Effect of V addition to Al and Al grain refined by Ti on chemical corrosion rates in NaOH solution with and without inhibitor at different temperatures

Adnan I O Zaid1, Ahmad M Al-Haj-Ali2 and G T A Allawi3
1Industrial Engineering Department, University of Jordan, Amman, Jordan
2,3Chemical Engineering Department, University of Jordan, Amman, Jordan
E-mail: a_kilani43@hotmail.com, ahmad.ay55@gmail.com, ghunaallawi@yahoo.com

Abstract. The paper presents the effect of vanadium addition to aluminum grain refined by titanium, in the range from 0.005 wt % to 0.236 wt %, on corrosion rate of these micro alloys in caustic soda (NaOH) solution at different temperatures. The corrosion rate decreased by the addition of any percent of vanadium at 25°C compared to pure Al. The corrosion rate increased with increase of solution temperature from 25 to 40 and 60°C at any percent of vanadium addition. However, addition of vanadium reduced the corrosion rate at these temperatures at most wt.% of V addition. The maximum achieved reduction in corrosion rate due to vanadium addition was 40 % at 0.148 wt % and 60°C. The addition of 3 % potassium dichromate as corrosion inhibitor to NaOH solution reduced the average corrosion rates at any wt.% of vanadium. The inhibition efficiency ranged from 44- 58% at 25°C and from 97-99% at 40 and 60°C.

1. Introduction
Aluminum (Al), as well as its micro alloys, has been extensively applied in industry due to their particular properties such as high strength-to-weight ratio, good appearance and corrosion resistance [1-2]. Aluminum and its alloys solidify in a coarse columnar structure of large grain size [3], which tends to reduce their mechanical strength and surface quality, therefore they are grain refined by different rare earth elements such as titanium (Ti) or Ti plus boron (B) to produce fine and equiaxed homogeneous structure, to enhance their mechanical properties and surface quality [4]. The literature on the effect of addition of different grain refiners to Al and its alloys to improve their metallurgical structure and their mechanical properties, e.g. hardness, fracture toughness and fatigue strength is voluminous. However, little research work is reported on the effect of these grain refiners on their chemical corrosion resistance [5]. Vanadium (V) enhances the grain refining efficiency of the Al micro alloys when added at a weight percentage of 0.1% or more, i.e., above the peritectic limit on the Al-V phase diagram [4]. Vanadium addition was also found to improves hardness, mechanical strength and surface quality of Al and its alloys [6]. A wide spectrum of corrosion problems are encountered in industry as a result of combination of materials, environments and service conditions. Corrosion may not have a deleterious effect on a material immediately but it affects its mechanical strength, physical appearance and it may lead to serious operational problems in future [7]. Corrosion attack on Al surfaces is usually quite obvious since the products of corrosion are white and generally more voluminous than the original base metal taking the forms of general etching, pitting or roughness of metal surfaces [8,9]. In highly alkaline solutions, e.g. sodium hydroxide (NaOH), the dissolution
process occurs easily and fast resulting in hydrogen gas (H₂) evolution [10]. First the reaction begins with the dissolution of the protective oxide film (hydration process at the film) and as a result hydroxide ions (OH⁻) are formed:

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \]  (1)

Then aluminum reacts with hydroxide ions in alkaline solution as follows:

\[ Al + 4OH^- \rightarrow Al(OH)_4^- + 3e^- \]  (2)

The overall main reaction taking place can be represented by the following equation:

\[ 2Al + 2OH^- + 6H_2O \rightarrow 2Al(OH)_4^- + 3H_2 \]  (3)

Potassium dichromate (K₂Cr₂O₇) is a common inorganic chemical reagent; it is a crystalline ionic solid with a very bright, red-orange color most commonly used as an oxidizing agent in various laboratory and industrial applications, [11]. As with all hexavalent chromium (Cr) compounds (chemical compounds that contain this element in the +6 oxidation state), dissolve as stable complexes in water, transport easily, and adsorb on oxide surfaces. The octahedral, d₃, trivalent compounds of Cr form very stable inert oxides; K₂Cr₂O₇ is a mild oxidizer, the reaction between aluminum and K₂Cr₂O₇ in alkaline media is given in the following equation:

\[ Al + Cr_2O_7^{2-} + 7H_2O + 3e^- \rightarrow Al(OH)_4^- + 2Cr^{3+} + 10OH^- \]  (4)

2. Materials and Experimental Procedures

2.1 Materials
Commercially pure Al of 99.8% having the chemical composition shown in Table1, high purity titanium and vanadium were used. Graphite crucibles were used for melting and graphite rods were used for stirring.

