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Scientific paper
UDC:620.193.4:669.721.5

Corrosion of friction welded areas of Mg-Mg, Mg-AZ91D Mg alloy and AZ91D-AZ91D Mg alloy in carbonate solutions

Studies on the corrosion of welded areas of friction welded magnesium and its alloy AZ91D are done in view of their applications as structural materials in automotive and aerospace engineering. Friction welding of magnesium-magnesium, magnesium-AZ91D alloy and AZ91D alloy-AZ91D alloy is carried out at the welding speed of 600 RPM which produced a burn length of 2 mm. Corrosion of this welded area is studied using E-log I polarization in 0.1 M ammonium carbonate solution. It is found that the welded areas are more corrosion resistant than their respective parent samples under similar experimental conditions. Scanning electron microscopic images confirm the grain refinement of welded zones. For better understanding, E-log I polarization studies of pure magnesium and its alloy are also done.

Key words: *friction welding; magnesium; AZ91D alloy; E-log I polarization; welded zones; corrosion*

1. INTRODUCTION

Magnesium is a metal with the lightest weight among all the structural materials. It and its alloy have many traits in application, including high specific strength and stiffness, low elastic modulus, excellent damping capacity, stronger vibration load resistance, fine processing or machinability, little dimensional change, etc. Its highest advantage is sought in marine applications. Mg is a highly active metal, commonly used for the cathodic protection of other less active metals. Magnesium and its alloys are increasingly used in aerospace and automotive applications because of their ultra lightness and high strength to weight ratio with a density that is two thirds of aluminum and one fourth of iron [1].

More than half of the annual production of magnesium is used as an irreplaceable alloying addition in aluminum alloys and nodular cast iron. The remainder is used mainly as castings in the aerospace and general transport industries, with some wrought products in specialized applications. In these engineering applications, magnesium is rarely used in unalloyed form. Because of their high strength/weight ratios, magnesium alloys are of particular interest to the aerospace and transport industries and these industries have provided great stimulus to the develop ment of magnesium alloys over the last 40 years. For example, thorium-containing alloys have found applications in missiles and spacecraft. Magnesium alloys provide promising alternatives to aluminum alloys for the manufacture of cast automotive components and there has been increased use in automobile production during the last few years of new corrosion resistant alloys with higher ductility. For instance, die cast magnesium components have been used for applications such as clutch housings, gear boxes, pedal brackets, instrument panel frames, integral seat frames and wheel hub cover components. One of the largest applications of magnesium alloys was in the Volkswagen engine where the magnesium alloy components performed very well. This could be attributable to a combination of good design which shielded the components from road splash, the engine heat keeping everything dry, and a nature film of oil and grease accumulating and excluding water [2].

In most of the structural applications, magnesium/ /alloy has to be welded to make components of specific design and orientation. One such useful technique is friction welding. Friction welding is a solid-state welding processes that generates heat through mechanical friction between a moving workpiece and a stationary component, with the addition of a lateral force called "upset" to plastically displace and fuse the materials. Technically, because no melt occurs, friction welding is not actually a welding process in the traditional sense, but a forging technique. However, due to the similarities between these techniques and traditional welding, the term has become common. Friction welding is used with metals and ther-

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moplastics in a wide variety of aviation and automotive applications.

The combination of fast joining times of the order of a few seconds, and the direct heat input at the weld interface, gives rise to relatively small heat affected zones. Another advantage of friction welding is that it allows dissimilar materials to be joined. This is particularly useful in the aerospace field, where it is used to join lightweight aluminum stock to high-strength steels. Normally the wide difference in melting points of the two materials would make it impossible to weld using traditional techniques, and would require some sort of mechanical connection instead (bolts, etc.). Friction welding provides a "full strength" bond with no additional weight. Another common use for these sorts of bi-metal joins is in the nuclear industry, where copper-steel joints are common in the reactor cooling systems.

In view of the utility of magnesium/alloy in automative and aeropace engineering, studies pretaining to the corrosion resistance of the friction welded areas is of fundamental as well as technological interest. Previous literature on this topic is virtually non-existent. In the present work, friction welding of two work pieces such as magnesium-magnesium, magnesium-AZ91D magnesium alloy and AZ91D magnesium alloy- AZ91D magnesium alloy and their corrosion behavior in ammonium carbonate solutions was carried out. E-log I polarization studies are done to study the corrosion behavior and micro structural analysis are carried out by SEM and optical microscopy.

