

Corrosion Behavior of V₂AlC and Cr₂AlC in 0.01 N Calcium Hydroxide at Four Temperatures

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ABSTRACT

Corrosion behavior of V₂AlC and Cr₂AlC materials have been investigated in 0.01N Ca(OH)₂ at pH=11.7 using Potentiostat to estimate corrosion parameters. The results show that V₂AlC material has more noble potential and lower current density than Cr₂AlC over temperatures include 303, 313, 323 and 333K. Polarization resistance which calculated according to Stern-Geary equation confirms the most resistance for V₂AlC in experimental conditions. The change in free energy was more negative for Cr₂AlC than V₂AlC, this means that V₂AlC has less ability to corrosion. The negative value of ΔS for V₂AlC 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 V₂AlC was more than for Cr₂AlC.

Keywords: MAX phase material, corrosion in Ca(OH)₂, kinetic of corrosion, Corrosion of V₂AlC, Corrosion of Cr₂AlC.

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 H₂SO₄ [17]. Also, Dong et al. studied the corrosion of Cr₂AlC compounds [18]. Rana et al. studied the corrosion behavior of V₂AlC and Cr₂AlC 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 V₂AlC and Cr₂AlC in 0.01 Ca(OH)₂ at four different temperatures (303,

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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 1100-1350°C for 6 hrs.

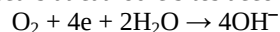
Characterization of fabricated materials was achieved using X-ray diffraction (XRD). Corrosion behavior of these materials was estimated with a WINKING M Lab 200 Potentiodynamic equipment at 5 mV.sec⁻¹ to obtain corrosion parameters such as corrosion potential and corrosion current density. All experiments 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

Figure (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 V₂AlC and Cr₂AlC 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:



While oxidation of metals can be take place at anodic sites as follows:



The data of corrosion were measured are listed in Table (1). These data indicate that V₂AlC has more noble corrosion potentials than Cr₂AlC, and lower corrosion current densities which give indication about the corrosion rate. The higher corrosion resistance of V₂AlC is due to the protective film of vanadium oxide on material surface. 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.

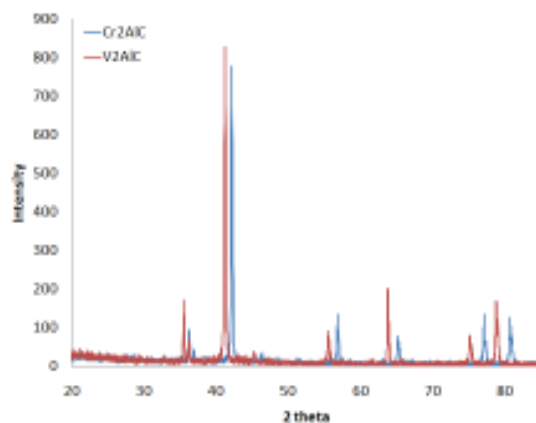


Fig. 1: XRD of prepared MAX phase materials.

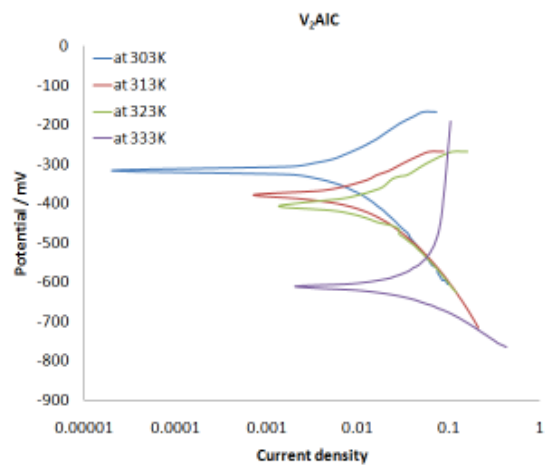


Fig. 2: Polarization curve of V_2AlC in 0.01N $Ca(OH)_2$ at four temperatures.

