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Effect of V Content on Corrosion Behavior of Al-V Alloys Produced by Mechanical Alloying and Subsequent Spark Plasma Sintering

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Al-V alloys produced via high-energy ball milling have been reported to show simultaneous improvement of corrosion resistance and mechanical properties compared to traditional Al alloys. In these alloys, V content plays a crucial role in increasing or decreasing the corrosion resistance. Therefore, the effect of V and microstructure on corrosion of high-energy ball milled and subsequently spark plasma sintered Al-xV alloys ($x = 2, 5, 10$ at%) has been studied. Cyclic potentiodynamic polarization tests and electrochemical impedance spectroscopic analysis revealed the increment of V content up to 5 at% enhanced the corrosion resistance of the alloy. However, highly heterogeneous microstructure in Al-10 at%V resulted in significant localized corrosion over the immersion time. The electrochemical impedance spectroscopy studies over 14 days of immersion revealed underlying corrosion mechanisms.

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Climate change and rising global temperatures due to greenhouse gas emissions are among the most critical concerns the world is facing in the 21st century. Since transportation is the primary greenhouse emission economic sector, researchers worldwide have focused on various solutions to reduce vehicle fuel consumption. Among the different possibilities, developing lightweight Al alloys, which can be long-lasting for years, is one of the viable solutions. However, Al alloys manufactured by traditional techniques such as casting show a tradeoff between corrosion and mechanical properties, restricting their application and longevity in many industries. Recent research has shown that the corrosion and mechanical performance of Al alloys can be optimized by suitable processing routes along with a specific composition. For example, nanocrystalline Al alloys produced by non-conventional techniques such as sputter deposition,^{1–7} ion implantation,^{8–12} and high energy ball milling (HEBM)^{13–18} exhibit excellent corrosion resistance. Among these techniques, HEBM has received significant attention because it is simple, economical, and capable of application in industrial production.

High-energy ball milling, widely known as mechanical alloying, is one of the production techniques that can be used to attain unique microstructural features such as grain refinement, extended solid solubility, and the uniform dispersion of alloying elements.^{15,19–22} Such microstructures significantly increased hardness,^{13–16,23,24} elastic modulus,^{25,26} and corrosion resistance.^{13,16–18,27–29} In addition, the excellent dispersion capability of various elements in HEBM led to feedstock modification for additive manufacturing applications.^{30–32}

In recent years, the corrosion behavior of HEBM Al alloys has been studied. For example, Esquivel et al. investigated the corrosion behavior of HEBM subsequently cold compacted binary Al-M (M-Cr, Mo, Ni, Ti, Mn, V, Nb) alloys.^{13,14} The extended solid solubility of alloying elements resulted in simultaneous corrosion resistance

and hardness enhancement. In addition, the formation of the nanocrystalline structure further contributed to improving the hardness of these Al-M alloys. Since HEBM Al-M alloys impart the grain refinement and extended solid solubility of the alloying element via gaining access energy during the ball milling, most of these alloys are in a metastable state. Therefore, they tend to decompose to a thermodynamically stable state upon adding excessive energy. Thus, choosing an appropriate alloying element to produce Al alloys using HEBM is crucial. Interestingly, the thermal stability and age-hardening properties of Al-V alloys were substantially higher as the diffusion coefficient of V in Al is extremely low, which can retain solid solution even at elevated temperatures such as 400 °C.³³ Besides, Al-5at %V exhibited excellent age-hardening characteristics as the hardness increased from 271 to 319 HV after heat treatment at 200 °C. Since Al-V alloys showed outstanding improvements in corrosion and mechanical properties compared to other Al-M alloys, the Al-V alloys have been investigated further.

The effect of milling parameters and V content on the microstructural evolution has been discussed previously.³⁴ Interestingly, the milling at 350 RPM for 100 h led to the formation of in situ consolidated specimens in Al-2V. The corrosion behavior of these in situ consolidated Al-2V alloys has been intensively studied, and the following mechanisms have been proposed for improved corrosion resistance:²⁷

- (1) Deposition of V on cathodic sites present inside the pits leads to the reduction of cathodic kinetics
- (2) Enrichment of V underneath the passive film, which reduces further dissolution of the substrate
- (3) Incorporation of V into the passive film improves the passive film stability

Even though this study presented the corrosion mechanisms for Al-2V alloys, the formation of various phases in HEBMed Al-V highly depends on the V content in the alloy and the post-consolidation technique.^{23,34} For instance, Christudasjustus et al.

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investigated the effect of spark plasma sintered (SPS) temperature on microstructure, hardness, and elastic modulus of Al-xV alloys ($x = 2, 5, 10$ at%). They showed that the SPS at 400 °C led to the porosity reduction.²⁵ Meanwhile, the decomposition of the super-saturated solid solution and the formation of V-lean and V-rich secondary phases were observed over the V content and the consolidation temperature increment. Therefore, studying the effect of V content and the various consolidation routes on corrosion performance is also crucial to understanding the corrosion mechanisms of Al-V alloys. Thus, in this study, the influence of V content and the SPS process on the corrosion mechanisms of HEBMed Al-xV alloys ($x = 2, 5, 10$ at%) have been studied using various electrochemical techniques.

