Corrosion Behavior of V$_2$AlC and Cr$_2$AlC in 0.01 N Calcium Hydroxide at Four Temperatures

Rana A. Majed Anaee[1*] and Ahmed M. Al-Ghaban[1]

[1]*Department of Materials Engineering, University of technology, Baghdad-Iraq.*

Authors' contributions

This work was carried out in collaboration between both authors. Author AMA manufactured the materials and author RAMA analyzed and interpreted and prepared the manuscript and also read and approved the final manuscript.

Original Research Article

ABSTRACT

Corrosion behavior of V$_2$AlC and Cr$_2$AlC materials have been investigated in 0.01N Ca(OH)$_2$ at pH=11.7 using Potentiostat to estimate corrosion parameters. The results show that V$_2$AlC material has more noble potential and lower current density than Cr$_2$AlC over temperatures include 303, 313, 323 and 333K. Polarization resistance which calculated according to Stern-Geary equation confirms the most resistance for V$_2$AlC in experimental conditions. The change in free energy was more negative for Cr$_2$AlC than V$_2$AlC, this means that V$_2$AlC has less ability to corrosion. The negative value of ΔS for V$_2$AlC confirms the later result. It`s known that corrosion rate depends on the value of the activation energy which is represents the energy maxima of intermediate transition states through which the entity must pass in transforming and the energy that must be acquired, from Arrhenius plots have been conducted that activation energy E$_a$ for V$_2$AlC was more than for Cr$_2$AlC.

Corresponding author: E-mail: dr.Rana.A.Anaee@uotechnology.edu.iq;

1. INTRODUCTION

The MAX phase materials are made up of an early transition metal M in the periodic table, an element from the A groups, usually IIIA and IVA, and a third element, X, which is either nitrogen or carbon, in the composition $M_{n+1}AX_n$, where n is 1, 2 or 3.

Many authors were interested fabrication of MAX phase materials and studied of some their physical and mechanical properties of the layered ternary compound [1-16]. On other hand, some authors highlighted corrosion of MAX phase materials at high temperatures (oxidation). While there are very little studies focused the corrosion at normal temperatures. V.D. Jovic et al. studied the corrosion behavior of select MAX phases in 1M of NaOH, HCl and H_2SO_4 [17]. Also, Dong et al. studied the corrosion of Cr_2AlC compounds [18]. Rana et al. studied the corrosion behavior of V_2AlC and Cr_2AlC in 0.01N NaCl solution [19]. Numerous authors studied the corrosion behavior in calcium hydroxide as a main component of the corrosion in concrete [20-25].

The present work involves studying the corrosion behavior of two MAX phase materials include V_2AlC and Cr_2AlC in 0.01 $Ca(OH)_2$ at four different temperatures (303, 313, 323 and 333K) by potentiostat to estimate the corrosion resistance of these materials and to estimate some thermodynamic and kinetic parameters.

2. EXPERIMENTAL PROCEDURE

MAX phase materials were fabricated using powder metallurgy by weighing V, Cr, C, and Al powders (99% pure) and mixing them using ball milled, cold pressing and sintering procedures at 1373-1623 K for 6 hrs.

Characterization of fabricated materials was achieved using X-ray diffraction (XRD). Corrosion behavior of these materials was estimated with a WINKING M Lab 200 Potentiodynamic equipment at 5 $mV.sec^{-1}$ to obtain corrosion parameters such as corrosion potential and corrosion current density. All experiments were performed at four temperatures 303, 313, 323 and 333K using jacket cell.

0.01N calcium hydroxide was used as diluted base solution at pH=11.7

3. RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction (XRD) of prepared materials which confirms the presence of MAX phases. Figs. (2) and (3) show the polarization curves of V_2AlC and Cr_2AlC respectively in calcium hydroxide at four different temperatures, these curves show the cathodic and anodic regions.