2. EXPERIMENTAL PART

2.1. Friction welding

Friction welding was performed in 15 ton capacity ETA make machine. Welding parameters are: friction pressure, 45 MPa; upsetting pressure, 90 MP ; welding speed 600 rpm; burn of length, 2 mm. 15 mm (diameter) X 60 mm (length) samples were machined from commercial ingot for the same study. Prior to welding, all the samples were thoroughly cleaned by acetone. After welding, flash was removed and the welded samples were cut into half vertically for further studies and characterization.

2.2. Instrumentation

All electrochemical experiments were conducted with a PGSTAT 302 Autolab system (Ecochemie, Utrecht, The Netherlands). It was connected to a PC running with Eco-Chemie GPES. The reference electrode was Ag/AgCl (3M KCl) and the counter electrode was a platinum foil supplied along with the instrument. The electrodes were arranged in a flat cell (Wear and Friction Tech, Chennai) such that 0.37 cm^2 area of the working electrode (sample) was exposed to the electrolytic medium.

SEM analysis was done using scanning electron microscope, TESCAN Vega equipped with an Econ 4 detector. Varian make atomic absorption spectrometer (AAS) was used to do the AAS analysis of alloy sample. Microstructural analysis by optical microscopy of welded AZ91D alloy and parent metal and alloy samples were carried out after sample preparation and etching with picric acid, ethanol and acidic acid mixture solution. Same samples were used for SEM analysis also.

3. RESULTS AND DISUCSSION

3.1. Material characterization

AZ91D magnesium alloy was analysed for its composition by AAS. The composition determined was as follows: Al, 8.67; Zn 0.89; Mn, 0.1; Si, 0.09; Mg, 90.25.

3.2. SEM analysis

SEM images of magnesium metal before and after corrosion are shown in Fig. 1A and B respectively. In Fig 1 A, the grain sizes of the metal are from 50-100 µm. The grain boundaries are clearly visible from the half white specks around the much darker grains. SEM image of corroded surface confirms the occurrence of corrosion at the grain boundaries indicated by the white precipitate thereof and bulk precipitate at some spots.

Fig. 2 A and B shows the SEM images of AZ91D cast alloy before and after corrosion respectively. Large irregular shaped grains are due to the magnesium solid solution. Much smaller white particles distributed at random are of β-$Mg_{17}Al_{12}$; the darker phase appearing in between the alpha phase magnesium is the mixed phase of both α and β [3-5]. After corrosion, the surface has corrosion products precipitated in the form of needles that could be clearly seen in Fig. 2B. Here the grains boundaries also show the corrosion precipitate at their edges but the needle shaped corrosion product suggest the uniform dissolution of the alloy followed by the precipitation.

SEM images of welded areas of magnesium-magnesium and magnesium-AZ91D alloy were shown in Fig. 3 A and B respectively. The morphology of the welded area of magnesium-magnesium resembles that of pure magnesium as in Fig. 1A. Quite interestingly, the morphology of the welded area of magnesium-alloy sample (Fig. 3B) shows the joining of two specimens very clearly; the metallic and alloy phases were distinctly visible along with their adherence at the welded zone.

