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EFFECT OF Scandium and Zirconium ADDITIONS ON CORROSION PROPERTIES OF Al-Mg-Mn Alloy

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ABSTRACT

This study investigates the hardness and corrosion resistance of Al-Mg-Mn alloy with minor additions of scandium (Sc) and zirconium (Zr) systematically. Stir casting with cold rolled condition was applied to the four compositions of this alloy, namely Al-4.2Mg-0.6Mn alloy, Al-4.2Mg-0.6Mn-0.2Sc-0.1Zr alloy, Al-4.2Mg-0.6Mn-0.4Sc-0.1Zr alloy, and Al-4.2Mg-0.6Mn-0.6Sc-0.1Zr alloy. Alloying with Sc and Zr has a strong influence on the hardness of Al-Mg-Mn alloys and introduce resistance to corrosion in 3.5wt.% NaCl solution.

Key words: Al-Mg-Mn-Sc-Zr; hardness, optical microscope; corrosion resistance; scanning electron microscopy; X-ray diffraction

1. INTRODUCTION

The development of light weight metals in the field of engineering and technology is due to the demand for such materials in aerospace, automotive and marine applications. Light weight metals such as aluminium alloys with magnesium and manganese are characterized by a low density and high resistance to corrosion [1, 2].

5XXX series aluminium alloys usually contains Aluminium (Al), Magnesium (Mg) Manganese (Mn) and other metals. Increase in the magnesium content in these 5XXX series alloys leads to increase in the ultimate tensile strength due to cold working; this involves in decrease in the plastic properties and Manganese and chromium increase in the corrosion resistant and wear resistant respectively [3-4]. However, these elements alone cannot achieve better mechanical properties. For improving these properties on Al-Mg-Mn alloys, investigational studies on adding transition elements of the periodic table like scandium (Sc), zirconium (Zr), hafnium (Hf), and titanium (Ti) etc., to 5XXX series aluminium were begun at the end of the 1960s, specifically on scandium additions [7-8]. From the literature, Al–Sc phase diagram shown in the Fig.1 provides the formation of Al_3Sc phase when Sc addition levels are 0.2wt.% to 0.6wt.%, that is Sc addition levels exceeding the eutectic composition [5-6]. However, Zr is another element for refining the structure of aluminium alloys can reduce the Sc addition levels because Zr shifts the eutectic position to a lower Sc level.

Thus the Al-Mg-Mn alloys, with minor additions of Sc and Zr is a new light-weight structural material, allowing scandium and zirconium unitedly results in $Al_3Sc_{1-x}Zr_x$ phases [9].

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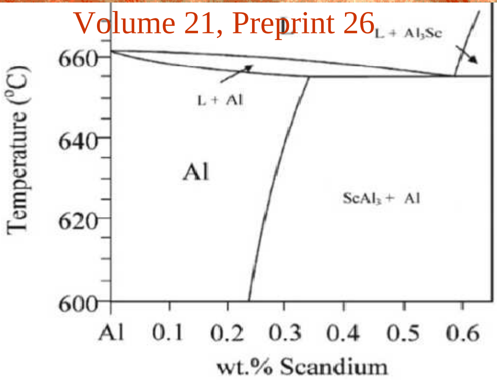

Fig. 1 Al–Sc phase diagram

In the present work an attempt was made to study the effect of systematic addition levels of Sc from (0.2wt.% to 0.6wt.%) with 0.1wt.% Zr to Al-Mg-Mn alloy on mechanical and corrosion properties.

2. EXPERIMENTAL METHODS

2.1 Materials

In the present work the four alloys Al-4.2Mg-0.6Mn alloy (hereafter named as specimen-1), Al-4.2Mg-0.6Mn-0.2Sc-0.1Zr alloy (hereafter named as specimen-2), Al-4.2Mg-0.6Mn-0.4Sc-0.1Zr alloy (hereafter named as specimen-3), and Al-4.2Mg-0.6Mn-0.6Sc-0.1Zr alloy (hereafter named as specimen-4) were produced by melting in an electrical resistance furnace (Fig. 3a). These alloys were prepared by stir casting, using Al-4.2Mg-0.6Mn metal and three master alloys (Al-10wt. %Mg, Al-2wt. %Sc and Al-5wt. %Zr) as shown in the Fig. 2(a)-(c), that were melted in alumina crucible and then poured into a metal mould, the casting process as shown in the Fig.3 (a)-(d). The final temperature of the melt was always maintained at 1000±15°C with the help of the electronic controller. Then the melt was homogenized under stirring at 900°C. Casting was done in cast iron metal mould preheated to 200°C [10-12]. Mould size is 150mm x 150mm x 6mm, then cold-rolled to 5 mm thick sheets. All the alloys were analyzed by spectrochemical methods simultaneously. The chemical compositions of the alloys are given in Table 1. Subsequently, specimens measuring 15 mm in square were prepared for hardness test (Fig. 4b), corrosion test (Fig. 5b), x-ray diffraction, optical and scanning electron microscope characterization.

