

Corrosion behaviour of Al-Fe-Ti-V medium entropy alloy

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Abstract. Alloys containing up to four multi-principal elements in equiatomic ratios are referred to as medium entropy alloys (MEA). These alloys have attracted the interest of many researchers due to the superior mechanical properties it offers over the traditional alloys. The design approach of MEA often results to simple solid solution with either body centered cubic; face centered cubic structures or both. As the consideration for introducing the alloys into several engineering application increases, there have been efforts to study the corrosion behaviour of these alloys. Previous reports have shown that some of these alloys are more susceptible to corrosion when compared with traditional alloys due to lack of protective passive film. In this research, we have developed AlFeTiV medium entropy alloys containing two elements (Ti and Al) that readily passivate when exposed to corrosive solutions. The alloys were produced in vacuum arc furnace purged with high purity argon. Open circuit potential and potentiodynamic polarisation tests were used to evaluate the corrosion behaviour of the as-cast AlFeTiV alloy in 3.5 wt% NaCl and 1 M H₂SO₄. The corrosion performance of the alloy was compared with Ti-6Al-4V alloy tested under similar conditions. The results show that unlike in Ti-6Al-4V alloy, the open circuit potential of the AlFeTiV alloy move towards the negative values in both 3.5 wt% NaCl and 1 M H₂SO₄ solutions indicating that self-activation occurred rapidly on immersion. Anodic polarisation of the alloys showed that AlFeTiV alloy exhibited a narrow range of passivity in both solutions. In addition, the alloys exhibited lower *E_{corr}* and higher *I_{corr}* when compared with traditional Ti-6Al-4V alloy. The traditional Ti-6Al-4V alloy showed superior corrosion resistant to the AlFeTiV alloy in both 3.5 wt.% NaCl and 1 M H₂SO₄ solutions.

1. Introduction

About twelve years ago, a paradigm shift in the design approach of metallic alloys led to the emergence of high entropy alloys (HEA) [1]. Unlike conventional alloy systems with a parent element, HEA are alloys with equimolar or equiatomic concentration of constituent elements [2]. The alloys have been reported to have superior mechanical properties and sometimes excellent corrosion resistance over the conventional alloys [3-4]. These properties have been attributed to the strong



binding energy among the constituent elements and the simple solid solution phase that is formed in the alloys due to high configurational entropy of mixture that was hypothesized by Boltzmann [5].

The unique properties showed by these alloys have continued to attract the interest of researchers since the mechanisms driving the behaviour of these alloys are not well understood. Consequently, there have been a lot of contradictions and controversies in the reports of scientists in open literature. For example, the general claim that HEA forms simple solid solution have been found to be inconsistent in some other alloys where intermetallic compounds and complex phases were found. Also, the initial definition of HEA as alloys containing at least five elements with equiatomic concentrations has been questioned by some researchers, they reported that some HEAs can be developed with just four elements with equimolar concentrations. These sets of alloys have been referred to as medium entropy alloys (MEA).

While the controversies on the definition and properties of medium and high entropy alloy continue, the alloys exhibit comparable hardness and tensile properties. With a lot of potential medium and high entropy alloys yet to be explored, we have developed an experimental Al₂₅Fe₂₅Ti₂₅V₂₅ medium entropy alloy with the aim of examining its corrosion behaviour.

In this study, the AlFeTiV medium entropy alloy was tailored to conventional Ti-6Al-4V alloy which exhibit excellent corrosion resistance in several corrosive environments. The alloy contains Al and Ti that readily passivate when exposed to some corrosive solution, the corrosion behaviour of these alloys were then investigated in two common industrial solutions in comparison with commercial Ti-6Al-4V alloy.

2. Experimental procedure

The experimental powders were produced from elemental powders of aluminium, iron, titanium and vanadium. A total of 20 g of mixed Al₂₅Fe₂₅Ti₂₅V₂₅ powders were pressed and then melted three times in an electric arc furnace purged with high purity argon to produce the Al₂₅Fe₂₅Ti₂₅V₂₅ ingot. The ingot was turned in between melts to ensure homogenization of the alloy. The as-cast alloy was then sectioned and mounted for microstructural examination, hardness and corrosion testing.