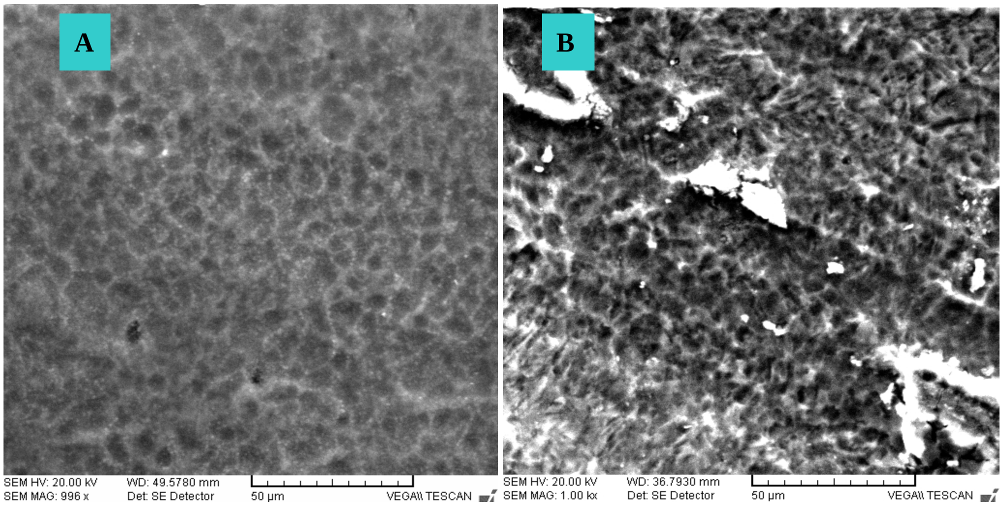

Figure 1. SEM images of magnesium metal (A) before corrosion (B) after corrosion

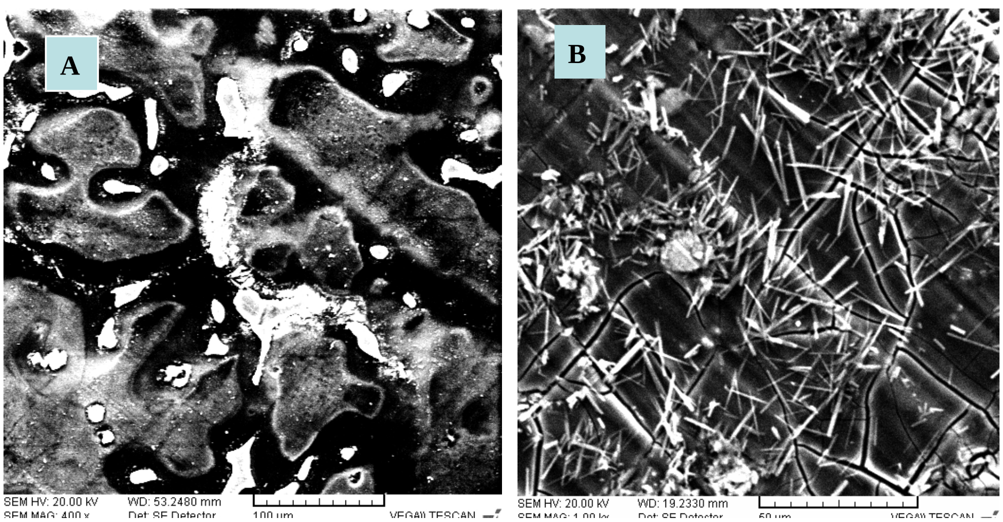

Figure 2. SEM images of AZ91D magnesium alloy (A) before corrosion (B) after corrosion

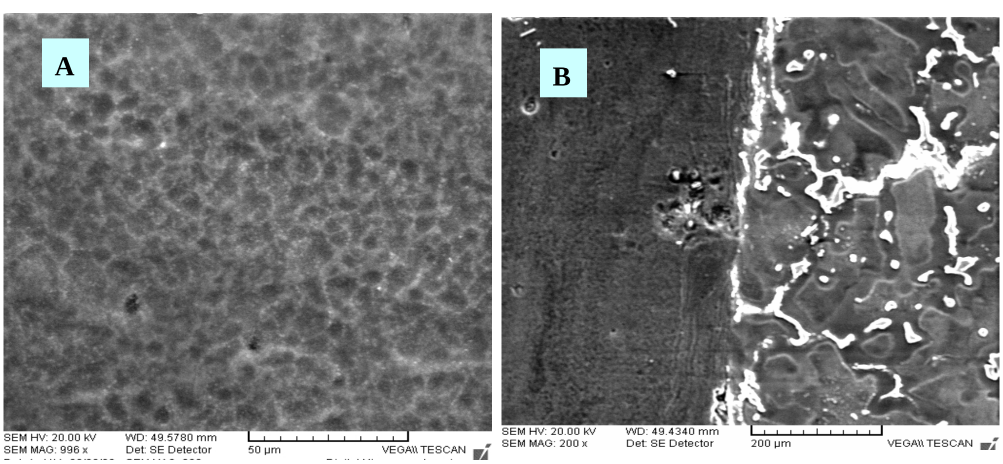

Figure 3. SEM images of welded zones of (A) pure magnesium-magnesium (B) pure magnesium- AZ91D magnesium alloy before corrosion

Fig. 4 A and B shows the optical and SEM microscopes of welded area of alloy-alloy sample. The optical image shows finely tuned grains with well defined grain boundaries. SEM image of the same sample shows a different morphology than that of pure alloy (cf. Fig. 2A). The distinction of α and β phases as (in the alloy) disappeared and the β phase appears as white dots distributed as clusters over the dark back ground of mixed phase.