Methods

Alloy synthesis and consolidation.—A Fritsch P-5/4, planetary ball mill was utilized to produce Al-xV ($x=2,5$ and 10 at%). Elemental aluminum (99.7% purity and $-50/+100$ mesh size) and vanadium (99.8% purity and 325 mesh size) powder were weighed inside the glove box, which maintained a high purity argon environment along with lower oxygen content (<25 ppm). 10 mm diameter steel balls were used as the milling media, and a 16:1 ball-to-powder ratio was maintained in each jar. The stearic acid was used as a process-controlling agent (1.5% of the total powder weight in each jar) to minimize the cold welding during the milling process. The jars were sealed inside the glove box, and high-energy ball milling was conducted at 280 RPM. The milling time for each composition was selected based on the authors' previous study, where the milling parameters were optimized to achieve the highest solid solubility of V in Al.^{20,34} The milling process was interrupted for 30 min after each 1 h of milling to minimize overheating during the milling. Al-V alloys were in powder form for all three alloys after ball milling, and the characteristics of each powder were described in the authors' previous publications.^{20,25,34}

The authors' previous publication described the microstructural evolution of SPSe Al-xV ($x=2,5$, and 10 at%), where the choice of SPS parameters was optimized to minimize the porosity while retaining the initial HEBM microstructure up to a certain level.²⁵ According to that, 600 MPa pressure along with the 400 °C consolidation temperature was selected as the optimum SPS condition. HEBMed Al-xV ($x=2,5$ and 10 at%) alloy powders were consolidated using 10–3 thermal technology LLC spark plasma sintering. The tungsten carbide dies, punches (10 mm diameter), and graphite foil were utilized to compact the samples. The SPS was conducted in an Ar inert environment with a heating rate of 50 °C min⁻¹ until reaching 400 °C. A uniaxial 600 MPa pressure was applied on the specimens while keeping 5 min of dwell time.

Immersion tests and scanning electron microscopic analysis.—Immersion tests were conducted on SPSe Al-xV ($x=2,5$, and 10 at%) for post-corrosion characterization. The specimens were ground to 1200 grit surface roughness using SiC papers and subsequently polished up to 0.05 μ m surface finishing using the diamond suspension. The polished samples were ultrasonicated in ethanol for 10 min. The immersion test was carried out in 0.1 M NaCl for two days for each sample. After immersion, specimens were washed with de-ionized water before scanning electron microscopic analysis (SEM). The SEM analysis of immersed SPSe Al-xV ($x=2,5$, and 10 at%) was conducted using FEI Verios 4601 at 20 kV accelerating voltage. In addition, backscattered electrons analysis (BSE) was performed on each sample to understand the post-corrosion characteristics of each sample.

Electrochemical tests.—The corrosion behavior of SPSe Al-xV ($x=2,5$ and 10 at%) alloys was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy tests. First, SPSe Al-xV ($x=2,5$ and 10 at%) alloys were mounted on epoxy resin and kept overnight for curing. Then, the samples were

grounded using SiC sandpapers starting from P400 to P1200 grit and subsequently ultrasonic cleaned in ethanol for 10 min. The adhesive polymer tape was punctured using a metal puncture with the desired diameter to obtain the required sample exposure area. Prior to the electrochemical tests, the punctured adhesive polymer tape was stuck on the sample surface, which helped maintain an accurate exposure area and prevent crevice corrosion during the tests. The specimen exposure area was 0.178 cm² for cyclic potentiodynamic polarization and electrochemical impedance spectroscopy tests. A standard three-electrode flat cell containing a Pt counter electrode was utilized for the experiments. In addition, a saturated calomel electrode (SCE) was used as a reference for all the electrochemical tests. VMP 300 biologic potentiostat and the EC lab software were used to acquire all the electrochemical data. Potentiodynamic polarization was repeated at least three times, whereas electrochemical impedance spectroscopy tests were conducted twice to ensure the test result's reproducibility.

Cyclic potentiodynamic polarization tests.—Cyclic potentiodynamic polarization (CPP) tests were performed on SPSe Al-xV ($x=2,5$ and 10 at%) alloys in 0.01 M NaCl aqueous solution. First, open circuit potential (OCP) was monitored for 30 min. Next, the specimen was anodically polarized starting from 50 mV_{SCE} below OCP and continued the polarization until the current density reached 200 μ A cm⁻². Then, the scanning direction was reversed until the potential reached 100 mV_{SCE} below OCP. A sweep rate of 0.167 mV s⁻¹ was used throughout the experiment.

Electrochemical impedance spectroscopy.—Electrochemical impedance spectroscopy (EIS) tests were carried out on SPSe Al-xV ($x=2,5$ and 10 at%) alloys in 0.01 M NaCl aqueous solution. The EIS data set was acquired after 30 min of immersion, and EIS tests were continued for 14 d, collecting the data every 12 h. A sinusoidal signal with 10 mV amplitude (with respect to OCP) was passed through during the experiment. The signal frequency was varied from 10⁵ Hz to 10⁻³ Hz, and three readings were taken at each frequency point. For each frequency decade, 10 data points were collected.

