

Corrosion Behavior of V_2AlC in Different Media

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Abstract

This work involves studying corrosion behavior of manufactured V_2AlC by Potentiostat to estimate corrosion resistance in different media include 0.01N of HCl, H_2SO_4 , NaCl and NaOH over temperatures range of 303–333 K. Polarization resistance values which calculated by Stern-Geary equation indicated that V_2AlC has the highest resistance in basic medium, while the lowest resistances were in acidic media. Activation energy has been calculated between 303 and 323 K, and the results indicate that the highest energy was in basic medium. The later result was good agreement with the result of corrosion resistance.

Keywords: MAX phase materials, Corrosion behavior, V_2AlC .

1. Introduction

From simple commodities to advanced technology, ceramics and metals are the most common materials being used, despite the fact that the two of them have almost opposite properties. Ceramics are good insulators, have good corrosion resistance, but are extremely brittle. On the other hand, metals are known as good electrical and thermal conductors, machinable, have high elastic moduli, but frequently show poor corrosion resistance. The search for materials which have the combination of both metal and ceramic properties is becoming more important in the 21st century. Transition Metal Carbides and Nitrides, developed by Jeitschko and Nowotny in 1960's, are ceramics which also have metal properties [1]. This new class of materials is called the MAX phases because of its compositions, where M stands for an early transition metal, A is an A-group element (mostly 13 or 14) and X is either C and/or N. MAX phases are a good electrical and thermal conductors, machinable, and exhibit good corrosion resistance. They have high elastic moduli, good damage tolerance, and excellent thermal shock resistance [2].

Many authors were interested fabrication of V_2AlC and studied of some their physical and mechanical properties. Zhimei et al. [3] performed theoretical studies of the bulk modulus of M_2AlC , where M_2 Ti, V, Cr by means of *ab initio* total energy calculations using the projector augmented wave methods. The bulk modulus of M_2AlC increases as Ti is substituted with V and Cr by

19% and 36%, respectively. This can be understood since the substitution of Ti by V and Cr is associated with an extensive increase in the M–Al and M–C bond energy. Hettinger et al. [4] investigated the electronic, magnetotransport, thermoelectric, thermal, and elastic properties of four M_2AlC phases: Ti_2AlC , V_2AlC , Cr_2AlC and Nb_2AlC . The electrical conductivity, Hall coefficient, and magneto-resistances are analyzed within a two-band framework assuming a temperature-independent charge carrier concentration. With room temperature thermal conductivities in the 25 W/m K range - 45 W/m K for V_2AlC , they are also good thermal conductors.

Yanchun et al. [5] synthesized new layered compounds, $(V_{0.5}Cr_{0.5})_3AlC_2$, $(V_{0.5}Cr_{0.5})_4AlC_3$, and $(V_{0.5}Cr_{0.5})_5Al_2C_3$ by reactive hot pressing V, Cr, Al, and graphite powders. The crystal structures of these new phases were determined using a combination of X-ray diffraction and scanning transmission electron microscopy. Chunfeng et al. [6] studied mechanical properties of V_2AlC such as flexural strength, fracture toughness and compressive strength. Also, they showed that V_2AlC could retain a high degree of Young's modulus up to 1200°C. Below 800°C, V_2AlC showed excellent thermal shock resistance. Darwin et al. [7] studied the influence of deposition temperature on phase formation of V_2AlC by magnetron sputtering from elemental targets. While Z.J. Yang et al. [8] studied electronic and phononic properties of V_2AlC .

The aim of present work is fabricate the V_2AlC by powder metallurgy and its corrosion behavior in different media with 0.01N concentration at four temperatures 303, 313, 323 and 333K.

2. Experimental Part

To fabricate the V_2AlC sample, V, C and Al powders (99% pure) were mixed in stoichiometric proportions, ball milled (BAIRD & TATLOCK) for 20 min at high level of speed for each sample, cold pressed using the hydraulic press machine type (Mega 50 Ton Max) and placed in a graphite die in a vacuum hot press (MTI Corporation GLS 1500X). The latter was evacuated and heated to 1100-

1350 °C for 6 h. The sample was held at the maximum applied uniaxial pressure ~3 ton for 10 min.

To characterize the prepared MAX phase material, X-ray Diffraction (XRD) analysis was used in order to find out the composition and phase identification of each sample using Shimadzu X-ray diffractometer (type XRD-6000/7000).

Potentiostatic and cyclic polarization measurements were carried out with WINKING MLab 200 Potentiostat from Bank-Elektronik with electrochemical standard cell and SCI electrochemical software at a scan rate 5 mV.sec⁻¹. Polarization experiments were started when the rate at which open circuit potential (E_{oc}) changed was less and more 300mV[9]. Saturated calomel electrode (SCE) was used as reference electrode and Pt as counter electrode, while working electrode was V₂AlC. The specimen was polished, degreased with acetone and rinsed with distilled water and then they put in holder to insulate all but one side with exposed surface area (1 cm²). The main results obtained were expressed in terms of the corrosion potentials (E_{corr}) and corrosion current density (i_{corr}) in addition to measure the Tafel slops by Tafel extrapolation method [10]. From the values of Tafel slopes and corrosion current density, the polarization resistances values can be calculate according to Stern-Geary equation as follow:

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

where b_c and b_a are cathodic and anodic Tafel slop respectively.

