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Corrosion Behavior of V_2AlC and Cr_2AlC Compared with SS 316L in NaOH at Four Temperatures

Rana A. Anaee* **Ahmed M. Al-Ghaban****
Russul F. Faleh***
*,**,****Department of Materials Engineering/ University of Technology*
*Email: Dr.rana_afif@yahoo.com
**Email: ahmed_gaban@yahoo.com
***Email: russulfadhelfaleh@gmail.com

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Abstract

This work involves the manufacturing of MAX phase materials include V_2AlC and Cr_2AlC using powder metallurgy as a new class of materials which characterized by regular crystals in lattice. Corrosion behavior of these materials was investigated by Potentiostat to estimate corrosion resistance and compared with the most resistant material represented by SS 316L. The experiments were carried out in 0.01N of NaOH solution at four temperatures in the range of 30–60^oC. Polarization resistance values which calculated by Stern-Geary equation indicated that the MAX phase materials more resistant than SS 316L. Also cyclic polarization tests confirmed the resistivity of MAX phase materials through disappears of hysteresis loop.

Key word: *MAX phase materials, Corrosion behavior, V_2AlC, Cr_2AlC.*

1. Introduction

Materials technology is a very vital part of modern technology. Technological development is often limited by the properties of materials and knowledge about them. Some properties, such as that determining corrosion behavior, are most difficult to map and to control [1]. In general, the development of modern society and industry has led to a stronger demand for engineers with specialized knowledge in corrosion. There are a number of reasons for this; The application of new materials requires new corrosion knowledge, Industrial production has led to pollution, acidification and increased corrosivity of water and the atmosphere, Stronger materials, thinner cross-sections and more accurate calculation of dimensions make it relatively more expensive to add a corrosion allowance to the thickness, The widespread use of welding has increased the number of corrosion problems, and other factors [2]

Many authors were interested fabrication of MAX phase materials and studied of some their physical and mechanical properties. Zhou et al. in 2001 determined the electronic and structural properties of the layered ternary compound Ti_3AlC_2 using the ab initio pseudopotential method based on density functional theory [3]. Wang and Zhou in 2002 investigated the isothermal oxidation behavior of Ti_2AlC at intermediate temperatures of 500, 600, 700, 800, and 900°C in flowing air by means of thermogravimetric analysis, X-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy (SEM)/energy dispersive spectroscopy [4], also they fabricated the microstructure of polycrystalline Ti_3AlC_2 by the solid–liquid reaction

synthesis and simultaneous in situ hot pressing process was investigated by SEM and TEM [5].

Zhimei et al. [6] performed theoretical studies of the bulk modulus of M_2AlC, where M_5Ti, 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.

Jochen et al. [7] calculated the equilibrium volume and the density of states (DOS) of Cr_2AlC for antiferromagnetic (AFM), ferromagnetic (FM) and paramagnetic (PM) configurations by ab initio total energy calculations. Based on a comparison of the cohesive energies as well as the DOS for all three magnetic configurations we have identified the FM configuration to be metastable. Furthermore, they report the structural characterization of polycrystalline Cr_2AlC thin films grown by magnetron sputtering. The charge density distribution suggests that the chemical bonding between Cr and C in Cr_2AlC is very similar to the one in cubic CrC.

Hettinger et al. [8] 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.

Yuri et al. [9] synthesized a near-single-phase Ti_3AlC_2 ternary carbide from 3Ti–1.1Al–1.8C powder blend, both by the wave propagation and thermal explosion (TE) modes of self-propagating high temperature synthesis. Zhimei et al. [10] studied M_2AlN phases, where M = Ti, V, and Cr, by means of *ab initio* total energy calculations. The bulk modulus of M_2AlN is generally higher than that of the corresponding M_2AlC phase, which may be explained by an extra electron in the former phases contributing to stronger chemical bonding.

Wubian et al. [11] fabricated Cr_2AlC ceramics by hot-pressing using Cr, Al and C powders as starting materials. The phase assemblages of the samples consisted of Cr_2AlC, as a major crystalline phase, together with a very small amount of Cr_7C_3 and an unknown phase. Its thermal and electrical as well as mechanical properties were determined. Wu-bian et al. [12] fabricated dense and predominantly single-phase samples of Cr_2AlC, together with a trace amount of Cr_7C_3 by hot pressing of a mixture of chromium, aluminum, and graphite powders at 14001C for 1 h. The hardness, Young's modulus, flexural strength, and compressive strength of Cr_2AlC samples were 5.2, 288 GPa, 483729, and 1159723 MPa, respectively, which are comparable with those of Ti_3AlC_2 and Nb_2AlC. The material exhibits good damage tolerance.

Denis et al. [13] studied the electronic structure of $Ta_{n+1}AlC_n$ (space group *P*63/*mmc, n* = 1–3) under uniform compression from 0 to 60 GPa and at temperatures from 0 to 1500 K using *ab initio* calculations.

Yanchun et al. [14] 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.

Wubian et al. [15] studied the isothermal oxidation behavior of Cr_2AlC ceramics oxidized in air at 1100 and 1250 ^oC for 20 h. Wubian et al. [16] studied the compressive properties of ternary compound Cr_2AlC at different temperatures and strain rates. Zhou et al. [17] synthesized dense bulk Cr_2AlC by hot-pressing of Cr, Cr_3C_2 and Al powders as starting materials. The results showed that Cr_2AlC grains have columnar and plate-like shapes, and that it is a good electrical and thermal conductor. Chang et al. [18] studied the Cr_2AlC ternary carbide in chemical and oxidation resistances as well as mechanical properties at high temperatures.