Fig. 2 Master alloys (a) Al-10wt. % Mg (b) Al-2wt. % Sc (c) Al-5wt. % Zr

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Fig. 3 shows the fabrication process (a) Electrical Resistance Furnace (b) Pouring molten mixture into the preheated permanent mould (c) Al-Mg-Mn-Sc-Zr ascast plate (d) Cold rolling of plate.

Table 1 Composition of Modified Al-Mg-Mn Alloy

Alloy type	Mg	Mn	Si	Cr	Zn	Ni	Li	Sc	Zr	Balance
Specimen-1	4.2	0.6	0.17	0.10	0.06	0.006	0.001	-	-	Al
Specimen-2	4.2	0.6	0.17	0.10	0.06	0.006	0.001	0.2	0.1	Al
Specimen-3	4.2	0.6	0.17	0.10	0.06	0.006	0.001	0.4	0.1	Al
Specimen-4	4.2	0.6	0.17	0.10	0.06	0.006	0.001	0.6	0.1	Al

All the specimens were polished with SiC paper and final polish with diamond paste on disc polishing machine. All the polished specimens were cleansed with acetone for microstructural studies [13].

3. EXPERIMENTAL PROCEDURE

3.1 Vickers micro hardness measurement

Hardness of the specimens was measured using a Vickers microhardness tester (Fig. 4(a)) and specimens of all four compositions (Fig. 4(b)) with 200 gf load and a dwell time of 15s. Average of five readings were measured and presented.

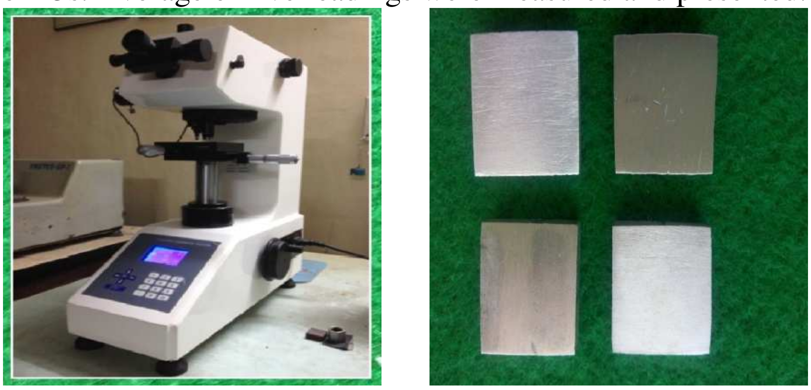

Fig. 4 shows the (a) Vickers's digital microhardness tester (b) specimens for hardness test

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The surface morphology of the specimens before and after corrosion was examined with an optical microscope and scanning electron microscope. Micro analytical studies were conducted by SEM-EDS.

3.3 *X-Ray diffraction Analysis*

X-ray diffraction analysis was carried out to find the presences of different elements in the Al-Mg-Mn-Sc-Zr alloys. It was carried out by X-Ray diffractometer.

3.4 *Corrosion Measurements*

The corrosion measurements were made according to ASTM G5-87 standards in 3.5 % NaCl solution [14]. Fig.5 (a) and (b) shows the corrosion setup and specimens respectively.

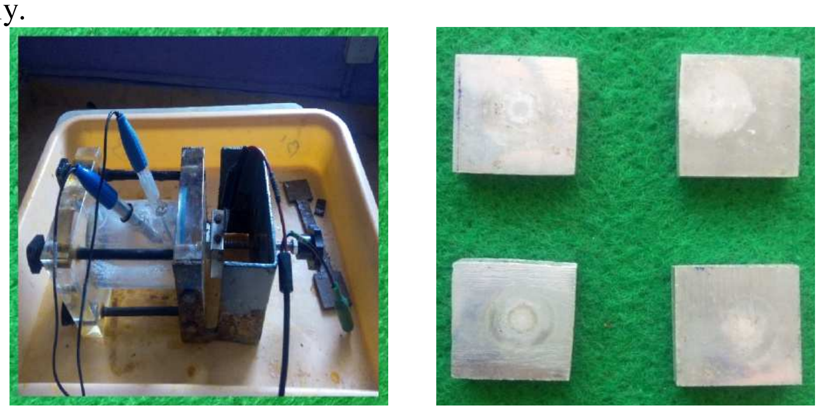

Fig. 5 (a) Corrosion test setup (b) specimens after corrosion test

4. RESULTS AND DISCUSSION

4.1 *Effect of Sc and Zr additions on Hardness*

The influence of Sc and Zr additions on hardness of the Al-Mg-Mn wt. % base alloy is presented in Fig. 6, which reveals significant effect of Sc and Zr additions upon the hardness of the alloy. This indicates that contribution of Sc and Zr in solid solution strengthening was significant.