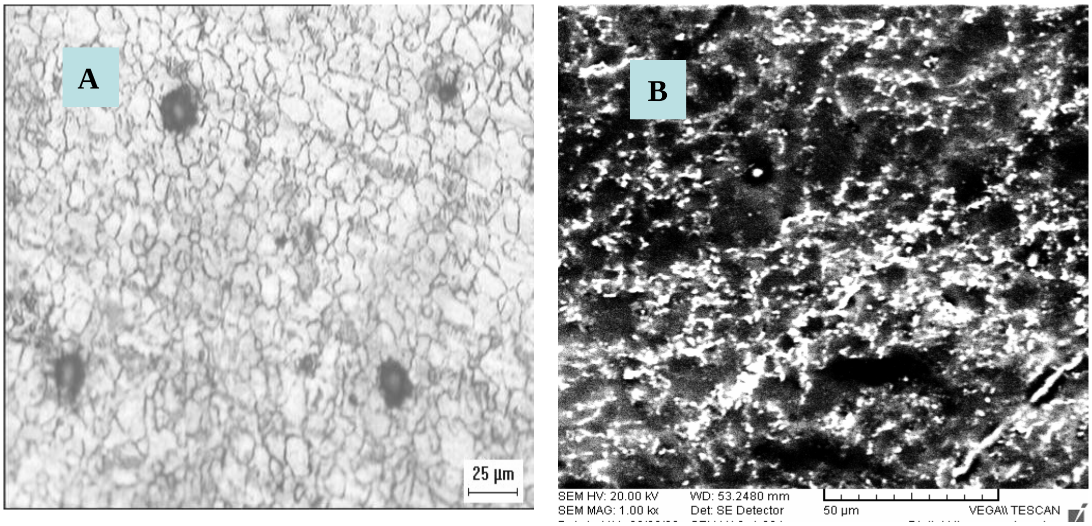

Figure 4. (A) Optical image of welded zones of AZ91D magnesium alloy- AZ91D magnesium alloy (B) SEM image of welded zone of AZ91D magnesium alloy- AZ91D magnesium alloy before corrosion

3.3 E-log I polarization studies

Prior to the presentation of E-log I polarization curves for the welded areas of magnesium-magnesium, magnesium-AZ91D magnesium alloy and AZ91D magnesium alloy- AZ91D magnesium alloy, the corrosion behavior of individual parent metal /alloy has to be studied for better understanding of the corrosion of welded regions which involve both pure metal and alloy. Comparison of corrosion potentials of parent metal and welded area under identical experimental conditions helps to evaluate the corrosion resistance of welded zones; in other words, corrosion potential of Mg/alloy serves as a reference scale.