Results and Discussion

Microstructural evolution and localized corrosion using scanning electron microscope.—The immersion tests for SPSe Al-xV ($x=2,5$, and 10 at %) were conducted for two days of immersion in 0.1 M NaCl. Figure 1 exhibits BSE images before and after immersion in the same areas for all three compositions. Before the immersion, tiny bright Fe-rich particles were observed in the Al-2V microstructure (Fig. 1a) because of the contamination from stainless steel milling media. Furthermore, the high-energy ball milling process is attributed to a uniform distribution of these Fe-rich particles within the Al-V alloy matrix. Since the Fe-rich phase is electrochemically more noble than the Al-rich matrix, these Fe-rich particles act as cathodic sites to the surrounding Al-rich matrix when exposed to NaCl electrolyte. Therefore, it is clear that the galvanic interaction takes place between Fe-rich particles and the surrounding matrix, leading to pitting initiation (Figs. 1b and 1c). In Al-2V, the average pit diameter and pitting area fraction were (1.83 ± 0.92) μ m and 10.7%, respectively. Interestingly, these pitting sites did not grow significantly compared to the pits formed in pure Al after immersion in 0.01 M NaCl for 30 min.³⁵ This could be attributed to (1) cathodic inhibition in pitting sites due to the deposition of V species on Fe-rich particles, (2) control of pit growth kinetics due to the enrichment of V underneath the pitting sites, which could lead to a higher repassivation tendency, as discussed in the authors' previous publications about the corrosion mechanisms of Al-V alloys.²⁷ The formation of V-lean and V-rich phases in SPSe Al-5V and Al-10V alloys have been reported previously.²⁵ However, in this study, Al-5V (Fig. 1d) reveals only the presence of the V-lean phase because of the small size of the V-rich phase, which is beyond

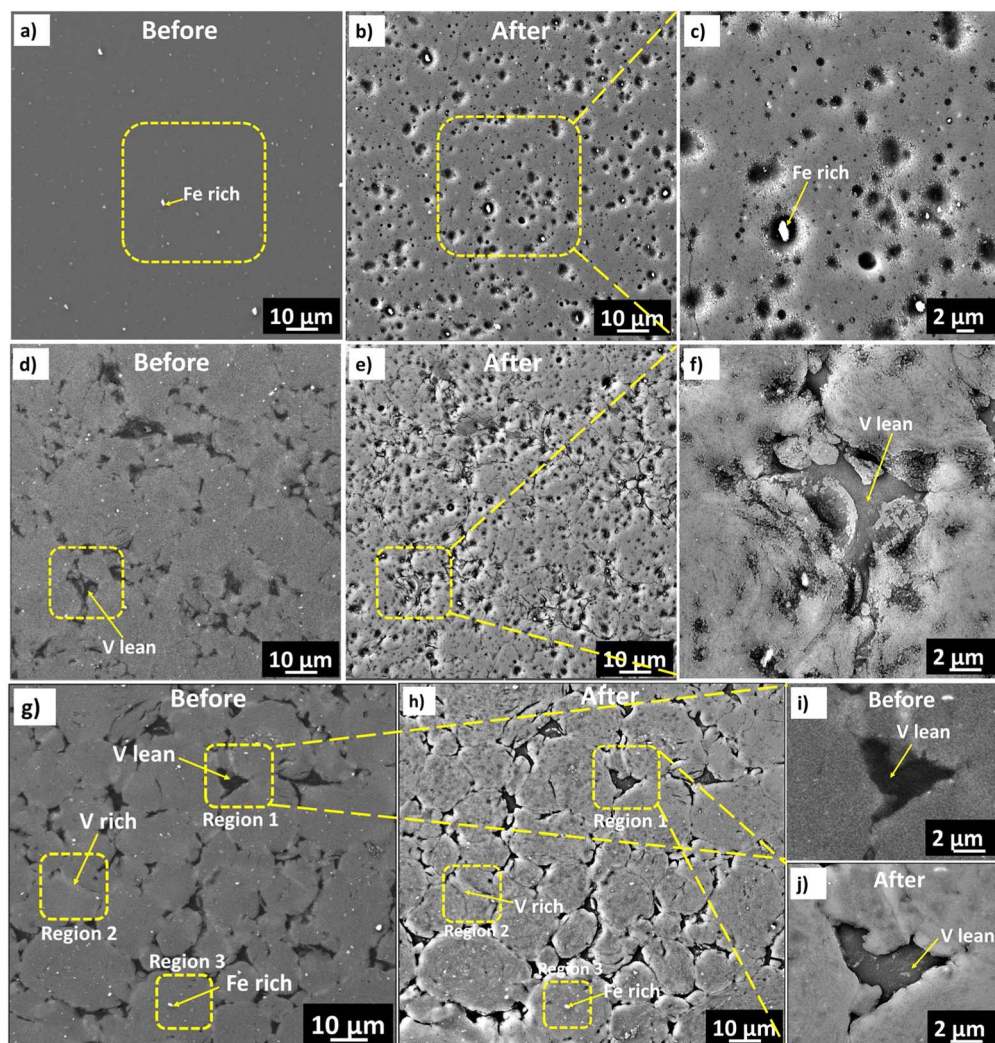


Figure 1. Backscattered electron images of before and after 2 days of immersion in 0.1 M NaCl showing: (a-c) Al-2V microstructure consisting of Fe-rich particles and pit initiation at Fe-rich sites with a zoomed-in region, (d-f) Al-5V microstructure revealing V-lean regions and pit initiation at V-lean sites with a zoomed-in region, (g-j) Al-10V microstructure showing V-rich, V-lean regions and Fe rich particles. Selected zoomed-in regions indicate before and after localized corrosion on the V-lean region.

the resolution limit. Figures 1e and 1f revealed the pitting initiation around Fe-rich particles and within the V-lean region. Since the V-lean phase and Fe-rich particles were distributed all over the matrix in Al-5V, pits were noted throughout the alloy. The average pitting diameter in Al-5V was estimated considering Fe-rich particles and was $(1.68 \pm 0.71) \mu\text{m}$, which is slightly smaller than that in Al-2V. Interestingly, these pitting sites also grew little compared to the pits formed in pure Al after immersion in 0.01 M NaCl for 30 min.³⁵ Nevertheless, reducing the average pit size in Al-5V, compared to Al-2V, suggests that increasing V content could gradually reduce galvanic interaction between the matrix and Fe-rich particles. On the other hand, the total pitting area fraction, including the V-lean region in Al-5V, was 16%, which is about a 6% increment compared to that in Al-2V. This pitting area fraction increment is mainly attributed to the corrosion in the V-lean region in Al-5V alloy. The electrochemical potential difference between the V-lean phase (more active) and the matrix could be ascribed to corrosion in the V-lean phase. However, the corrosion in the V-lean phase is insignificant enough to cause severe pitting damage in Al-5V. Since V-based species act as cathodic inhibitors in ball-milled Al-V alloys, it is possible that there was cathodic inhibition in V-lean pitting sites, which needs to be validated in future studies.