Reduction of oxygen occurs at cathodic sites according to the following reaction:

$$O_2 + 4e + 2H_2O \rightarrow 4OH^-$$
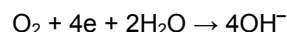
While oxidation of metals can be take place at anodic sites as follows:

$$M \rightarrow M^{n+} + ne$$
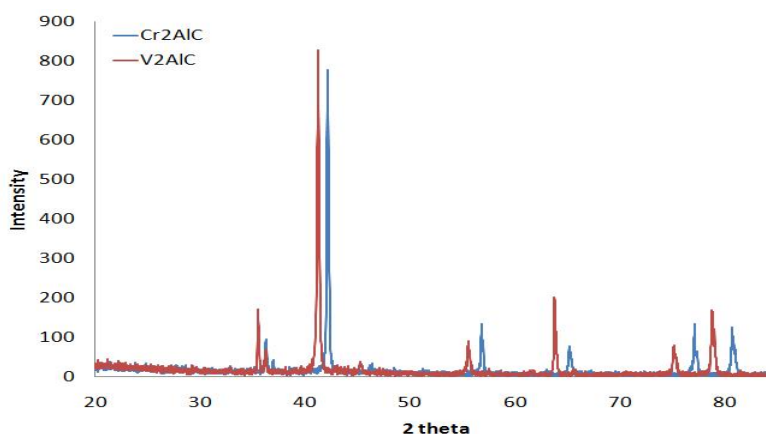
Fig. 1. XRD of prepared MAX phase materials

V$_2$AlC
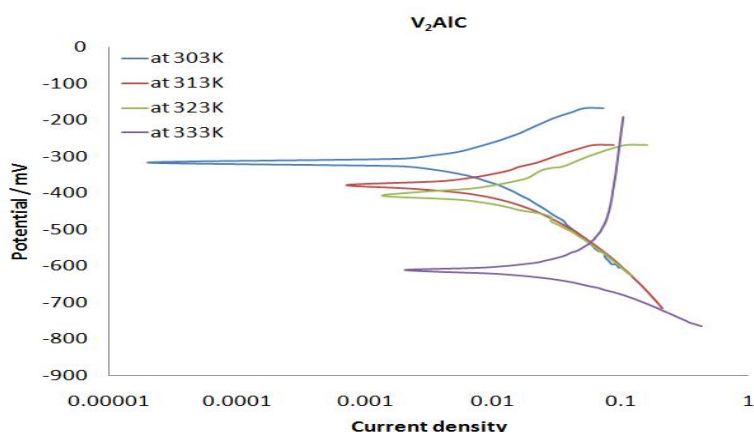
Fig. 2. Polarization curve of V$_2$AlC in 0.01N Ca(OH)$_2$ at four temperatures
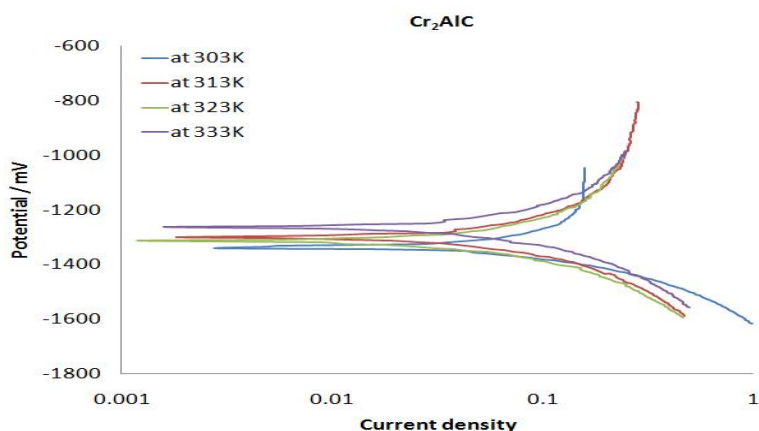
Cr$_2$AlC

Fig. 3. Polarization curve of Cr$_2$AlC in 0.01N Ca(OH)$_2$ at four temperatures

The data of corrosion were measured are listed in (Table 1). These data indicate that V$_2$AlC has more noble corrosion potentials than Cr$_2$AlC, and lower corrosion current densities which give indication about the corrosion rate. The higher corrosion resistance of V$_2$AlC is due to the protective film of vanadium oxide on material surface, oxygen incorporation occur by oxygen replaces carbon in V$_2$AlC but is incorporated interstitially in the Al layer of Cr$_2$AlC, even for carbon-deficient Cr$_2$AlC [26]. At pH=11.7, Al is passive therefore it is do not allow to carbon vacancies to be form. Cathodic Tafel slope is lower than anodic once, this means that the change in potential with current density was lower at cathodic sites than anodic once which may be due to form calcium salts on cathodic sites.