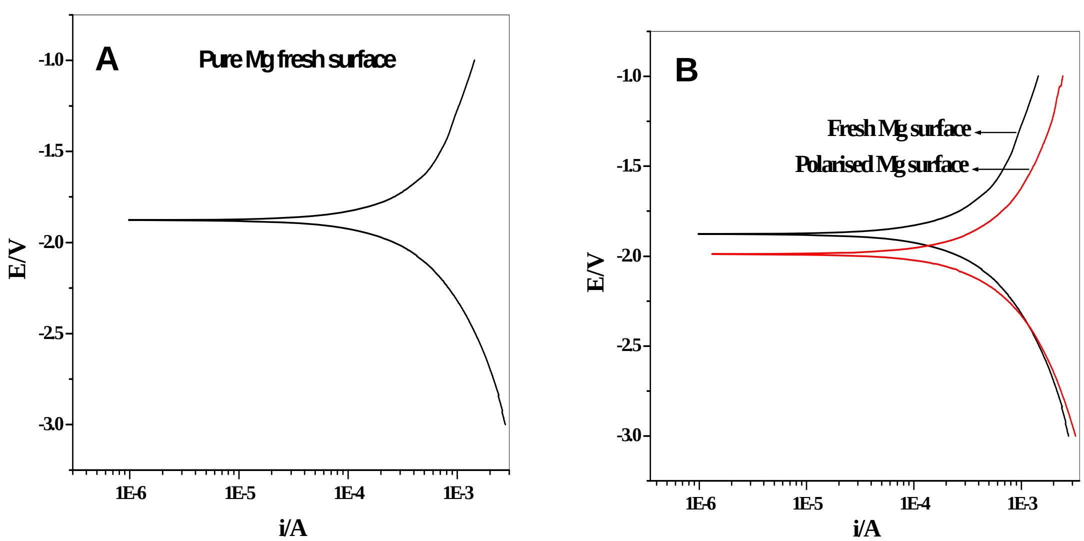

Figure 5. E-log I polarization curves for (A) magnesium fresh surface (B) polarized magnesium surface in 0.1 M ammonium carbonate solution (scan rate = 0.1 Vs^{-1})

Fig. 5A shows the E-log I polarization curve of freshly polished Mg surface in 0.1 M ammonium carbonate solution recorded at the scan rate of 100 mVs^{-1}. After a few scans, the potentiodynamic curve was recorded; the polarized curve was shown in Fig. 5B. For a virgin magnesium surface, the corrosion potential was -1.88 V while for the polarized surface, the corrosion potential was -1.99 V. The shift in potential for the polarized sample in the negative direction is due to the formation of passive film on the surface of the electrode. In the carbonate solution, the following reactions takesplace:

$$Mg \rightarrow Mg^{2+} + 2e \text{ (anodic reaction)} \quad (1)$$

$$2H_2O + 2e \rightarrow H_2 + 2OH^- \text{ (cathodic reaction)} \quad (2)$$

$$Mg + 2H_2O \rightarrow Mg(OH)_2 \quad (3)$$

$$Mg + CO_3 \rightarrow MgCO_3 \quad (4)$$

Table 1 shows the corrosion currents and potentials calculated from the polarization curves. Composition of corrosion products on magnesium vary from one location to another and from indoor to outdoor exposure. X-ray diffraction analysis of corrosion products scraped from magnesium ingots after 18 months of exposure in rural atmosphere have shown the presence of various hydrated carbonates of magnesium, including $MgCO_3.H_2O$, $MgCO_3.5H_2O$ and $3MgCO_3.Mg(OH)_2.3H_2O$. These analyses indicate that the primary reaction in corrosion of magnesium is the formation of magnesium hydroxide, followed by a secondary reaction with carbonic acid to convert the hydroxide to a hydrated carbonate [5].

Table 1. Parameters derived from the E-log I polarization curves for the metal, alloy, weld samples

S. No.	Specimen	E_{corr} (V)	I_{corr} (x 10^{-4} A/cm^2)
1	Magnesium -fresh surface	-1.874	3.03
2	Magnesium - polarized surface	-1.999	3.21
3	Magnesium -cast	-1.804	3.91
4	Mg-Mg welded area	-1.477	2.20
5	AZ91D alloy	-1.378	1.47
6	AZ91D - Mg welded area	-1.338	1.77
7	AZ91D - AZ91D welded area	-1.329	2.10

Fig. 6A shows the E-Log I polarization curves for the untreated magnesium (commercial grade) and cast magnesium. Cast Mg is the one melted in an induction furnace, poured in a steel crucible and cooled down by natural process to room temperature. The corrosion potential of cast Mg was -1.804 V which is more positive than that of pure untreated Mg (-1. 87 V). This result indicates that the heat treated Mg or the cast Mg is more resistant to corrosion in ammonium carbonate solutions than the untreated one. It is expected as heat treatment induces larger cathodic grains and lesser anodic grain boundaries.