In Al-10V, V-lean and V-rich phases and Fe-rich particles were detected (Fig. 1g). However, the V-lean phase was more dominant

than the V-rich phases and Fe-rich particles. This V-lean phase formation is attributed to the partial decomposition of the V-solid solution.²⁵ Similar to Al-5V alloy, the V-lean phase is distributed all over the matrix in Al-10V. After the immersion, notable corrosion was not observed around Fe-rich particles in Al-10V (Fig. 1h). Thus, it is clear that having higher V content in Al-10V alloy leads to a considerable reduction of the anodic nature of the alloy matrix, as compared to Al-5V, resulting in the least galvanic interaction between Fe-rich particles and Al-10V alloy matrix. Interestingly, considerable corrosion was noticed on the V-lean phase (Figs. 1h and 1j). Figures 1i and 1j show the high magnification microstructure of V-lean regions before and after immersion, revealing that the V-lean region was more susceptible to localized corrosion in Al-10V. This observation is consistent with the authors' previous studies, further evidencing the corrosion initiation in the V-lean phase at the interface between the Al-10V alloy matrix and the V-lean phase after exposing the alloy to 0.1 M NaCl.³⁶ This corrosion in the V-lean phase could be attributed to a higher electrochemical potential difference between the more noble matrix and the V-lean phase. The area fraction of the corroded V-lean region in Fig. 1h was estimated to be about 10%, which is about a 4% rise compared to that in Al-5V. Since the area fraction of the V-lean phase in Al-10V is higher than that in Al-5V and the electrochemical potential difference between a more noble alloy matrix and the V-lean phase

in Al-10V is higher than that in Al-5V, it is expected to have a higher degree of corrosion in V-lean sites over the long hours of immersion.

Corrosion behavior of SPSed Al-xV alloys using cyclic potentiodynamic polarization and electrochemical impedance spectroscopy.—Figure 2 shows the representative CPP curves for SPSed Al-xV (x= 2,5, and 10 at%) alloys and pure Al after 30 min and 14 days of immersion in 0.01 M NaCl. The average OCP and current density at $-580 \text{ mV}_{\text{SCE}}$ from 30 min and 14 days of immersion were selected as representative conditions (Table I). This selected polarization potential lies in the passive window in many of the alloys in both 30 min and 14 days immersion CPP curves. After 30 min of immersion, the average OCP of pure Al was significantly noble than that of all three SPSed Al-xV (x= 2,5, and 10 at%) alloys. The average current densities at $-580 \text{ mV}_{\text{SCE}}$ were 0.6 ± 0.2 , 0.6 ± 0.1 , 0.5 ± 0.2 , and $0.2 \pm 0.1 \mu\text{A cm}^{-2}$ for Al-2V, Al-5V, Al-10V, and pure Al, respectively. These values indicate that the effect of V content in the alloy has no significant influence on the current densities at $-580 \text{ mV}_{\text{SCE}}$ after 30 min of immersion. However, compared to pure Al, SPSed Al-xV alloys showed almost three times higher current densities, indicating better passivity in pure Al than that of SPSed Al-xV alloys after 30 min of immersion. Active OCP and higher current densities $-580 \text{ mV}_{\text{SCE}}$ after 30 min of immersion in SPSed Al-xV alloys could be attributed to the electrochemical heterogeneities in their microstructures. The pitting potential (E_{pit}) of Al-2V was $\sim -266 \text{ mV}_{\text{SCE}}$ after 30 min of immersion, which is 98, 12, and 288 mV higher than that of Al-5V, Al-10V alloys, and pure Al, respectively. A significant improvement of pitting potential in SPSed Al-xV alloys compared to that in pure Al could be attributed to the (1) cathodic reaction control due to the deposition of V on cathodic sites and (2) controlled pit growth and repassivation in the early stage of pits due to the V enrichment underneath pits.^{24,27}

Interestingly, the average current densities at $-580 \text{ mV}_{\text{SCE}}$ were significantly reduced in Al-2V ($0.08 \pm 0.03 \mu\text{A cm}^{-2}$) and Al-5V ($0.06 \pm 0.03 \mu\text{A cm}^{-2}$) after 14 days of immersion, as compared to them in 30 min of immersion. The E_{pit} for Al-2V and Al-5V were $(183 \pm 47) \text{ mV}_{\text{SCE}}$ and $(207 \pm 44) \text{ mV}_{\text{SCE}}$, respectively, after 14 days of immersion. This indicates almost 449 mV and 571 mV increments of E_{pit} in Al-2V and Al-5V compared to that in 30 min of immersion. The reduced current density and increased E_{pit} in Al-2V and Al-5V reveal enhanced corrosion resistance over long hours of immersion. On the other hand, in Al-10V and pure Al, the average current densities at $-580 \text{ mV}_{\text{SCE}}$ were $(6.42 \pm 0.8) \mu\text{A cm}^{-2}$ and $(1.98 \pm 1.10) \mu\text{A cm}^{-2}$, which are about 13 and 10 times higher than that of 30 min of immersion, respectively. The E_{pit} of pure Al was $-542 \text{ mV}_{\text{SCE}}$ after 14 days of immersion, which is almost similar to that in 30 min of

immersion.³⁵ However, a distinguishable E_{pit} was not observed in Al-10V after 14 days of immersion. This exhibits the deterioration of the corrosion resistance of Al-10V over the immersion time.