The Al₂₅Fe₂₅Ti₂₅V₂₅ and commercial Ti-6Al-4V samples used for microstructural examination was mounted, grounded and polished following standard metallographic procedures. The samples were etched for 15 second in standard Kroll's reagent, rinsed with acetone in an ultrasonic bath and dried in compressed air. The elemental composition of the Al₂₅Fe₂₅Ti₂₅V₂₅ was taken prior to etching of the alloy to avoid the dissolution of some of the elements in the alloy.

Back-scattered electron images of the etched sample were taken using field emission scanning electron microscope (Jeol FE-SEM JSM-7600F) while phase analysis of the as-cast AlFeTiV was carried out using the PW1710 Philips X-ray diffractometer with Cu K α radiation at 40 kV and 40 mA to identify the constituent phases. Diffractograms were collected over a range of 2 θ between 10 and 90°, with a step size of 0.02. A search-match routine was performed using X'Pert High Score Plus software for phase identification.

The hardness of the sample was measured on FM700 microhardness testing machine using a load of 300 kgf and a dwell time of 15 s.

Open circuit potential (OCP) and potentiodynamic polarisation techniques were used in investigating the corrosion performance of the MEA in 3.5 wt% NaCl and 1 M sulphuric acid solutions. The solutions were prepared using analytical grade chemicals and distilled water. A three-cell set-up which consisted of silver-silver chloride as reference electrode, graphite rod as counter electrode and both Al₂₅Fe₂₅Ti₂₅V₂₅ and Ti-6Al-4V alloys as working electrodes was connected to an AUTOLAB potentiostat (302N model) with general purpose electrochemical system (GPES 4.9) software. Before potentiodynamic measurement, the OCP of the alloys was traced for 3600 s in 1 M sulphuric acid and 3.5 wt% sodium chloride solutions to allow stability. The potentiodynamic scan was traced from -1.5 to 2.0 V at a scan rate of 0.2 mV/s in both solutions. Electrochemical parameters such as E_{corr}, I_{corr} and corrosion rate were calculated using Tafel extrapolation technique.

3. Results and discussion

The microstructure of the as-cast Al₂₅Fe₂₅Ti₂₅V₂₅ alloy (nominal composition) is shown in figure. 1. The alloy contains typical as-cast dendritic and interdendritic regions marked as A and B respectively. Interdendritic and dendritic regions constituting FCC and BCC phases have been reported in some HEA alloys.

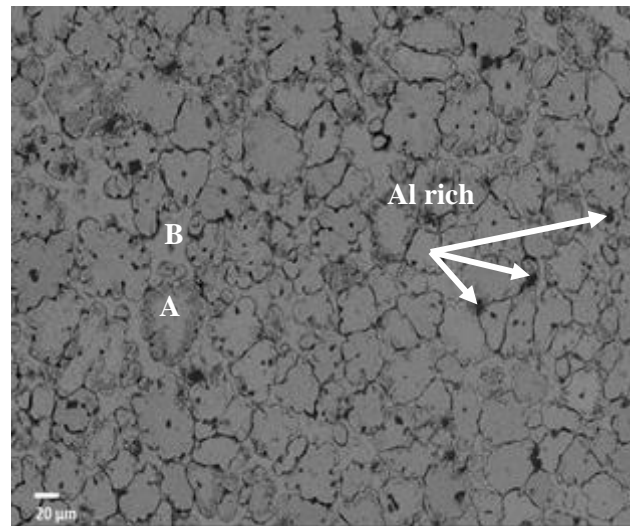


Figure 1. SEM-BSE of as-cast Al₂₅Fe₂₅Ti₂₅V₂₅ medium entropy alloy.

XRD peaks in figure 2 indicate that a mixture of FCC and BCC solid solutions are present in the alloy. The segregation of dark Al rich spots is also observed in the SEM micrograph. The EDX area analysis (figure 3) shows that there is a loss in aluminium during melting of the alloy. This led to the reduction in the aluminium concentration in the alloy. The hardness of the alloy was 692.5 ± 21 HV (6.79 ± 0.2 GPa) which is comparable to hardness values of some HEAs [6].