2.2 Preparation of the master and binary alloys
The binary Al-Ti and Al-V master alloys were laboratory prepared and used for preparing the five different microalloys which are used throughout this work are shown in Table2.

The grain refinement process started by manufacturing the binary Al-Ti and Al-V master alloys by adding the calculated amount of pure Ti or V to the molten Al in the graphite crucible at 1100 °C under cryolite flux to avoid oxidation. The temperature was kept constant for 30 minutes, then the crucible was brought out from the furnace, and stirred for two minutes before casting the alloy into a plate form of less than 10mm thickness by spreading it over a thick cast iron plate. The preparation of the different microalloys by melting the predetermined quantity of Al and the calculated amount of the binary master alloy was added to the molten Al bath, stirred and its temperature was raised to 820 °C, then lowered to 750 °C for 10 minutes and finally the crucible was brought out of the furnace, stirred for two minutes and left to solidify and cool inside the crucible, outside the furnace.

| Table 1. Chemical composition (wt %) of commercially pure Aluminium [5] |
|-----------------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Element | Fe     | Si     | Cu     | Mg     | Ti     | V      | Zn     | Mn     | Na     | Al     |
| Wt. %   | 0.09   | 0.05   | 0.005  | 0.004  | 0.004  | 0.008  | 0.005  | 0.001  | 0.005  | Bal.   |
Table 2. Chemical composition of aluminum and its different microalloys (wt.\%)

| Specimen No. | Ti  | V  | Al  |
|--------------|-----|----|-----|
| 1            | 0.15| 0  | Rem.|
| 2            | 0.15| 0.005| Rem.|
| 3            | 0.15| 0.053| Rem.|
| 4            | 0.15| 0.112| Rem.|
| 5            | 0.15| 0.148| Rem.|
| 6            | 0.15| 0.236| Rem.|

2.3 Corrosion Testing Procedure
Cylindrical specimens having 10 mm diameter and 25 mm² working surface area were prepared from Al and its five micro alloy, immersed in 1 % HCl solution at room temperature for two minutes to remove any protective or oxide layer, rinsed in distilled water, kept in acetone for one minute, dried in hot air and then fixed in position in the PVC teflon holder, shown in figure 1. The specimens were then immersed in 0.2 M NaOH solution of pH 13.3 at 25, 40 or 60 °C in a stand still condition, (without stirring). After a specified period of time (taken as 24 hr), the specimens were removed from the teflon holder, rinsed with acetone, dried and kept in the desiccator for two hours and weighted again from which the weight loss per mm² is calculated in each specimen. Each test was repeated twice to guarantee the repeatability of the results within an accepted difference of 3%. The average corrosion rate was then obtained.

![Figure 1. PVC teflon holder with the metal specimens](image)

2.3.1 Corrosion Rate Measurement.
The weight loss technique involves exposing a specimen of material to a process environment for a given duration, then removing the specimen for analysis. The weight loss taking place over the period of exposure in the corrosive medium [2], is being expressed as a corrosion rate according to the following expression:

\[
CR = \frac{\Delta W}{t \cdot A}
\]

where CR is the corrosion rate, \(\Delta W\) is weight loss (mg), \(t\) is the time (yr), \(A\) is the surface area exposed in the corrosive medium (mm²).

2.4 Surface Examination Procedure
Microstructural examination of the surface of each specimen was examined by light microscope before and after corrosion test. Photographs of the etched specimens were taken using optical microscope. Detailed procedure of etching and surface examination is described elsewhere [2].
3. Results and Discussion

3.1 Effect of vanadium addition

Figures 2, 3 and 4 show the effect of vanadium addition on the corrosion rate of commercially pure aluminum grain refined by Ti, (Al-0.15 % Ti) at solution temperatures of 25, 40 and 60 °C, respectively. It can be seen from Fig.2 that, except at infinitesimally small percent of V addition (less than 0.05%), vanadium addition has generally resulted in a decrease in corrosion rate comparable with the commercially pure Al specimen. The maximum decrease in corrosion rate was 38 % and the minimum was 11 % at 0.053 and 0.148 wt % vanadium addition respectively. This is attributed to the small grain size caused by the grain refinement caused by the addition of Ti or V either alone or together, which results in increasing the number of grain boundaries and reducing the surface roughness, both of which reduces corrosion rate, references, [3,6].