Overall, it is clear that the corrosion resistance of Al-2V and Al-5V alloys was significantly enhanced over the immersion time, as compared to that in pure Al. Therefore, it can be proposed that the corrosion observed around Fe-rich particles in Al-2V (Fig. 1c and Fe-rich particles and the V-lean phase (Fig. 1e) would have been inhibited over the long hours of immersion. In contrast, the V-lean phase in Al-10V (Fig. 1g) caused drastic corrosion over the immersion time. Furthermore, having higher V content in Al-10V alloy leads to a considerable reduction of the anodic nature of the alloy matrix as compared to Al-5V. This is further supported by more noble OCP in Al-10V compared to Al-2V and Al-5V alloys. Thus, the potential difference between the more noble matrix and the V-lean region in Al-10V is significantly higher than that of the Al-5V matrix and its V-lean phase. Therefore, it can be proposed that the corrosion resistance deterioration over the immersion in Al-10V is mainly due to the higher electrochemical potential difference between the alloy matrix and the V-lean phase.

The time-dependent corrosion behavior of SPSed Al-xV (x= 2, 5, and 10 at%) alloys was investigated using EIS analysis and is presented in Fig. 3. The total impedance ($|Z|$) of Al-2V and Al-5V increased significantly over the immersion time and reached the highest impedance after 336 h of immersion (Figs. 3a–3d). In contrast, Al-10V, the highest total impedance was recorded after 30 min of immersion and dropped intensely over the immersion time (Figs. 3e and 3f).

As shown in Fig. 4, two types of equivalent circuits were used to characterize the electrochemical parameters: Al-2V and Al-5V electrochemical data were fitted using the first circuit (Fig. 4a). In contrast, the first and second (Fig. 4b) circuits were utilized to characterize Al-10V alloy. Interestingly, a frequency relaxation has been observed at around 10^5 Hz in all Bode plots (Figs. 3b, 3d and 3f). This relaxation is attributed to an artifact of the electrochemical cell, as high-frequency data fitting deviated from a three-time constant equivalent circuit. Therefore, equivalent circuits with two-time constants have been applied in this study: one was at high frequencies while the other one was at low frequencies. The Zview software, with the help of the above-mentioned equivalent circuits, was used to evaluate the electrochemical parameters, as presented in Tables II–IV. In the equivalent circuits, R_s is the solution resistance. CPE_{film} corresponds to the constant phase element (CPE) of the surface film. The surface film's resistance was noted as R_{film} . CPE_{dl} and R_{ct} indicate the double layer constant phase element and charge transfer resistance, respectively. In this analysis, a frequency-dependent non-ideal capacitive behavior is represented by the CPE.

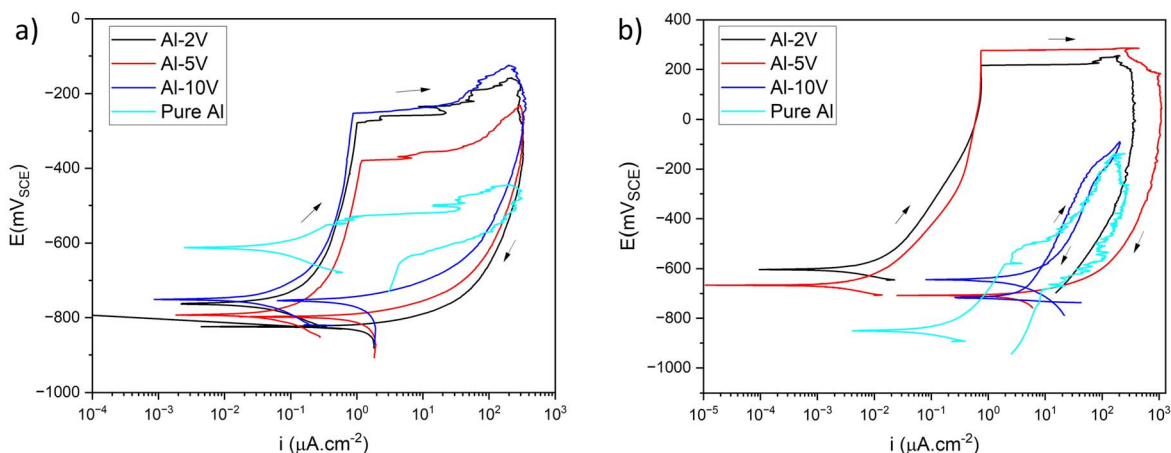


Figure 2. Representative CPP curves for Al-xV (x=2,5 and 10 at%) as compared with the pure Al control specimens in 0.01 M NaCl after (a) 30 min, and (b) 14 days of immersion. It should be noted that after 30 min of immersion, CPP curves for Al-10V alloy and pure Al CPP curves are reproduced from the authors' previous publications.^{35,36}