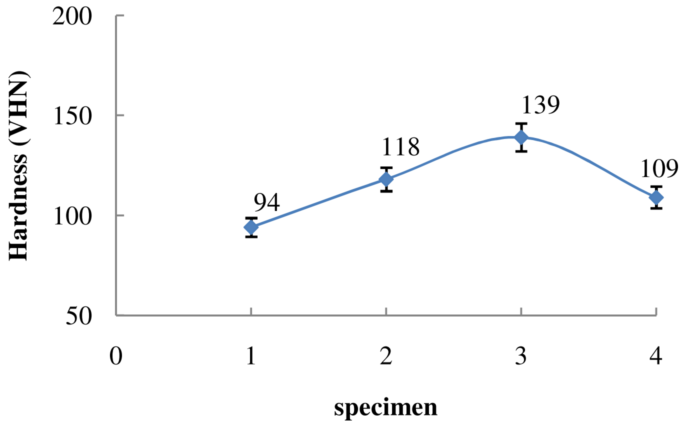

Fig. 6 Vickers hardness measured from specimen-1 to specimen-4.

The hardness of alloys was increased by Sc and Zr additions; however, this effect was significant up to 0.4 wt. % Sc and 0.1wt. % Zr i.e., specimen-3. This gradual increase of hardness was caused by the addition of Sc and Zr apparently, which would have promoted the formation and the dispersion of $Al_3Sc_{1-x}Zr_x$ with the increase of Sc wt. % [15]. The addition of 0.6 wt. % Sc and 0.1 wt. % Zr i.e., specimen-4 lead to a decrease in average hardness by ~15 $HV_{0.2}$ [16].

The Journal of Corrosion Science and Engineering
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4.2 Effect of Sc and Zr additions on Microstructure

The effect of varying amounts of Sc on the phases present in Al-Mg-Mn is presented in Fig. 6. The increasing Sc content leads to the formation of an $Al_3Sc_{1-x}Zr_x$ phase. The phase fraction of the $Al_3Sc_{1-x}Zr_x$ phase increased linearly with Sc content to a maximum of ~0.6 wt. %.

The microstructure of the alloys as investigated using optical microscope revealed that Sc addition altered the morphology of intermetallics (Fig. 7). Intermetallics appeared to be fragmented because of the Sc and Zr addition [17].

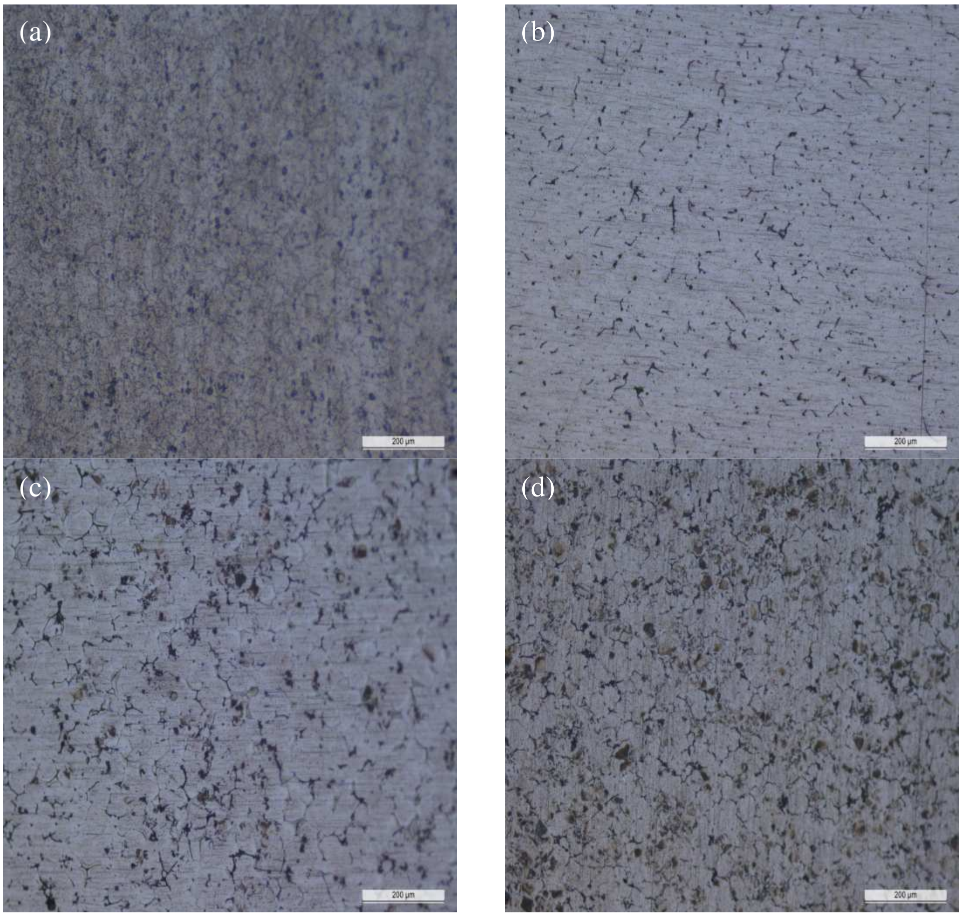

Fig. 7 OM image showing the surface of alloys before corrosion
(a) specimen-1, (b) specimen-2, (c) specimen-3, and (d) specimen-4 alloys.