The data of polarization resistance R$_p$ which was calculated according to Stern-Geary equation

[27], indicate that the resistance of V$_2$AlC was more than that for Cr$_2$AlC.

$$R_p = \left(\frac{dE}{di}\right)_{i=0} = \frac{b_a b_c}{2.303(b_a + b_c)i_{corr}}$$

where b$_a$ and b$_c$ are anodic and cathodic Tafel slopes respectively.

Thermodynamic laws tell us that there is a strong tendency for high energy state in a system to transform into low energy state. It is this tendency of metals to recombine with components of the environment that leads to the phenomenon known as corrosion. The free–energy change accompanying an electrochemical reaction can be calculated by the following equation [28]:

$$\Delta G = -nFE$$

where *ΔG* is the free–energy change, *n* is the number of electrons involved in the reaction, *F* is the Faraday constant, and *E* equals the cell potential (E=E$_{corr}$).

At constant temperature, the change in free energy more negative for Cr$_2$AlC than for V$_2$AlC, this means that V$_2$AlC has less ability to corrosion. Also increasing temperature has more effect on *ΔG* for V$_2$AlC than that for Cr$_2$AlC.

From the values of *ΔG* at several temperatures, the change in the entropy (*ΔS*) of corrosion process could be derived according to the well–known thermodynamic relation:

$$\Delta S = -\frac{d(\Delta G)}{dT}$$

From Fig. 4, can be seen that the increasing of temperature more affect on change in free energy for V$_2$AlC compared with Cr$_2$AlC. The change in free energy, ΔG, is related to ΔH, the change in the enthalpy, and ΔS, the change in entropy of the corrosion reaction at a constant temperature, T, by the equation [29]:

$$\Delta G = \Delta H - T\Delta S$$

The change in entropy was negative for V$_2$AlC, while positive value for Cr$_2$AlC, this means that the corrosion of V$_2$AlC gave stable corrosion products such as protective layer of metal oxide. Values of (ΔS) reflect the change in the order and orientation of the solvent molecules around the hydrated metal ions in the corrosion medium when metal atoms were corroded and subsequently hydrated in the solution.

The positive value of ΔS suggests a lower order in the solvated states of the metal ions as compared with the state of metal atoms in the crystal lattice of the corroding electrodes. Value of the enthalpy of corrosion (ΔH) reflects the enthalpy changes associated with the corrosion reaction and ranged from negative to positive values indicating exothermic or endothermic nature of corrosion reaction. The positive values of ΔH refer to endothermic process of corrosion for MAX phase material. Thermodynamic parameters are listed in Table (2).

The rate (r) of corrosion in a given environment is directly proportional with its corrosion current density (i$_{corr}$) in accordance with the relation [30]:

$$r = 0.13 \left(e/\rho \right) i_{corr}$$

Here (*e*) is the equivalent weight of the metal and (*ρ*) is its density. For the increasing values of (i$_{corr}$) with a temperature follow Arrhenius equation, it is reasonable as:

$$i_{corr} = A\exp(-E_a / RT)$$

Where *A* and *E$_a$* are the pre- exponential factor and energy of activation of the corrosion process respectively. Values of *E$_a$* were derived from the slopes of the (log i$_{corr}$) versus (1/T) linear plots as in Fig. (5). The values of activation energy and log A for V$_2$AlC higher than that for Cr$_2$AlC, this result confirms that corrosion resistance of V$_2$AlC more than that of Cr$_2$AlC. Values of activation energy and pre- exponential factors are listed in Table (3).
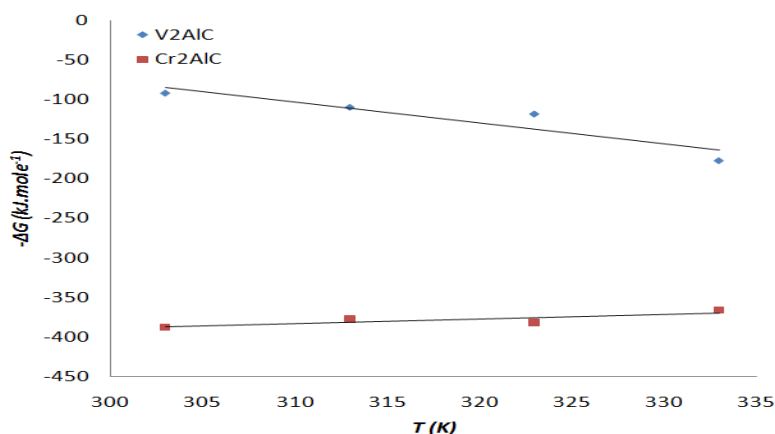