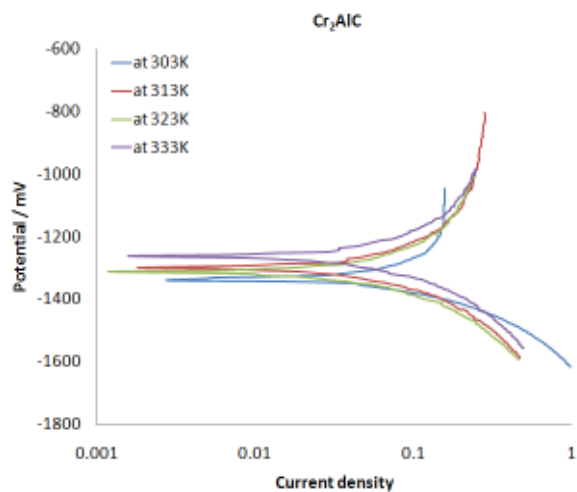


Fig. 3: Polarization curve of Cr_2AlC in 0.01N $Ca(OH)_2$ at four temperatures.

Table 1. Corrosion parameters for V₂AlC and Cr₂AlC in 0.01N Ca(OH)₂ at four temperatures.

Material	Temp. K	E_{corr} mV	i_{corr} μA.cm⁻²	-b_c mV.dec⁻¹	+b_a mV.dec⁻¹	R_p×10³ Ω.cm²
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

The data of polarization resistance R_p which was calculated according to Stern-Geary equation [26], indicate that the resistance of V₂AlC was more than that for Cr₂AlC.

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

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 [27]:

$$\Delta G = -nFE$$

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 Cr₂AlC than for V₂AlC, this means that V₂AlC has less ability to corrosion. Also increasing temperature has more effect on ΔG for V₂AlC than that for Cr₂AlC.

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 V₂AlC compared with Cr₂AlC. 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 [28]:

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

The change in entropy was negative for V₂AlC, while positive value for Cr₂AlC, this means that the corrosion of V₂AlC 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.

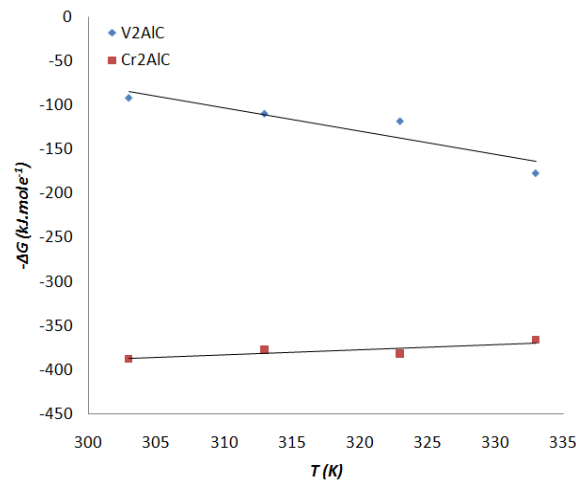


Fig. 4: The relationship between ΔG and T for MAX phase materials.

Tables 2. The thermodynamic quantities for V_2AlC and Cr_2AlC 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_2AlC	303	91.60	-2.65819	0.29
	313	109.55		0.34
	323	118.12		0.36
	333	177.35		0.52
Cr_2AlC	303	387.58	0.587106	1.28
	313	377.65		1.21
	323	382.00		1.18
	333	366.56		1.10

The rate (r) of corrosion in a given environment is directly proportional with its corrosion current density (i_{corr}) in accordance with the relation [29]:

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

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:

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

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 ($\log i_{\text{corr}}$) versus ($1/T$) linear plots as in Fig. (5). The values of activation energy and $\log A$ for V_2AlC higher than that for Cr_2AlC , this result confirms that corrosion resistance of V_2AlC more than that of Cr_2AlC .

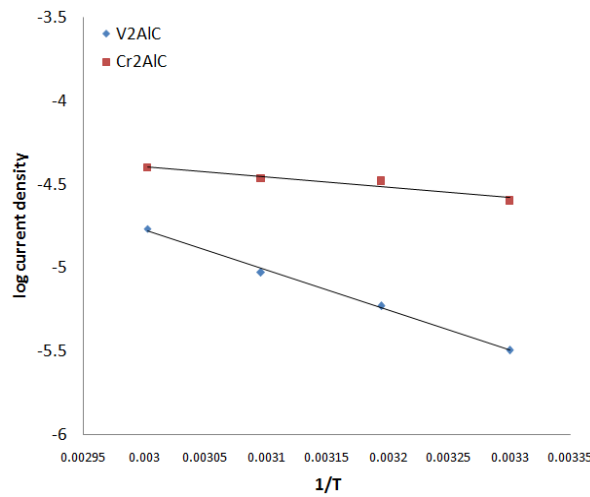


Fig. 5: Arrhenius plot for MAX phase materials.