Electrolyte solutions were 0.01N of HCl (pH=2), H₂SO₄ (pH=2.3), NaCl (pH=7) and NaOH at (pH=12) which used for corrosion tests. All experiments were achieved at four temperatures include 303, 313, 323 and 333 K which adjusted by water bath in jacket cell.

3. Results and Discussion

The X-ray powder diffraction patterns collected at 1 atm for V₂AlC is shown in Fig.(1). All major peaks were assigned to the hexagonal structure with the space group *P63 /mmc*. A few low intensity impurity peaks were not identified.

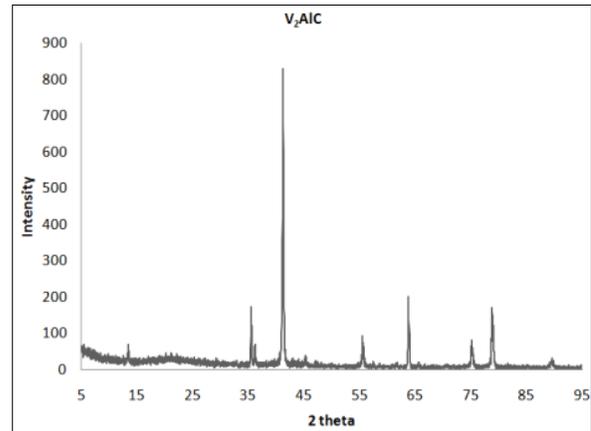


Figure 1. XRD for prepared V₂AlC material.

Figure (2) shows the polarization test of V₂AlC in different media at four temperatures, and indicates the cathodic and anodic regions. At cathodic sites, reduction reactions can occur. While at anodic sites, dissolution of metals in material takes place. Corrosion parameters were calculated by Tafel extrapolation method, which are found in Table (1). These parameters indicate that the most noble corrosion potentials were in basic solution of 0.01N NaOH, i.e., at pH=12, while the most active potentials were in salt solution at pH=7 due to aggressiveness of chloride ions which breakdown passive layers. Corrosion potentials are thermodynamic parameters which are a criterion for the extent of the corrosion feasibility under the equilibrium potential (in opposite sign) of the cell consisting of the working electrode and the auxiliary electrode when the rate of anodic dissolution of working electrode material becomes equal to the rate of the cathodic process that takes place on the same electrode surface.

The corrosion current density (i_{corr}) is a kinetic parameter and represents the rate of corrosion under specified equilibrium condition. Any factor that enhances the value of (i_{corr}) results in an enhanced value of the corrosion rate on pure kinetic ground. The results in Table (1) showed that the corrosion current densities take the following sequence:

$$i_{corr} \text{ in } 0.01N \quad NaOH < NaCl < H_2SO_4 < HCl$$

This means that the lowest corrosion rates occur in basic medium which promote the presence of hydroxide ions which produce vanadium hydroxide and then vanadium oxide to protect material surface.