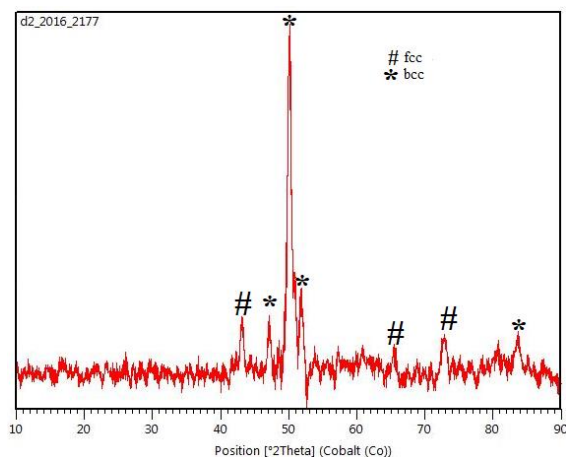


Figure 2. XRD pattern of as-cast Al₂₅Fe₂₅Ti₂₅V₂₅ medium entropy alloy.

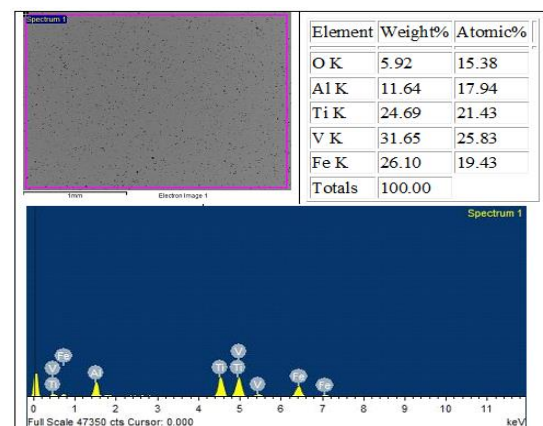


Figure 3. EDX spectra of Al₂₅Fe₂₅Ti₂₅V₂₅ medium entropy alloys.

The high hardness of the alloy can be attributed to the presence of BCC solid solutions in the alloys. Increasing aluminium content has been reported to promote the transition of FCC to BCC phase in some HEAs due to lattice distortions [7]. In addition, it was reported that refractive elements such as Ti and V impacts high hardness in high entropy alloys [8].

The linear polarization curves for alloys immersed in 3.5 wt% sodium chloride and 1 M sulphuric acid solutions are presented in figure 4. In both solutions, the traditional Ti-6Al-4V alloys showed superior corrosion resistance in comparison with the Al25Fe25Ti25V25 medium entropy alloys. Ti-6Al-4V alloy has higher E_{corr} values and a wider range of passivity in the anodic region in both solutions. An active to passive behaviour could be observed in 1 M H_2SO_4 . The range of the passivity exhibited by the Al25Fe25Ti25V25 alloy was narrower than that of the Ti-6Al-4V alloy. Narrow range of passivity was also reported in CrMnFeCoNi high entropy alloys [9]. The Al25Fe25Ti25V25 alloy showed a lower breakdown potential in sulphuric acid than in sodium chloride solution whereas the traditional Ti-6Al-4V did not show any breakdown potential up to 2 V.

In sodium chloride solution (figure 4a), both alloys displayed spontaneous passivation since no evidence of active to passive transition nose is observed. However, the Al25Fe25Ti25V25 alloy showed transient currents in the passive region. These transient currents are signatures of unstable passive film which indicates the dissolution and building of the films in the anodic region. The passivation current of the Al25Fe25Ti25V25 alloy is slightly lower than the conventional alloy in sodium chloride solution. In sulphuric acid medium (figure 4b), the traditional alloy displayed an active to passive transition nose while the Al25Fe25Ti25V25 alloy showed transient current close to the active nose. The passivation current and critical current density of the conventional Ti-6Al-4V alloys is slightly lower than that of the Al25Fe25Ti25V25 alloy.