A higher magnification SEM images of these alloys (specimen-3 to specimen-4) as presented in the Fig. 8 revealed the presence of uniformly distributed particles in Sc and Zr-containing alloys and it convenient to keep scandium and zirconium content levels upto specimen-3 and appearance of non dendrites primary intermatallics observed in the specimen-4 [18], which were not present in the specimen-1.

The Journal of Corrosion Science and Engineering
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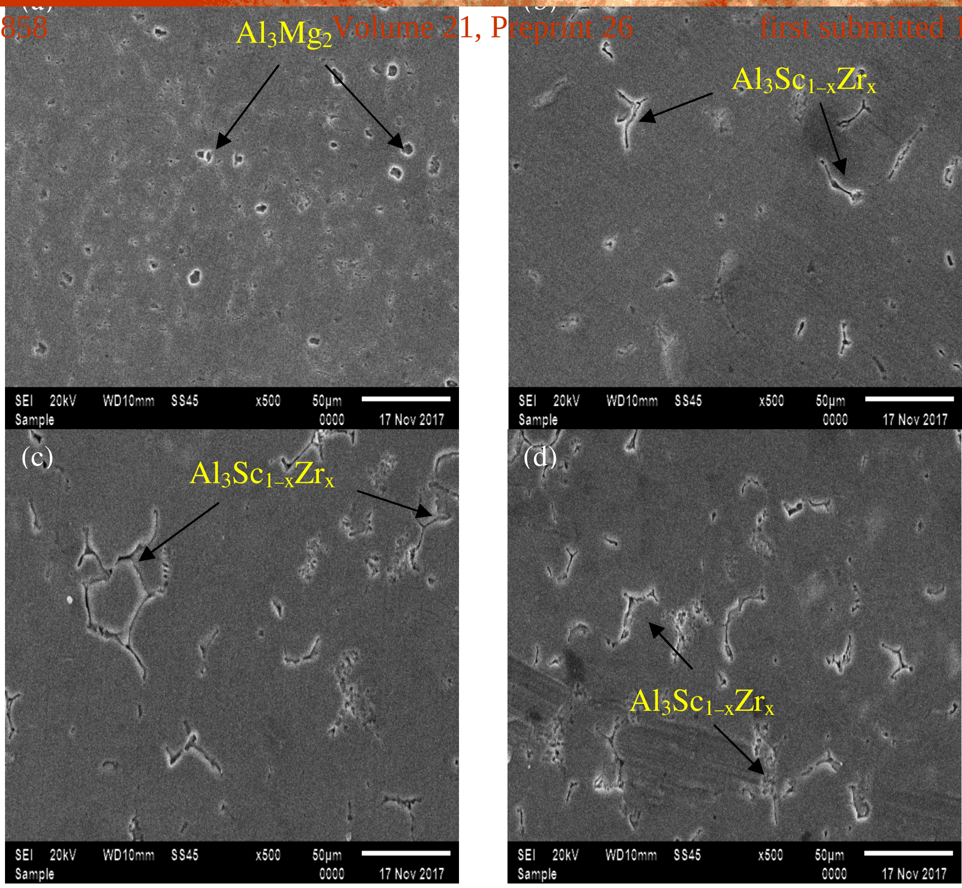

Fig. 8 SEM images showing the surface of alloys before corrosion *(a) specimen-1, (b) specimen-2, (c) specimen-3, and (d) specimen-4 alloys.*

Fig. 9 presents a high-magnification image of intermetallics and corresponding area map as collected using energy dispersive x-ray spectroscopy (EDS). Presence of Al, Mg and Mn elements observed in Fig.9(a), in addition to Al, Mg, Mn elements, Sc and Zr-containing intermetallic though its peaks not observed from Fig. 9(b)-(d), it is evident from EDS elemental analysis table 2 [19].