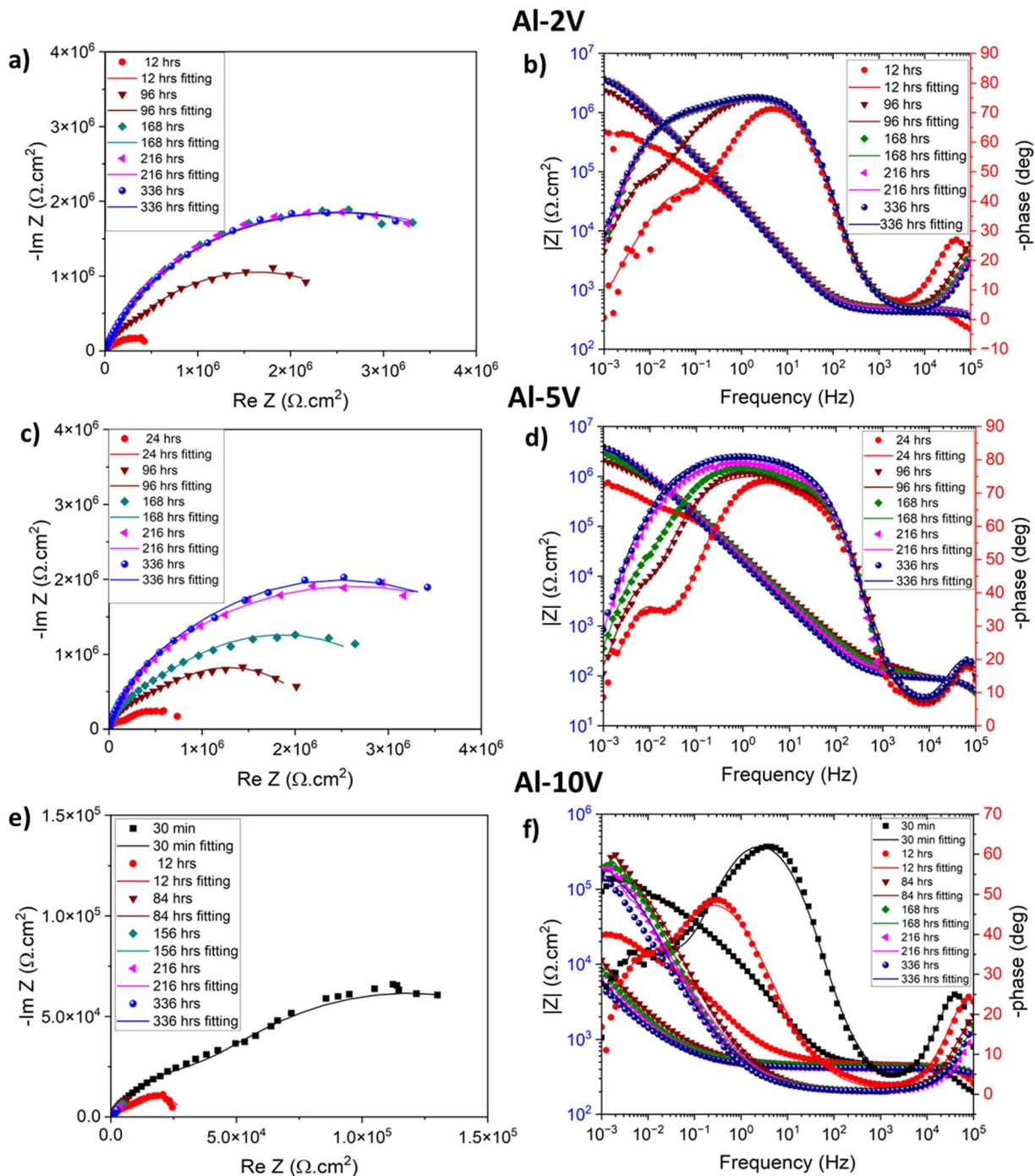


Figure 3. Electrochemical impedance spectroscopic analysis for Al-xV (x=2,5 and 10 at%) alloys at OCP for 14 days immersion in 0.01 M NaCl, showing Nyquist diagram for (a) Al-2V, (c) Al-5V, (e) Al-10V and Bode plot for (b) Al-2V, (d) Al-5V, and (f) Al-10V.

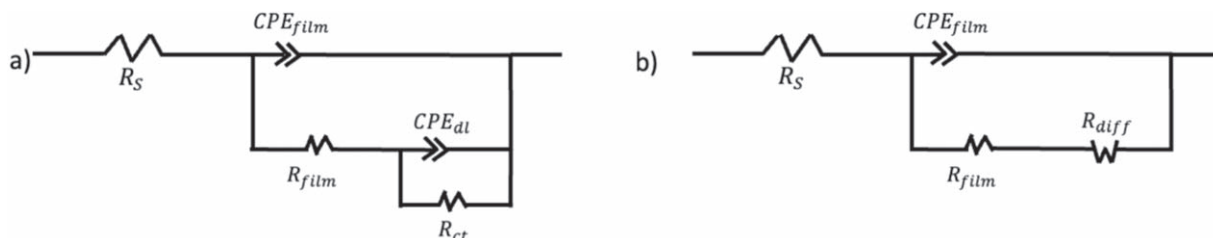


Figure 4. The equivalent circuit diagrams used for the EIS data fitting: (a) Al-2V and Al-5V, and Al-10V, (b) Al-10V.