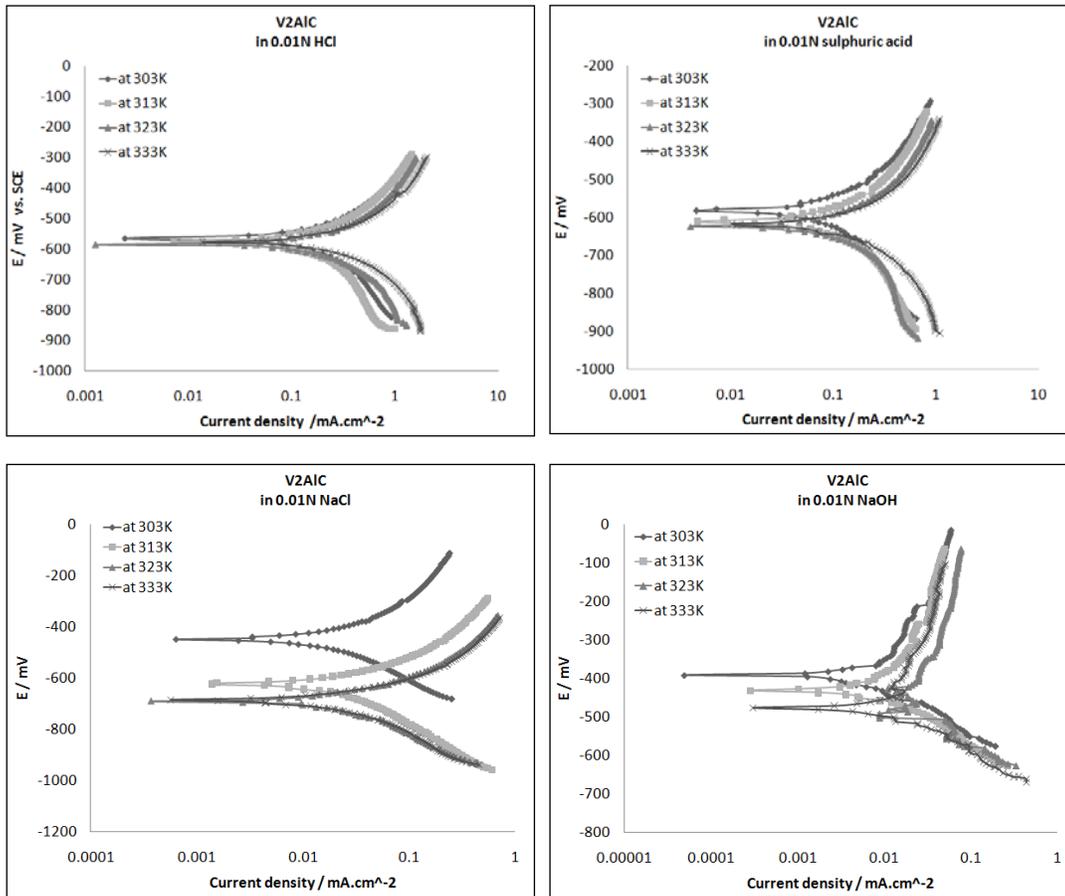


Figure 2: Tafel plots of V₂AlC in different media at four temperatures.

The term (R_p) corresponds to the resistance (R) of the metal/solution interface to charge–transfer reaction. It is also a measure of the resistance of the metal to corrosion in the solution in which the metal is immersed. The values of R_p are presented in Table (1). These data indicate that the polarization resistance was good agreement with the results of corrosion current density. Generally, the sequence of R_p take the order:

$$R_p \Omega.cm^2 \text{ NaOH} > \text{NaCl} > \text{H}_2\text{SO}_4 > \text{HCl}$$

In general, the polarization resistance decreases with increasing temperature due to increasing kinetic energy of particle and its ability to surmount the energy barrier.

From the corrosion current densities (corrosion rates) at different temperatures, the values of the activation energy can be calculated according to the following equation[11]:

$$\log \frac{S_2}{S_1} = \frac{E_{app}^*}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

where S_1 and S_2 are the corrosion rates at the temperature T_1 and T_2 (K) respectively and E_{app}^* is the activation energy.

The data of activation energy indicate that the highest energy was in basic medium, this result agreement with the data of polarization resistance. Therefore, it can be seen that V₂AlC has good corrosion resistance in basic medium.

Table 1. Corrosion parameters for V₂AlC in different media at four temperatures.

Medium	Temp./ K	-E _{corr} / mV	i _{corr} / μA.cm ⁻²	-b _c / mV.dec ⁻¹	+b _a / mV.dec ⁻¹	R _p x10 ³ / Ω.cm ²
0.01N HCl	303	564.1	70.09	118.4	102.1	0.340
	313	575.5	84.29	150.7	116.7	0.339
	323	585.8	98.15	116.6	110.4	0.251
	333	577.7	116.83	99.2	106.7	0.191
0.01N H ₂ SO ₄	303	581.1	48.54	141.3	117.5	0.574
	313	610.8	49.39	114.8	114.3	0.504
	323	623.8	49.74	95.1	99.3	0.424
	333	617.9	61.54	94.3	91.5	0.328
0.01N NaCl	303	448.5	6.97	92.7	91.1	2.862
	313	621.8	9.02	104.9	79.6	2.179
	323	686.3	10.72	115.1	92.2	2.074
	333	690.8	11.54	123.2	84.5	1.886
0.01N NaOH	303	394.7	5.23	147.8	151.4	6.209
	313	431.0	5.50	86.4	183.2	4.635
	323	497.1	10.32	93.9	98.9	2.029
	333	473.5	11.45	130.5	364.8	3.645

Table 2. Activation energy of corrosion for V₂AlC in different media between 303 and 323 K.

Medium	E _a / cal.mol ⁻¹
0.01N HCl	2.251
0.01N H ₂ SO ₄	0.163
0.01N NaCl	2.877
0.01N NaOH	4.543

4. Conclusions

From the study of corrosion behavior of V₂AlC in different media, can be concluded that this material has good corrosion resistance in basic medium compared with acidic and salt media. This conclusion was confirmed through polarization test which due to homogenously structures and regular crystal in lattice of this ceramic material. The corrosion parameters indicated that the most noble potential, lowest current density, highest resistance and highest activation energy were in basic medium.

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