Table 3. Values of activation energy (E_a), pre- exponential factors (A) for V_2AlC and Cr_2AlC in 0.01N $\text{Ca}(\text{OH})_2$.

Material	E_a (kJ.mol^{-1})	Log A
V_2AlC	19.95	2.424
Cr_2AlC	12.80	0.337

4. CONCLUSION

Corrosion behavior of V_2AlC and Cr_2AlC materials have been investigated in 0.01N $\text{Ca}(\text{OH})_2$ as attempt to find reproducible industrial materials embedded in concrete. The data of corrosion test indicated that V_2AlC more resistance than Cr_2AlC , i.e., the corrosion potentials were more noble for V_2AlC with less current densities. Thermodynamic and kinetic calculations showed the corrosion process is less

spontaneous for V_2AlC than that for Cr_2AlC through the change in free energy value, also the negative value of ΔS for V_2AlC compared with the positive value for Cr_2AlC in addition to get more activation energy E_a for V_2AlC than that for Cr_2AlC .

5. REFERENCES

- 1- Zhou YC, Wang XH, Sun ZM, Chen SQ. Electronic and structural properties of the layered ternary carbide Ti_3AlC_2 . J. Mater. Chem. 11. 2001; 2335–2339.
- 2- X.H. Wang and Y.C. Zhou. Intermediate-temperature oxidation behavior of Ti_2AlC in air. J. Mater. Res. 17(11). 2002; 2974–2981.
- 3- Wang X.H., Zhou Y.C. Microstructure and properties of Ti_3AlC_2 prepared by the solid–liquid reaction synthesis and simultaneous in-situ hot pressing process. Acta Materialia. 50. 2002; 3141–3149
- 4- Zhimei Sun, Rajeev Ahuja and Sa Li, and Jochen M. Schneider. Structure and bulk modulus of M_2AlC . $M=Ti, V$, and Cr . Appl. Phys. Lett. 83(5). 2003;899-901.
- 5- Jochen M. Schneidera,, Zhimei Suna, Raphael Mertensa, Fatih Uestela, and Rajeev Ahujac. Ab initio calculations and experimental determination of the structure of Cr_2AlC . Solid State Communications. 130. 2004;445–449.
- 6- Hettinger J. D., Lofland S. E., Finke P., Meehan T., Palma J., Harrell K., Gupta S., Ganguly A., El-Raghy T., and Barsoum M. W. Electrical transport, thermal transport, and elastic properties of M_2AlC ($M=Ti, Cr, Nb$, and V). Physical Review B 72. 2005;115-120.
- 7- Yuri Khoptiar, Irena Gotman,w and Elazar Y. Gutmanas. Pressure-Assisted Combustion Synthesis of Dense Layered Ti_3AlC_2 and its Mechanical Properties. J. Am. Ceram. Soc. 88(1). 2005; 28–33.
- 8- Zhimei Sun, DenisMusic, Rajeev Ahuja and Jochen M Schneider. *Ab initio* study of M_2AlN ($M = Ti, V, Cr$). J. Phys.: Condens. Matter. 17. 2005; L15–L19.
- 9- Wubian Tian, Peiling Wang, Guojun Zhang, Yanmei Kan, Yongxiang Li, and Dongsheng Yan. Synthesis and thermal and electrical properties of bulk Cr_2AlC . Scripta Materialia. 54. 2006; 841–846.
- 10- Wu-bian Tian, Pei-ling Wang, Guo-jun Zhang, Yan-mei Kan, and Yong-xiang Li. Mechanical Properties of Cr_2AlC Ceramics. J. Am. Ceram. Soc. 90(5). 2007;1663–1666.
- 11- Denis Music, Jens Emmerlich and Jochen M Schneider. Phase stability and elastic properties of $Ta_{n+1}AlC_n$ ($n = 1–3$) at high pressure and elevated temperature. J. Phys.: Condens. Matter. 19. 2007; 136207 (9pp).
- 12- Yanchun Zhou, Fanling Meng, and Jie Zhang. New MAX-Phase Compounds in the $V–Cr–Al–C$ System. J. Am. Ceram. Soc. 91(4). 2008; 1357–1360.
- 13- Wubian Tian, Peiling Wang, Yanmei Kan, and Guojun Zhang. Oxidation behavior of Cr_2AlC ceramics at 1100 and 1250°C. J Mater Sci.43. 2008;2785–2791.
- 14- Wubian Tian, ZhengMing Sun, and Hitoshi Hashimoto. Compressive deformation behavior of ternary compound Cr_2AlC . J Mater Sci. 44. 2009; 102–107.
- 15- Zhou W.B, Mei B.C., and Zhu J.Q. On the synthesis and properties of bulk ternary Cr_2AlC ceramics. Materials Science-Poland. 27(4/1). 2009; 973-980.
- 16- Chang-Sam Kim, Sung Ik Hwang, Jung-Soo Ha, Seung-Min Kang and Deock-Soo Cheong. Synthesis of a Cr_2AlC - Ti_2AlC ternary carbide. Journal of Ceramic Processing Research. 11(1). 2010;82-85.