![Figure 2. Corrosion rate vs. vanadium percent of specimens at solution temperature of 25°C.](image)

![Figure 3. Corrosion rate vs. vanadium percent of specimens at solution temperature of 40°C.](image)

Increasing the temperature of the NaOH solution to 40 and then to 60 °C resulted in higher rates of corrosion for a given micro alloy (fixed wt.% V). However, as the wt. % of vanadium is increased in the microalloy, the corrosion rate decreased significantly at the three solution temperatures. At the higher temperatures, the trend remained the same but addition of V became more effective as the temperature of the NaOH solution is increased. As can be deduced from Fig.3, the maximum reduction in the corrosion rate was approximately 28 % at 0.112 wt % V, and the minimum reduction was approximately 5% at 0.053 wt % V at 40 °C. Figure 4 indicates that the maximum reduction in the corrosion rate was approximately 40 % at 0.112 wt % V, compared to the minimum reduction of approximately 6 % at 0.148 wt % V at 60 °C. All reduction percentages are obtained from comparison with the performance of pure aluminum with zero wt % V.
3.2 Effect of Solution Temperature

In Figure 5, the average corrosion rates of micro alloys vs. wt% V at the three temperatures 25, 40 and 60 °C are compared. The Figure reveals that at for a given micro alloy, the average corrosion rates at 60 °C is approximately 280 mg/mm².yr compared to 140 at 40 °C and 15 mg/mm².yr at 25 °C. In making this comparison, the corrosion rate at 0.05 wt. % V is excluded due to the different behavior exhibited by this micro alloy. The corrosion rate rises sharply from zero wt.% to 0.053 wt. % V before declining to values virtually below those of vanadium-free micro alloy. The reduction in average corrosion rates reached a maximum of 40% at 0.112 wt% V at 40 °C and a minimum of 6% at 0.148 wt.% V at 60 °C.

3.3 Surface Micrographs

Figure 6a shows the original microstructure of the commercially pure Al at magnification of X400 while figure6B is a photomicrograph showing the microstructure of commercially pure Al after an exposure of 24 hrs to 0.2 M NaOH solution at 60°C at the same magnification. The difference between the two graphs indicates clearly the corrosion action in the forms of pitting as well as wiping off the grains and their boundaries.
Figure 6a. Microstructure of commercially pure aluminum. (B) Microstructure of commercially pure aluminum after exposure of 24 hrs to 0.2 M NaOH solution at 60°C. (C) Original microstructure of Al-0.15 % Ti-0.112 % V micro alloy. (D) Microstructure of Al-0.15 % Ti-0.112 % V micro alloy after exposure of 24 hrs to 0.2 M NaOH solution at 60°C (all magnifications at X400).

Figure 6c is a photomicrograph of the original microstructure of Al-0.15 % Ti-0.112 % V micro alloy at magnification of X400. It shows the grain refinement effect of 0.112 wt % vanadium addition where the grains are much finer than those of commercially pure Al depicted by Figure 6A. A photomicrograph showing the microstructure of Al-0.15 % Ti-0.112 % V micro alloy after an exposure of 24 hrs to 0.2 M NaOH solutions at 60°C at magnification of X400 is shown in figure 6D. This Figure shows that the grains and their boundaries are wiped off. This agrees with the results obtained in the previous Figures for the corrosion rate of Al and its micro alloys in the NaOH solution.

3.4 Effect of Inhibitor and Inhibition Efficiency

Figure 7 shows the effect of V addition at different wt.% to commercially pure Al grain refined by Ti on the corrosion rate in NaOH solution at different temperatures in the presence of 3 wt% potassium dichromate (K₂Cr₂O₇) as inhibitor. It can be seen from this Figure that the corrosion rate increases as the V percent increases, but remained much less than the corrosion rate in the absence of the K₂Cr₂O₇ inhibitor. A comparison between Fig.7 and Fig.5 reveals that the highest corrosion rate in presence of inhibitor is only 8 mg/mm².yr whereas that in absence of inhibitor is 330 mg/mm².yr. In making this comparison, the corrosion rate data at 0.05 wt. % V is excluded as indicated earlier.
The presence of K₂Cr₂O₇ as an inhibitor caused significant reduction in the corrosion rate (that is, promotes corrosion resistance) at all rates of V addition as compared to the uninhibited NaOH solution at the three temperatures considered. This effect is due to adsorption of K₂Cr₂O₇ molecules on the Al surfaces thus forming a barrier layer that minimizes metal dissolution and release of its ions into solution. In Figures 8, 9 and 10 show comparison among the average corrosion rate vs. V addition percent at temperatures of 25, 40 and 60 °C, respectively in both blanks in the uninhibited and inhibited NaOH solutions. These Figures indicate that addition of K₂Cr₂O₇ at 3 wt.% to the strong alkaline solution of NaOH was effective in corrosion inhibition at any these temperature for all of the micro alloys at any wt.% vanadium. The inhibition effect is obviously an increasing function of temperature as shown from the corrosion rate curves at 25 and 40 °C. After 40 °C, the temperature effect on inhibition effect diminishes as indicated by comparing the corrosion rate curves at 40 and 60 °C. This can be explained by the enhancing effect of temperature on the adsorption of inhibitor molecules on Al surface. Based on these observations, it is suggested that below 40 °C, corrosion rate is highly temperature dependent as metal dissolution requires high energy of activation. Over 40 °C, the amount of activation energy becomes much less, thus further temperature increase will not have significant effect on corrosion rate.
The corrosion inhibition efficiency, IE, is defined as [13]:

$$\text{IE } \% = \frac{\text{CR}_b - \text{CR}_{wi}}{\text{CR}_b} \times 100\%$$