Table 2 SEM-EDS elemental analysis of Al-Mg-Mn-Sc-Zr Alloys

Element	**Weight %**			
	Specimen-1	**Specimen-2**	**Specimen-3**	**Specimen-4**
Al	94.87	94.28	94.43	94.49
Mg	4.51	4.73	4.47	4.25
Mn	0.62	0.69	0.60	0.56
Sc	-	0.20	0.40	0.60
Zr	-	0.10	0.10	0.10
Totals	100.00	100.00	100.00	100.00

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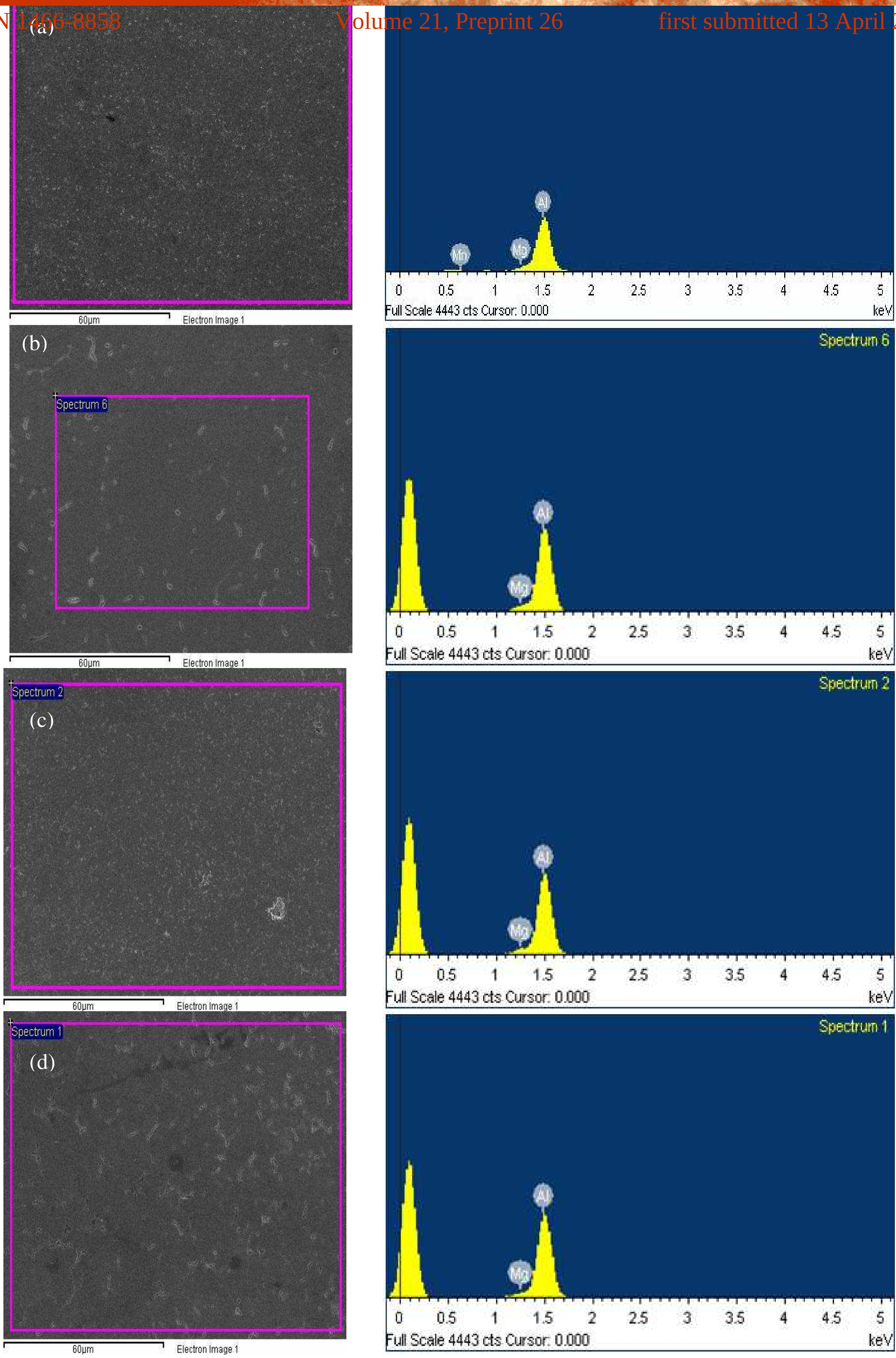

Fig. 9 SEM-EDS image showing the surface of alloys before corrosion
(a) specimen-1,(b) specimen-2,(c) specimen-3, and (d) specimen-4 alloys.

The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 21, Preprint 26 first submitted 13 April 2018

The XRD trace for Al-Mg-Mn-Sc-Zr alloys presented in Fig. 10 confirms the presence of Sc and Zr reinforcement with the Al-Mg-Mn matrix alloy. Sc and Zr containing peaks is observed to be increasing with increment of Sc and Zr content while the Al peak is decreasing [20].