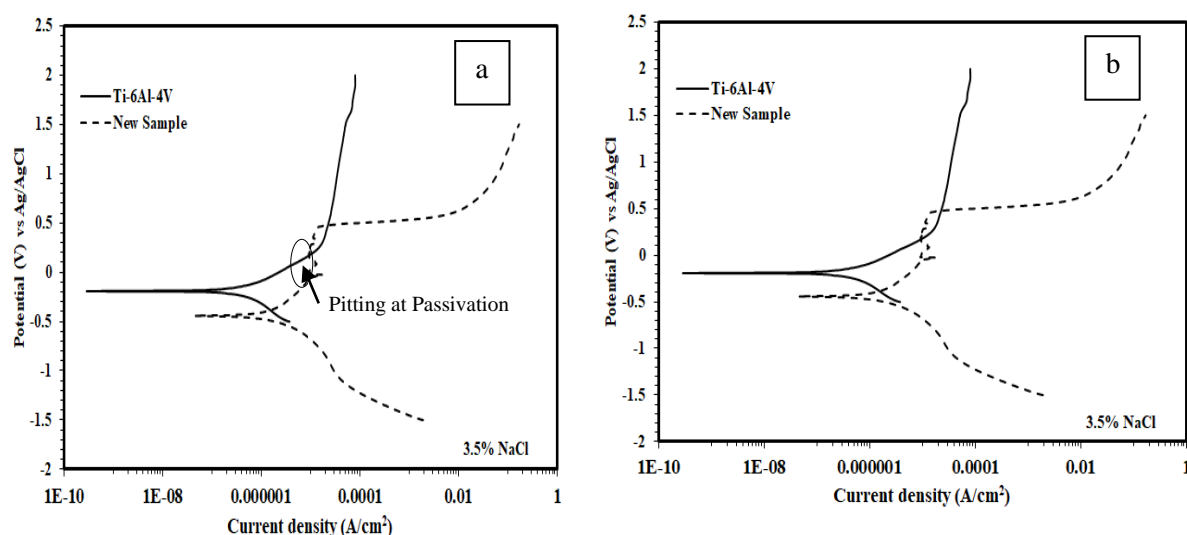


Figure 4. Polarisation curves for Al25Fe25Ti25V25 and Ti-6Al-4V in (a) 3.5 wt% sodium chloride solution and (b) 1 M sulphuric acid.

Table 1. Corrosion data obtained from potentiodynamic polarization curves.

Sample	E_{corr} (V)	I_{corr} ($\mu A/cm^2$)	Corrosion rate
3.5% NaCl			
Ti-6Al-4V	-0.283	0.33	2.828E-3
Al25Fe25Ti25V25	-0.442	0.49	4.010E-3
1 M H_2SO_4			
Ti-6Al-4V	-0.038	0.177	1.517E-2
Al25Fe25Ti25V25	-0.453	49.19	3.997E-1

Table 1 presents the E_{corr} , I_{corr} and Corrosion rate value derived from the Tafel extrapolation. The E_{corr} of Ti-6Al-4V alloy in both media are nobler when compared to Al25Fe25Ti25V25 alloy. Furthermore, the corrosion current density, I_{corr} , measured for Ti-6Al-4V are lower as shown in Figure 4.

Generally, the presence of Cl^- in the chloride containing solution significantly affect the pitting behaviour of Al25Fe25Ti25V25 alloy and thus, pitting within passivation range. In H_2SO_4 solution, the presence of H^+ influences the oxide film formation, lowering the pitting potential of Al25Fe25Ti25V25 alloy, thus affecting the corrosion behaviour ($I_{corr} = 49.19 \mu A/cm^2$). This explains the high corrosion rate reported for Al25Fe25Ti25V25 alloy ($3.997E-1$).

4. Conclusion

The corrosion behaviour of Al25Fe25Ti25V25 medium entropy in comparison with commercial Ti-6Al-4V alloy was evaluated in sodium chloride and sulphuric acid media. The Al25Fe25Ti25V25 medium entropy alloy exhibited inferior corrosion resistance in comparison with the conventional Ti-6Al-4v alloy due to unstable protective film. The substantial amount of the principal elements such as Al, V and Fe must have promoted defects in the passive film thereby causing severe attack of the corrosive solution on the alloy. Additionally, the segregated Al rich spots seen in the microstructure of the Al25Fe25Ti25V25 alloy could serve as a preferred site for corrosion attack to occur.

5. Acknowledgement

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6. References

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