(6)

Where CR$_b$ is the corrosion rate in blank (uninhibited) solution and CR$_{wi}$ is the corrosion rate in solution with inhibitor, both in (mg/mm$^2$.yr) units. The effect of V addition on the inhibition efficiency at different temperatures is shown in Table3. It can be seen from the result in this table that the presence of K$_2$Cr$_2$O$_7$ as an inhibitor in NaOH solution improved the inhibition efficiency of the solution by 90-99.5% for commercially pure Al and 97-99% in case of addition of Al-vanadium micro alloys. IE is obviously a function of temperature.

**Table 3.** Effect of V Addition on the Inhibition Efficiency in NaOH-K$_2$Cr$_2$O$_7$ Solution at Different Temperatures

| wt. % Vanadium | Inhibition Efficiency, IE % @ 25 °C | @ 40 °C | @ 60 °C |
|---------------|-----------------------------------|--------|--------|
| 0             | 90                                | 98.58  | 99.53  |
| 0.005         | 92.68                             | 98.77  | 99.36  |
| 0.053         | 50                                | 96.85  | 98.88  |
| 0.112         | 43.75                             | 96.92  | 98.44  |
| 0.148         | 57.5                              | 98.34  | 98.44  |
| 0.236         | 53.13                             | 99.6   | 98.66  |

4. Conclusions

The addition of vanadium in small weight percentages (0.053-0.236) to micro alloys of aluminum and Al grain refined by Ti is beneficial in improving their corrosion resistance in highly alkaline (pH=13.3) NaOH solution, both blank (uninhibited) and in presence of potassium dichromate at 3%. The corrosion rates of these micro alloys increased with temperature increase in the range 25-60°C in
absence of the inhibitor, however, in the presence of inhibitor, the corrosion rates decreased with temperature resulting in inhibition efficiency much higher at 40-60 C than at 25 C.

5. References

[1] Kalpakjian S and Schmid S R 2002 Manufacturing Processes for Engineering Materials (4th ed.), New Jersey: Pearson Education In.

[2] Fontana M G 1986 Corrosion Engineering, New York, McGraw-Hill international editions, 3rd Edition.

[3] Abdel-Hamid A A 1985 On the Mechanism of Grain Refinement of Aluminum by Small Addition of Ti and B The Second Arab Aluminum Conference, Arabal, Cairo.

[4] Abdel-Hamid A A 1989 Effect of Other Elements on the Grain Refinement of Al by Ti or Ti and B Part1: A critical Review Egypt.

[5] Zaid A I O, Allawi G T Aand Al-Haj-Ali A 2012 Key Engineering Materials, 510-511 481-486.

[6] Zaid A I O and Abdel-Hamid A A1999 Effect of Vanadium on Mechanical Behavior, Mechananability and Wear Resistance of Aluminum Grain Refined by Ti & B International Symposium on Advanced Materials ISAM-99, Islamabad.

[7] Zaki Ahmad 2006 Principles of Corrosion Engineering and Corrosion Control Elsevier, Amsterdam.

[8] Pierre R Roberge 2008 Corrosion Engineering: Principles and Practice, McGraw-Hill.

[9] Kaufman J G 2005 Corrosion of aluminum and aluminum alloys ASM Handbook 13B, Corrosion Materials ASM International Materials Park, OH 95 – 124.

[10] Emregul K C and Abbas A Aksut 2000 The Behavior of Aluminum in Alkaline Media, Corrosion Science 42 2051-2067.

[11] Cotton F A, Wilkinson G and GausP L 1995 Basic Inorganic Chemistry, 3rd Edition, Wiley.

[12] Allawi G T 2011 Effect of Vanadium Addition on the Chemical Corrosion Resistance of Commercially Pure Aluminum Grain Refined by Titanium at Different Temperatures, M.Sc. Thesis, Dept. of Chemical Engineering University of Jordan, Amman 120.

[13] El Maghraby A A 2009 The Open Corrosion Journal 2 189-196.