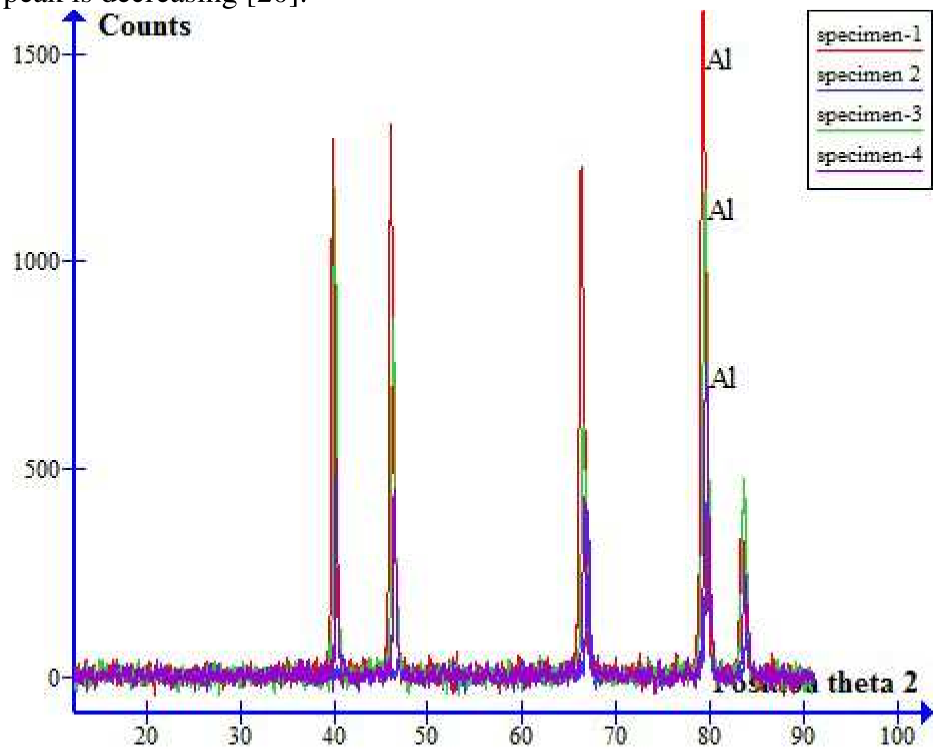

Fig. 10 XRD Patterns *(a) specimen-1,(b) specimen-2, (c) specimen-3, and (d) specimen-4 alloys.*

4.4 Effect of Sc and Zr on corrosion

The influence of Sc and Zr added Al-Mg-Mn alloy was studied for corrosion resistance. Fig.11 represents the polarization curves of the specimens which were aged for one hour in 3.5% NaCl solution [21]. The corrosion potential obtained from the polarization curves, are summarized in Table 3.

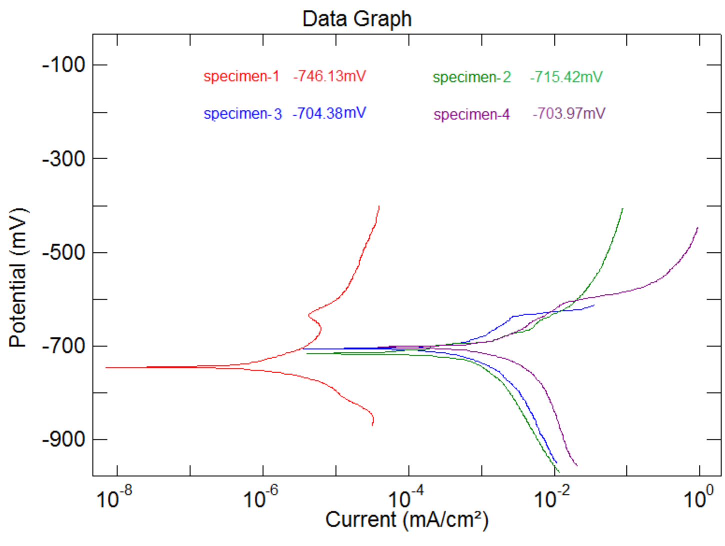

Fig.11 Polarization curves

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Specimen type	Ecorr (mv)
specimen-1	-746.13
specimen-2	-715.42
specimen-3	-704.38
specimen-4	-703.97

For corrosion resistance, the electrochemical behavior of the Sc and Zr added Al-Mg-Mn alloys with the Al-Mg-Mn alloy were compared. Anodic dissolution was experienced based on E_{corr} of Al-Mg-Mn alloy. In contrast to this, E_{corr} values in Sc and Zr added Al-Mg-Mn alloys, were experienced less anodic dissolution due to $Al_3Sc_{1-x}Zr_x$ phases [22].

As shown in table 3, the corrosion potential (E_{corr}) of specimen-4 is much lower than those of specimen-1 to specimen-3. Thus, the corrosion susceptibility of the alloys were ranked in the order from high to low as follows: specimen-1, specimen-2, specimen-3, and specimen-4.