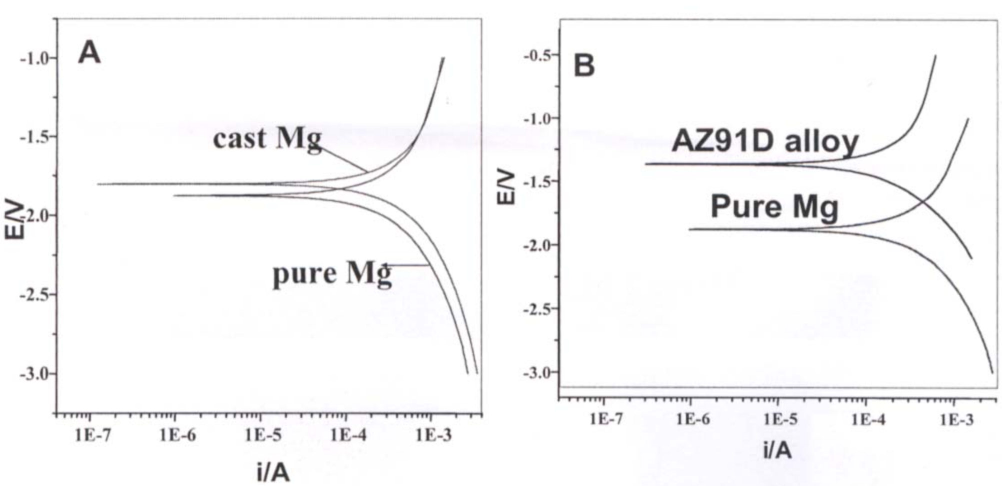

Figure 6. E-log I polarization curves for (A) pure and cast magnesium (B) pure magnesium and AZ91D magnesium alloy in surface in 0.1 M ammonium carbonate solution (scan rate = 0.1 Vs^{-1})

AZ91 is an alloy normally containing 9% Al and 1% Zn. AZ91D is the fourth alloy of its series. It is well known that alloying reduces the corrosion of pure metals. Fig. 6B shows the E-Log I polarization curves for the pure magnesium metal and AZ91D magnesium alloy recorded under similar experimental conditions. Table 1 shows the parameters derived from the curve. The alloy shows better corrosion resistance, indicated by the corrosion potential at -1.365 V, corresponding to a positive shift of 510 mV. The corrosion morphology of magnesium and its alloys differs and depends on the alloy chemistry and environmental conditions. Pure magnesium is known to undergo transgranular corrosion while the attack on the alloys is more uniform [6].

Two pieces of magnesium were friction welded to a burn length of 2 mm and this specific area was exposed to the electrolyte in a flat cell and potentiodymanic polarization was carried out at the scan rate of 0. 1 Vs^{-1}. Three subsequent scans were recorded. Fig. 7 shows the results. The welded area showed corrosion potential of -1.477 V; this value suggests the fact that the metal-metal welded zone has higher corrosion resistivity than pure metal (-1.8 V). This is expected as the welded zone undergoes heat treatment during the friction welding process, which changes the microstructure of the metal in-situ, thereby tending to be more corrosion resistant. Also the subsequently recorded scans did not differ much from the first one unlike pure magnesium (cf. Fig. 5B) which is a measure of stable surface.

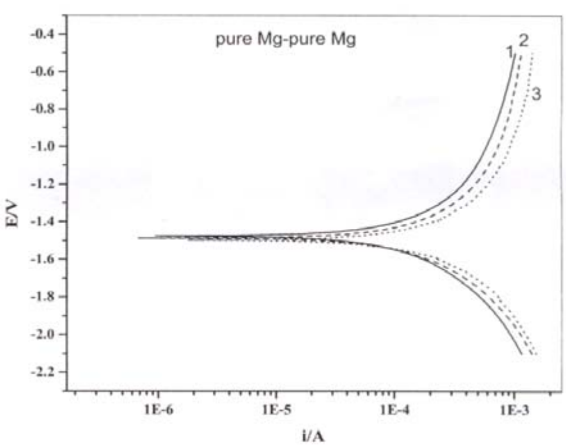

Figure 7. E-log I polarization curves for the welded area of magnesium - magnesium sample in 0.1 M ammonium carbonate solution (scan rate = 0.1 Vs^{-1}); 1,2,3 denote the successive scans recorded

Fig. 8 shows the E-log I polarization curves recorded for the welded area of magnesium metal-AZ91D alloy in three successive scans. The corrosion potential was -1.338 V. In this case, one working piece was pure metal and another was the alloy. On joining the two by friction welding, the welded area is expected to reflect the characteristics of both work pieces. Interestingly, the corrosion potential noted reflects the characteristics of the alloy rather than the pure metal (cf. Table 1). In fact, it was 40 mV more positive than that of the parent alloy. It shows the combined result of welding effect and alloying benefit.