Table I. The average electrochemical parameters for Al-xV (x-2,5 and 10 at%) alloys and pure Al after 30 min and 14 days of immersion in 0.01 M NaCl. It should be noted that the Al-10V alloy E_{pit} value after 30 min of immersion and pure Al electrochemical data are reproduced from the authors' previous publications.^{35,36}

Immersion time (h)	Composition	OCP (mV _{SCE})	i at -580 mV _{SCE} polarization potential ($\mu\text{A}\cdot\text{cm}^{-2}$)	E_{pit} (mV _{SCE})
0.5	Al-2V	-802 ± 57	0.6 ± 0.2	-266 ± 13
	Al-5V	-824 ± 45	0.6 ± 0.1	-364 ± 36
	Al-10V	-754 ± 66	0.5 ± 0.2	-278 ± 25
	Pure Al	-620 ± 8	0.2 ± 0.1	-554 ± 10
336	Al-2V	-670 ± 91	0.08 ± 0.03	183 ± 47
	Al-5V	-717 ± 71	0.06 ± 0.03	207 ± 44
	Al-10V	-684 ± 56	6.42 ± 0.18	–
	Pure Al	-890 ± 20	1.98 ± 1.10	-542 ± 57

Table II. EIS fitting results for the data presented in Fig. 3 for Al-2V.

Immersion time (h)	R_s ($\Omega\cdot\text{cm}^2$)	CPE_{film} ($\mu\text{F}\cdot\text{cm}^{-2}$)	$\text{CPE}_{\text{film-p}}$	R_{film} ($\text{k}\Omega\cdot\text{cm}^2$)	CPE_{dl} ($\mu\text{F}\cdot\text{cm}^{-2}$)	$\text{CPE}_{\text{dl-p}}$	R_{ct} ($\text{k}\Omega\cdot\text{cm}^2$)	Chi-Squared ($\chi \cdot 10^{-2}$)
12	190	7.3	0.87	100	19.5	0.72	450	0.3
36	194	6.9	0.87	277	16.1	0.76	963	0.4
96	205	6.7	0.86	731	10.1	0.78	2337	0.1
168	202	7.1	0.87	522	2.0	0.72	4431	0.04
216	198	7.2	0.87	395	2.0	0.69	4683	0.02
336	170	7.7	0.88	264	2.1	0.66	4930	0.02

Table III. EIS fitting results for the data presented in Fig. 3 for Al-5V.

Immersion time (h)	R_s ($\Omega\cdot\text{cm}^2$)	CPE_{film} ($\mu\text{F}\cdot\text{cm}^{-2}$)	$\text{C}_{\text{film-p}}$	R_{film} ($\text{k}\Omega\cdot\text{cm}^2$)	CPE_{dl} ($\mu\text{F}\cdot\text{cm}^{-2}$)	$\text{CPE}_{\text{dl-p}}$	R_{ct} ($\text{k}\Omega\cdot\text{cm}^2$)	Chi-Squared ($\chi \cdot 10^{-2}$)
12	159	8.3	0.85	247	70.6	0.95	434	0.1
96	161	7.5	0.85	1164	26.6	0.92	1055	0.1
168	142	8.0	0.86	1674	27.2	0.95	1660	0.1
216	122	8.9	0.89	2524	5.4	0.69	2723	0.2
336	47	10.6	0.89	3502	57.1	0.99	1297	0.2

Table IV. EIS fitting results for the data presented in Fig. 3 for Al-10V.

Immersion time (h)	R_s ($\Omega\cdot\text{cm}^2$)	CPE_{film} ($\mu\text{F}\cdot\text{cm}^{-2}$)	$\text{C}_{\text{film-p}}$	R_{film} ($\text{k}\Omega\cdot\text{cm}^2$)	CPE_{dl} ($\mu\text{F}\cdot\text{cm}^{-2}$)	$\text{CPE}_{\text{dl-p}}$	R_{ct} ($\text{k}\Omega\cdot\text{cm}^2$)	Chi-Squared ($\chi \cdot 10^{-2}$)
0.5	188	22	0.78	57	102	0.78	149	0.2
12	196	243	0.68	19	2899	0.9	15	0.2
Immersion time (h)	R_s ($\Omega\cdot\text{cm}^2$)	CPE_{film} ($\mu\text{F}\cdot\text{cm}^{-2}$)	$\text{C}_{\text{film-p}}$	R_{film} ($\text{k}\Omega\cdot\text{cm}^2$)	R_{diff} ($\text{k}\Omega\cdot\text{cm}^2$)	Time _{diff} (s)	$\text{CPE}_{\text{diff-p}}$	Chi-Squared ($\chi \cdot 10^{-2}$)
84	227	1871	0.66	0.7	36	278	0.67	0.3
156	240	2377	0.64	0.4	36	318	0.70	0.3
216	213	3094	0.63	0.1	35	379	0.7	0.2
336	245	3164	0.61	1.6	40.4	326	0.70	0.2

In Al-2V, the highest R_{film} was $731 \text{ k}\Omega \text{ cm}^2$, observed after 96 h with a gradual increment from 12–96 h. After 96 h, R_{film} declined over the immersion time and reached $264 \text{ k}\Omega \text{ cm}^2$ after 336 h. On the other hand, R_{film} of Al-5V was $247 \text{ k}\Omega \text{ cm}^2$ after 12 h of immersion, increased significantly over time, and reached the highest ($3502 \text{ k}\Omega \text{ cm}^2$) after 336 h of immersion, which is the highest value among all three alloys. In contrast, the maximum R_{film} ($57 \text{ k}\Omega \text{ cm}^2$) was observed after 30 min of immersion in Al-10V and dropped primarily over the immersion time. In comparison, the authors' previous publication revealed that the highest R_{film} of pure Al in the same experimental conditions was $101 \text{ k}\Omega \text{ cm}^2$, which is $630 \text{ k}\Omega \text{ cm}^2$, $3401 \text{ k}\Omega \text{ cm}^2$ lower than that of Al-2V and Al-5V, respectively.³⁵ Furthermore, the authors showed that the increment of the V content up to 5 at% caused the strong enrichment of V within and underneath the passive film.³⁶ These enrichments act as a barrier layer for

the chloride ion penetration and the prevention of dissolution of the passive film. Therefore, it can be proposed that the V content increment up to 5 at% resulted in the passive film resistance enhancement over the immersion time, as indicated by the R_{film} .