Effect of Sc and Zr addition can be observed in the alloy specimens where corrosion damage was observed in the alloy without Sc and Zr (Fig. 12 (a)-(d)). This corrosion damage which was rarely observed in Sc and Zr-containing alloys [23]. SEM observations showed that corrosion occurring in the surrounding area of the Sc and Zr-containing intermetallic phases was minimal, in comparison to that of Al-Mg-Mn intermetallic (Fig. 12).

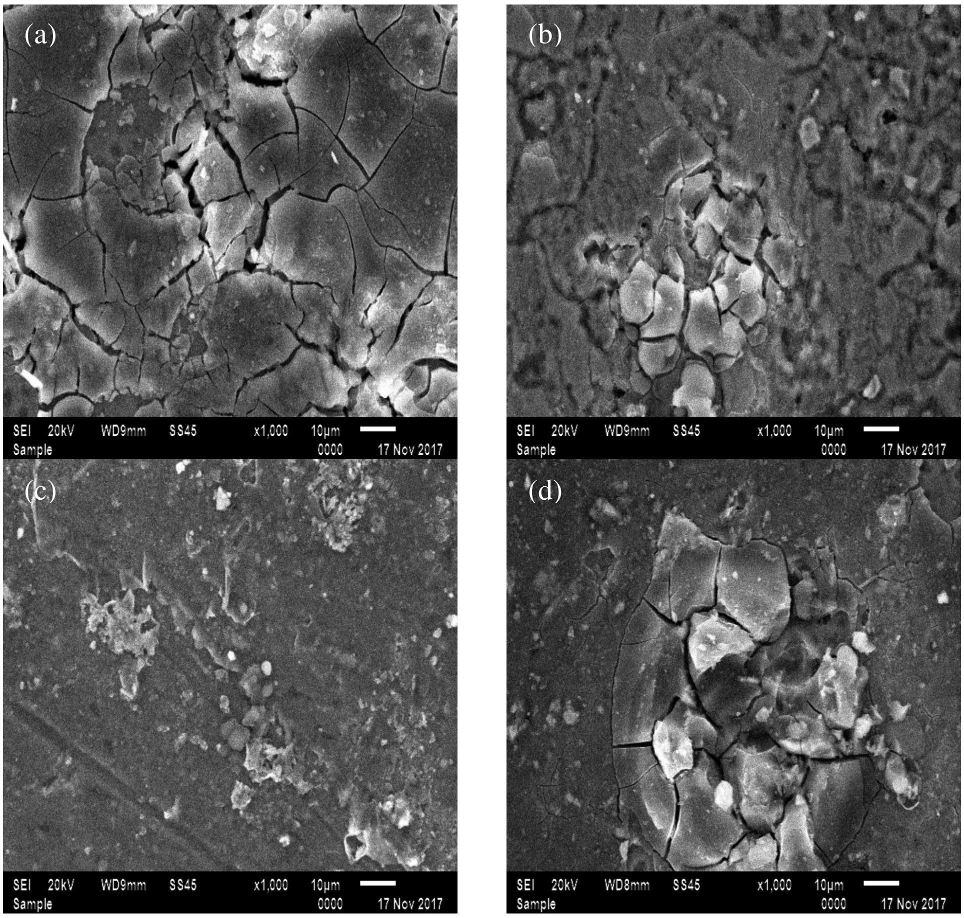

Fig. 12 SEM images of *Three-dimensional surfaces of as-rolled (a) specimen-1, (b) specimen-2, (c) specimen-3, and (d) specimen-4 alloys after corrosion.*