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- 17- Jovic V.D., Jovic B.M., Gupta S., El-Raghy T. and Barsom M.W. Corrosion behavior of select MAX phases in NaOH, HCl and H₂SO₄. Corrosion Science. 48. 2006; 4274-4282.
- 18- Dong Bok Lee, Thuan Dinh Nguyen, and Sang Whan Park. Corrosion of Cr₂AlC in Ar/1%SO₂ Gas Between 900 and 1200 °C. Oxidation of Metals. 75(5-6). 2011; 313-323.
- 19- Rana Afif Majed, Ahmed M. Al-Ghaban, Russul F. Faleh. Corrosion Behavior of V₂AlC and Cr₂AlC MAX phase Materials in 0.01N NaCl. Asian Journal of Engineering and Technology. 2(3). 2014; 244-254.
- 20- Amir Poursaee. Corrosion of steel bars in saturated Ca(OH)₂ and concrete pore solution. Concrete Research Letters. 1(3). 2010;90-97.
- 21- Ramirez E., Gonzalez J. A., Bautista A. The protective efficiency of galvanizing against corrosion of steel in mortar and in Ca(OH)₂ saturated solutions containing chlorides. Cement and Concrete Research. 26. 1996; 1525.
- 22- Gonzalez J. A., Miranda J. M., Otero E., Feliu S. Effect of electrochemically reactive rust layers on the corrosion of steel in a Ca(OH)₂ solution. Corrosion Science. 49. 2007; 436.
- 23- Nakayama N. Inhibitory effects of nitrilotris (methylenephosphonic acid) on cathodic reactions of steels in saturated Ca(OH)₂ solutions. Corrosion Science. 42. 2000; 1897.
- 24- Nakayama N., Obuchi A. Inhibitory effects of 5-aminouracil on cathodic reactions of steels in saturated Ca(OH)₂ solutions. Corrosion Science. 45. 2003; 2075.
- 25- Gonzalez J. A., Cobo A., Gonzalez M. N., Otero E. On the effectiveness of realkalisation as a rehabilitation method for corroded reinforced concrete structures. Materials and Corrosio. 51. 2000; 97.
- 26- Rana A. Majed, Hanaa Al-Kaisy, and Hind B. Al-Atrakchy. Effect of Chloride Ions on the Corrosion Behavior of Al-Zn Alloy in NaOH Solution at Four Different Temperatures. Al-Khwarizmi Engineering Journal. 4(4). 2008; 26-36.
- 27- Sherir L. L. Corrosion. Metal/Environment Reactions. 2nd ed. 1. 1976; 4:12.
- 28- Naema A. Hikmat, Ahlam M. Farhan and Rana A. Majed. Effect of Deaeration on the Corrosion of Pure Aluminum and Its Three alloys in NaOH solution at pH=11. Eng. & Tech. Journal .27(8). 2009; 1532-1543.
- 29- Rana A. Majed. Galvanic Corrosion of Dental Alloys and Amalgam in Artificial Saliva Containing Citric Acid. Eng. & Tech. Journal. 31(12). 2013; 2299-2310.