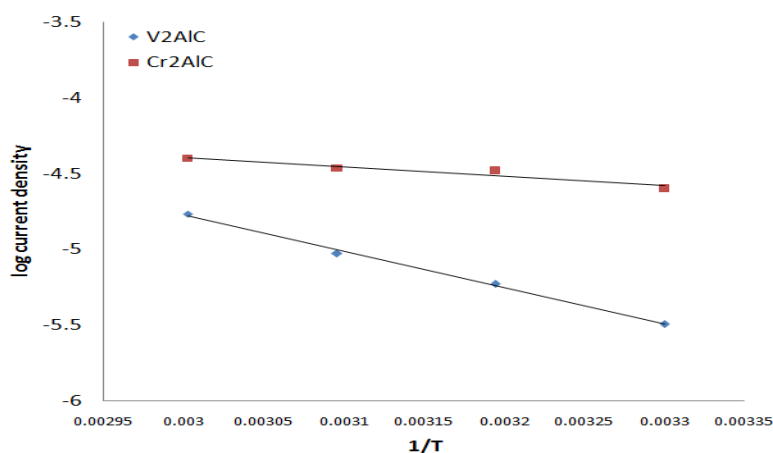**Fig. 4. The relationship between ΔG and T for MAX phase materials**

Fig. 5. Arrhenius plot for MAX phase materials

Table 1. Corrosion parameters for V$_2$AlC and Cr$_2$AlC in 0.01N Ca(OH)$_2$ at four temperatures

Material	Temp. K	E_{corr} mV	i_{corr} $\mu A.cm^{-2}$	$-b_c$ $mV.dec^{-1}$	$+b_a$ $mV.dec^{-1}$	$R_p x10^3$ $\Omega.cm^2$
V$_2$AlC	303	316.4	3.19	111.6	117.5	7.79
	313	378.4	5.88	110.0	128.8	4.38
	323	408.0	9.31	132.2	133.8	3.10
	333	612.6	17.00	82.8	124.5	1.27
Cr$_2$AlC	303	1338.8	32.31	85.7	128.7	0.69
	313	1304.5	32.95	139.1	176.8	1.03
	323	1319.5	34.29	147.6	199.2	1.07
	333	1266.2	39.56	167.6	214.9	1.03

Tables 2. The thermodynamic quantities for V$_2$AlC and Cr$_2$AlC in 0.01N Ca(OH)$_2$ at four temperatures

Material	T (K)	$-\Delta G$ (kJ.mole^{-1})	ΔS (kJ.mol^{-1}.K^{1})	ΔH (kJ.mole^{-1})
V$_2$AlC	303	91.60	-2.65819	0.29
	313	109.55		0.34
	323	118.12		0.36
	333	177.35		0.52
Cr$_2$AlC	303	387.58	0.587106	1.28
	313	377.65		1.21
	323	382.00		1.18
	333	366.56		1.10

Table 3. Values of activation energy (E$_a$), pre-exponential factors (A) for V$_2$AlC and Cr$_2$AlC in 0.01N Ca(OH)$_2$

Material	E_a (kJ.mol^{-1})	Log A
V$_2$AlC	19.95	2.424
Cr$_2$AlC	12.80	0.337

4. CONCLUSION

Corrosion behavior of V$_2$AlC and Cr$_2$AlC materials have been investigated in 0.01N Ca (OH)$_2$ as attempt to find reproducible industrial materials embedded in concrete. The data of corrosion test indicated that V$_2$AlC more resistance than Cr$_2$AlC, i.e., the corrosion potentials were more noble for V$_2$AlC with less current densities. Thermodynamic and kinetic calculations showed the corrosion process is less spontaneous for V$_2$AlC than that for Cr$_2$AlC through the change in free energy value, also the negative value of ΔS for V$_2$AlC compared with the positive value for Cr$_2$AlC in addition to get more activation energy E$_a$ for V$_2$AlC than that for Cr$_2$AlC.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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