In Al-2V and Al-5V, the charge transfer resistance (R_{ct}) was almost similar after 12 h and surged over the immersion time. After 336 h, the highest individual R_{ct} ($4930 \text{ k}\Omega \text{ cm}^2$) was recorded in Al-2V, which is $3633 \text{ k}\Omega \text{ cm}^2$ higher than that in Al-5V and almost 19 times higher than that in pure Al in similar conditions.³⁵ In comparison, the highest R_{ct} was $149 \text{ k}\Omega \text{ cm}^2$ after 30 min of immersion in Al-10V, which was degraded over the immersion time until 12 h. This indicates the localized corrosion resistance reduction over the V content in the alloy. After 12 h, the corrosion mechanisms have been changed in Al-10V, as the equivalent circuit

switched from circuit 1 (Fig. 4a) to circuit 2 (Fig. 4b). This change is attributed to the accelerated dissolution at the localized points and enhanced ionic transportation between the localized corrosion points and the bulk electrolyte, resulting in the lowest corrosion resistance in Al-10V over long hours of immersion. This observation is further supported by the CPP test after 14 days of immersion, confirming the enhanced corrosion current density over the immersion in Al-10V.

It is clear that the highest charge transfer resistance increment over the immersion time in Al-2V alloy among all SPS samples. Since Fe-rich particles caused the localized corrosion in Al-2V, it can be suggested that the localized corrosion inhibition takes place in Al-2V alloys probably due to the deposition of V on Fe particles, as proposed in the authors' previous publications.^{24,27} On the other hand, higher V content in the Al-10V alloy matrix could tend to be more cathodic because of V's higher electrochemical nobility than that in Al, as indicated in the galvanic series.³⁷ This could increase the potential difference between the matrix and the V-lean phase, leading to a stronger galvanic interaction. Such an effect can result in higher localized corrosion susceptibility in Al-10V than in Al-5V. Therefore, the corrosion resistance of Al-10V alloy deteriorates over the immersion time, which results in the corrosion mechanisms changing over the immersion time in the EIS analysis.

The authors' previous publications have shown the formation of a multi-layered passive film, where the top layer was mostly Al oxide and the bottom layer was a combination of Al and V oxides in HEBM Al alloys.^{29,36} As the V content increases in the alloy, the formation of a passive film with a high amount of oxidized V was noted. Therefore, it can be suggested that the reduction of point defects over the V content increment could be attributed to the point defect annihilation due to the formation of oxidized V-based species in the passive film.²⁷ Interestingly, after 30 min of immersion, the CPP test data further supported this claim, showing the highest passive film stability, indicated by the higher pitting potential in Al-10V. However, the actual passive film resistance of these alloys was explored in long-term EIS analysis (R_{film}), suggesting a V content increment of up to 5 at% led to a significant enhancement of the passive film resistance of the alloy over the immersion time.

Conclusions

The influence of V on corrosion of Al-xV (x= 2,5, and 10 at%) alloys produced by high energy ball milling and subsequently spark plasma sintered was investigated, and the following key conclusions are present:

- (1) The immersion test indicated that the presence of Fe-rich particles is mainly attributed to the localized corrosion in spark plasma sintered Al-2V and Al-5V. At the same time, forming the V-lean phase resulted in further corrosion in spark plasma sintered Al-5V and localized corrosion initiation in Al-10V.
- (2) Potentiodynamic polarization and electrochemical impedance spectroscopic analysis revealed a significant enhancement of corrosion resistance in Al-2V and Al-5V alloys compared to that in pure Al over the long hours of immersion, showing that the influence of Fe-rich particles in spark plasma sintered Al-2V and Al-5V on localized corrosion over long hours immersion time is considerably lower. On the other hand, in spark plasma sintered Al-10V exhibited severe corrosion over long hours of immersion, possibly due to a strong galvanic interaction between the V-lean phase and the more noble matrix.
- (3) Electrochemical impedance spectroscopic analysis showed a significant charge transfer resistance increment over the immersion time in spark plasma sintered Al-2V, which is mainly attributed to a substantial corrosion resistance enhancement in the alloy. However, the charge transfer resistance dropped significantly when the V content was higher than 2 at%. On the other hand, the surface film resistance was increased with the V content up to 5 at%, causing the highest surface film resistance over long hours of immersion in Al-5V among all three alloys, primarily enhancing corrosion resistance in Al-5V alloy.

- (4) Overall, the effect of heterogeneous microstructure is dominant if the V content is higher than 5 at%, leading to severe corrosion. Thus, selecting an appropriate alloying content with the optimum processing parameters is crucial to developing corrosion-resistant Al alloys via HEBM.

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CRediT Authorship Contribution Statement

C.S. Witharamage: Conceptualization, Methodology, Investigation, Formal analysis, Data curation, Writing - original draft, Writing - review & editing. J. Chirstudasjustus: Methodology, Investigation, Formal analysis, Writing - review & editing. G. Walunj: Investigation, review & editing. T. Borkar: Writing - review & editing. R.K. Gupta: Conceptualization, Methodology, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

No potential conflict of interest was reported.

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