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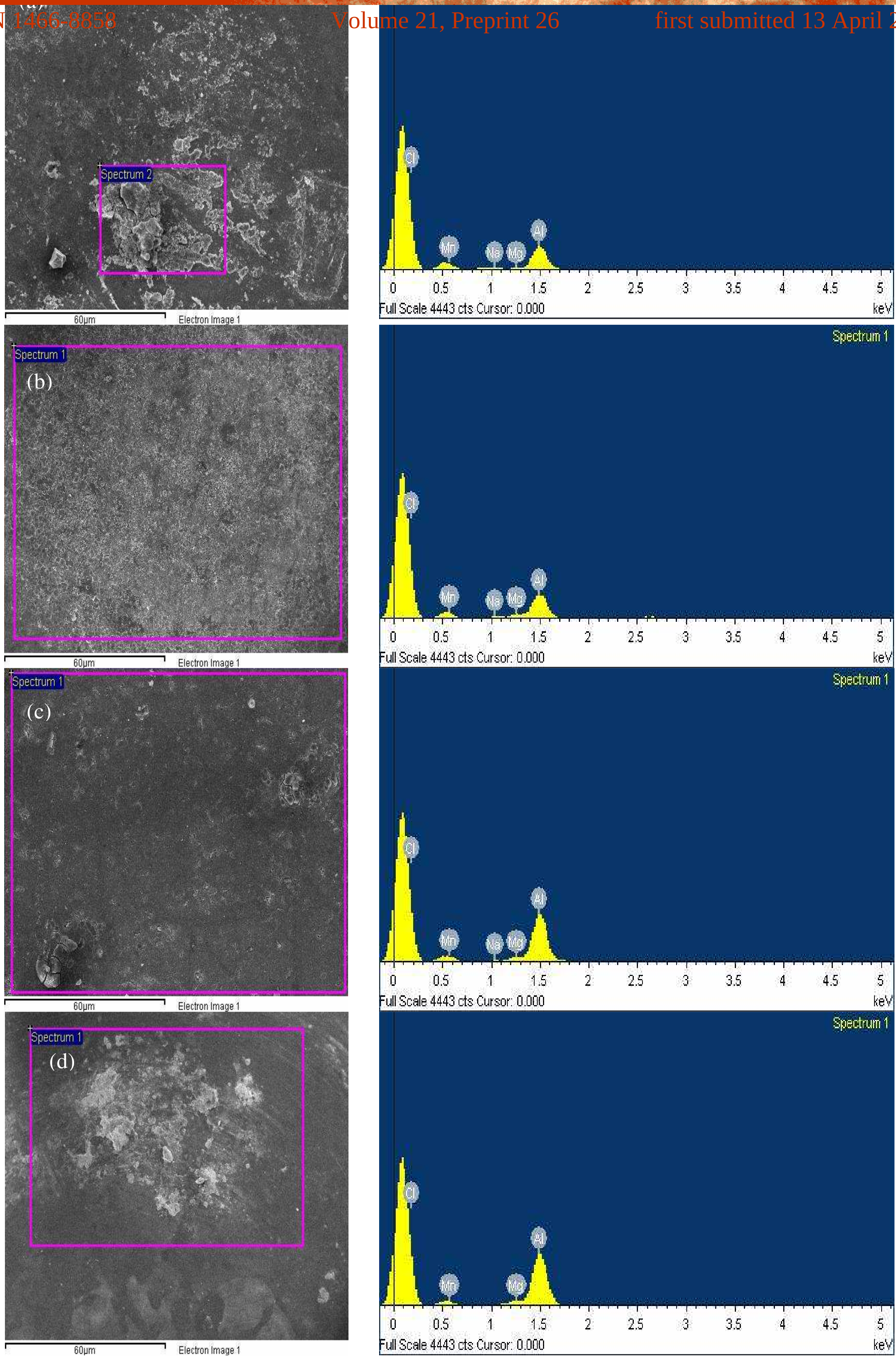

Fig. 13 SEM EDS images of *Three-dimensional surfaces of as-rolled (a) specimen-1, (b) specimen-2, (c) specimen-3, and (d) specimen-4 alloys after corrosion.*

ISSN 1466-8858 Volume 21, Preprint 26 first submitted 13 April 2018

elemental analysis using SEM EDS [23-24]. Therefore, the morphology of the surfaces and corrosion occurring around intermetallic phases after corrosion test were observed using SEM EDS (Fig. 13(a)-(d)). Table 5 shows the EDS elemental analysis of Al-Mg-Mn-Sc-Zr Alloys after corrosion.

Table 5 EDS elemental analysis of Al-Mg-Mn-Sc-Zr Alloys after corrosion

Element	Weight %			
	Specimen-1	**Specimen-2**	**Specimen-3**	**Specimen-4**
Al	92.66	82.19	73.71	86.85
Mg	6.70	4.57	11.16	6.56
Mn	0.64	1.27	1.55	1.73
Sc	-	1.38	1.86	1.39
Zr	-	0.56	0.67	0.13
Na	-	5.93	6.21	2.25
Cl	-	4.11	4.83	1.10
Totals	100.00	100.00	100.00	100.00

3 Conclusions

On the basis of the results obtained from the investigations, the following are the main conclusions:

i. Al-Mg-Mn-Sc-Zr alloys were successfully fabricated by stir casting technique.
ii. Minor additions of 0.2 - 0.6 wt. % scandium and 0.1wt. % Zr introduces a relatively high level of strength in Al-Mg-Mn as shown by the improvement in hardness.
iii. Vickers hardness measurement shows a gradual increase of hardness was observed with its peak at specimen-3, and then decreased afterwards.
iv. Microstructural and characterisation of Al-Mg-Mn–Sc–Zr alloy confirmed the appearances of Al3Sc and spherical Al3Sc1−xZrx particles and their growth in association with minor additions of 0.2 - 0.6 wt. % scandium and 0.1wt. % Zr.
v. Scandium (0.2–0.6 wt. %) and Zirconium (0.1wt.%) addition introduce an appreciable increase in the corrosion resistance of Al-Mg-Mn alloys.

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