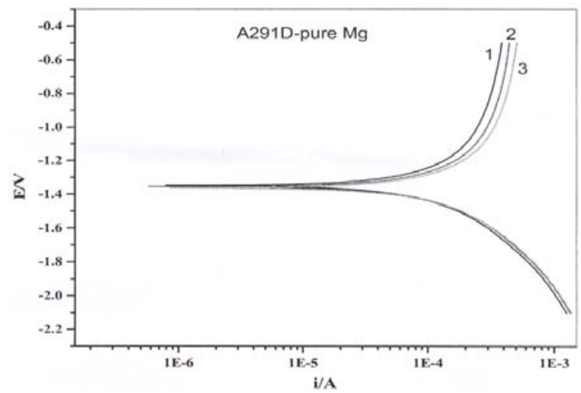

Figure 8. E-log I polarization curves for the welded area of AZ91D alloy -magnesium sample in 0.1 M ammonium carbonate solution (scan rate = 0.1 Vs^{-1}); 1,2,3 denote the successive scans recorded

Two pieces of alloy joined by friction welding was also subjected to potentiodynamic polarization in 0.1 M ammonium carbonate solution (Fig. 9). The corrosion potential of the welded area was -1.329 V; this potential is ~50 mV more positive than that of parent alloy. Significantly, there is no marginal difference in the corrosion potentials of welded areas of Mg-Mg and Mg-alloy samples.

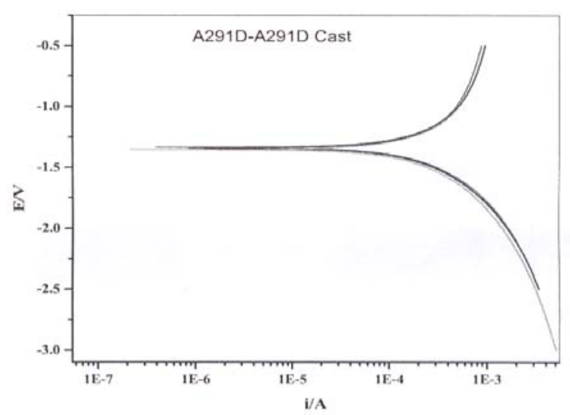

Figure 9. E-log I polarization curves for the welded area of cast AZ91D alloy - AZ91D alloy sample in 0.1 M ammonium carbonate solution (scan rate = 0.1 Vs^{-1})

4. CONCLUSIONS

Studies on the **c**orrosion resistivity of friction welded zones of magnesium-magnesium, magnesium-AZ91D alloy and AZ91D alloy-AZ91D alloy in ammonium carbonate solutions reveals the following facts:

- Friction welded area of magnesium-magnesium sample was more resistant to corrosion than the parent metal
- AZ91D alloy was also more corrosion resistant than the parent magnesium metal
- Friction welded areas of magnesium-alloy and alloy-alloy were significantly resistive to corrosion than their parent samples
- Morphology of welded zones of magnesium-magnesium and magnesium-alloy did not differ much from the parent samples but that of alloy-alloy showed a noticeable change in grain refinement.

REFERENCES

[1] Y. Kojima, *Mater. Sci. Forum* 350 (2000) 3

[2] S. Schumann, F. Friedrich, “The Use of Magnesium in Cars- Today and in the Future,” *Magnesium alloys and their Applications*, ed. B. L. Mordike and K. U. Kainer, (Frankfort, Germany: Werkstoff-Informationsgesel-schaft mbH, 1998), 3-13

[3] A.H. Feng, Z.Y. Ma, *Scripta Materialia,* 56 (2007) 397

[4] Y. Wang , G. Liu, Z. Fan, *Acta Materialia,* 54 (2006) 689

[5] D. Q. Sun, D. X. Sun, S. Q. Yin, J. B. Li, *ISIJ International*, 46 (2006)1200

[6] G. L. Makar, J. Kruger, *Int. Mat. Rev*. 38 (1993) 138

[7] G. L. Makar, J. Kruger, A. Joshi, in *Advances in Magnesium Alloys and Composites* (Eds. H. G. Paris, W. H. Hunt), International Magnesium association and the Non-Ferrrous Metals Committee, TMS, Phoenix, Arizona, January 26, 1998, pp. 105