materials Science and Engineering (2017), 1-10.

[6] J. Gandra, R. M. Miranda, P. Vilaca: "Effect of overlapping direction in multipass friction stir Processing", Materials Science and Engineering A, Vol. 528, (2011), 5593-5599

[7] A. A. Nia, H. Omidvar, S. H. Nourbakhsh:" Effects of overlapping multi-pass friction stir process and process and rapid cooling on the mechanical properties and microstructure of AZ31 magnesium alloy" , Materials and Design, Vol. 58, (2014), 298-304.

[8] CHANG C I, DUA X H, HUANG J C."Achieving ultrafine grain size in Mg-Al-Zn alloy by friction stir processing [J]". Scripta Mater, 2007, 57: 209-212.

[9] DU X H, WU B L. "Using friction stir processing to produce ultrafine-grained microstructure in AZ61 magnesium alloy [J]". Trans Nonferrous Met Soc China, 2008, 18: 562-565.

[10] A. Hütter, W. Huemer, C. Ramskogler, F. Warchomicka,"Surface Modification of pure magnesium and magnesium alloy AZ91 byFriction Stir Processing", Key Engineering Materials Vols. 651-653, (2016) 796-801.

[11] F. Khodabakhshi, S. M. Arab, P. Š, and A. P. Gerlich, "Materials Characterization Fabrication of a new Al-Mg / grapheme nanocomposite by multi-pass friction- stir processing : Dispersion , microstructure , stability , and strengthening," vol. 132, no. August, pp. 92–107, 2017.

[12] A. D. Akinwekomi et al., "Processing and characterization of carbon nanotube-reinforced magnesium alloy composite foams by rapid microwave sintering," Mater. Sci. Eng.A, vol. 726, no.April, pp. 82–92, 2018.

[13] A. Adetunla and E. Akinlabi, "Influence of reinforcements in friction stir processed magnesium alloys: insight in medical applications", Volume6, Number 2 (2018), doi.org/10.1088/2053-1591/aaeea8.

[14] MORISADA Y, FUJII H, NAGAOKA T, FUKUSUMI M., "Nanocrystallized magnesium alloy-uniform dispersion of C60 molecules [J]". Scripta Mater, 2006, 55: 1067-1070.

[15] MORISADA Y, FUJII H, NAGAOKA T, FUKUSUMI M. "MWCNTs/AZ31 surface composites fabricated by friction stir processing [J]". Mater SciEng A, 2006, 419: 344-348

[16] MORISADA Y, FUJII H, NAGAOKA T, NOGI K, FUKUSUMI M. “Fullerene/A5083 composites fabricated by material flow during friction stir processing [J]”. Composites: Part A, 2007, 38: 2097-2101.

[17] CHEN Ti-jun(陈体军), ZHU Zhan-ming(朱战民), LI Yuan-dong(李元东), MA Ying(马颖), HAO Yuan(郝远),” Friction stir processing of thixoformed AZ91D magnesium alloy a fabrication of Al-rich surface”,Elsevier, DOI: 10.1016/S1003-6326(09)60093-60095.

[18] SONG G, ATRENS A. “Corrosion mechanisms of magnesium alloys [J].”AdvEng Mater, 1999, 1: 11-33.

[19] SONG G, ATRENS A, WU X L, ZHANG B.”Corrosion behavior of AZ21, AZ501 and AZ91D in sodium chloride “[J]. Corrosion Science , 1998, 40: 1769-1791.

[20] SONG G, ATRENS A, DARGUSCH M. “Influence of microstructure on the corrosion of die cast AZ91D” [J]. Corrosion Science, 1999, 41:249-273.

[21]Unikrishnan M A, Edwin Raja Dhas,”Friction stir welding of magnesium alloys- A review”, DOI: 10.5121/msej.2015.2402, MSEJ,vol.2,no.4,December 2015.

[22] R.M. Miranda,J.Gandra and P.Vilaca,http://dx.doi.org/10.5772/55986

[23]R.SMishra,Z.Y.Ma,I.Charit,MaterialScienceandEngineerinA,www.elsevier.com/locate/msea

[24]Yong X.Gan, Daniel Solomon and Michael Reinbolt,”Friction stir processing of particle reinforced composite material”, Materials 2010.3.329.350;doi:10.3390/ma3010329

[25]A. Hütter, W. Huemer, C. Ramskogler, F. Warchomicka, “Surface Modification of pure magnesium and magnesium alloy AZ91 byFriction Stir Processing”, Key Engineering Materials Vols. 651-653, (2016) 796-801

[26]J.P. LalithGnanavel, S. Vijayan;”Friction Stir Processing of Magnesium Alloys- Review”; Journal of Chemical and Pharmaceutical Sciences, ISSN: 0974-2115

[27] B RatnaSunil,G.PradeepkumarReddy,HemendraPatle,RavikumarDumpala,”Review :Magnesium based surface metal matrix composites by friction stir processing”, Journal of Magnesium and alloys 4 (2016) 52-61

[28] P.Rey,D.Gesto,J A Del Valle,D.Verdera and O A Ruano,” Fine andUltra fine grained AZ61 and AZ91 Magnesium alloys obtained by Friction Stir Processing”,Material Secience forum 706-709(2012) 1002-1007

[29] Rajeev *Dang, AlaukikSaxena, AmitSingla,"Microstructural study, Hardness behavior and Friction stir processing of Magnesium based Metal matrix composites", IJSR,vol:4,Issue:10,ISSN 2277-8179*

[30] GhaderFaraji, ParvizAsadi ,"Characterization of AZ91/ Alumina nano composite produced by FSP", Material Science and Engineering A 528(2011)2431-2440, www.elsvier.com

[31] GhaderFaraji,OmidDastani and S. AsgharAkabariMousavi," Effect of process parameters on microstructure and micro- hardness of AZ91/Al2O3 surface composite produced by FSP",ASM international 1059-9495,Nov 29, 2010

[32] J.Iwaszko,K.Kudla,K.Fila,"Friction stir processing of AZ91 magnesium alloy with SiC particles",Archives of Materilas Science and Engineering, vol 77,issue 2, feb'2016,page 85-92.

[33] ParvizAsadi&GhaderFaraji& Mohammad K. Besharati, "Producing of AZ91/SiC composite by friction stir processing (FSP)", *Int J AdvManufTechnol (2010) 51:247–260*

[34] *A H Feng and Z Y Ma, "Enhanced mechanical properties of Mg-Al-Zn cast alloy via friction stir processing",doi:10.1016/j.scriptamat.2006.10.035*