The aim of present work is fabricate the V_2AlC and Cr_2AlC materials by powder metallurgy and study their corrosion behavior in basic medium of 0.01N NaOH solution and comparison their behavior with SS 316L which act as most metallic resistant alloy at four temperatures 30, 40, 50 and 60^oC.

2. Experimental Procedure

To fabricate the V_2AlC and Cr_2AlC samples V, Cr, 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.

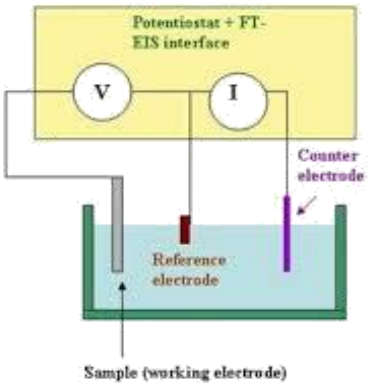
To characterize the prepared MAX phase material, X-ray Diffraction (XRD) analysis was used in order to find out the composition and phase identification of each sample using Shimadzu X-ray diffractometer (type XRD- 6000/7000).

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[19]. Saturated calomel electrode (SCE) was used as reference electrode and Pt as counter electrode, while working electrodes were V_2AlC, Cr_2AlC and SS 316L. The three electrodes arranged as shown in Fig. 1. The specimens were 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 cm^2). 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 [20]. From the values of Tafel slopes and corrosion current density, the polarization resistances values can be calculate according to Stern-Geary equation as follow:

$$R_p = \left(\frac{dE}{di}\right)_{i=0} = \frac{b_a * b_c}{2.303 * i_{corr} * (b_a + b_c)} \quad \dots (1)$$

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

Electrolyte solution was 0.01N NaOH at (pH=12) which used for corrosion tests. All experiments were achieved at four temperatures include 30, 40, 50 and 60°C which adjusted by water bath in jacket cell as shown in Fig. 1-b.



(a)

(b)

Fig. 1. Set up of corrosion test, (a) Electrical circuit, (b) Standard cell.

3. Results and Discussion

The X-ray powder diffraction patterns collected at 1 atm for V_2AlC and Cr_2AlC are shown in Fig.(2). For two materials, all major peaks were assigned to the hexagonal structure with the space group *P*63 /*mmc*. A few low intensity impurity peaks were not identified.

The variation of potentials with time for MAX phase materials and SS 316L (for comparison only) in basic medium of sodium hydroxide are shown in Figure (3) for 600 sec. at scan rate 5 $mV.sec^{-1}$, these figures indicate that there are protective film may be formed on material surfaces in basic medium for prepared MAX phase materials. Generally, the potentials of V_2AlC more noble than these for Cr_2AlC and SS 316L at constant temperature due to breakdown and repairing of Cr_2O_3 in the last two materials. In the other word, polarization

characteristics recoded in 0.01N NaOH show that V_2AlC undergoes active dissolution at potentials more positive than other materials, ex., E_{corr} of V_2AlC was -473.5 mV at 60°C, while for Cr_2AlC and SS 316L were -1191.8 and -1200.7 mV respectively at the same temperature (see Table 1).

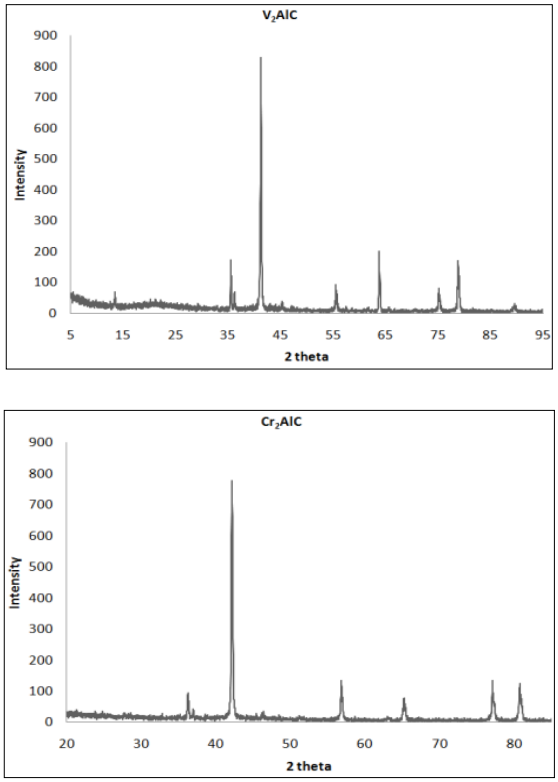


Fig. 2. XRD for prepared MAX material.

Figure (4) shows the polarization test of three materials in 0.01N NaOH solution at four temperatures, indicating the cathodic and anodic regions. The variation of potentials with current densities for V_2AlC and Cr_2AlC curves more than for SS 316L due to stable protective film in MAX phase materials compared with SS 316L in addition to the high resistance needed to rupture the regular crystals in structure. Corrosion parameters were calculated by Tafel extrapolation method are found in Table (1) and the order of corrosion current densities take the following sequence:

i_{corr} in 0.01N NaOH

V_2AlC < Cr_2AlC < SS 316L

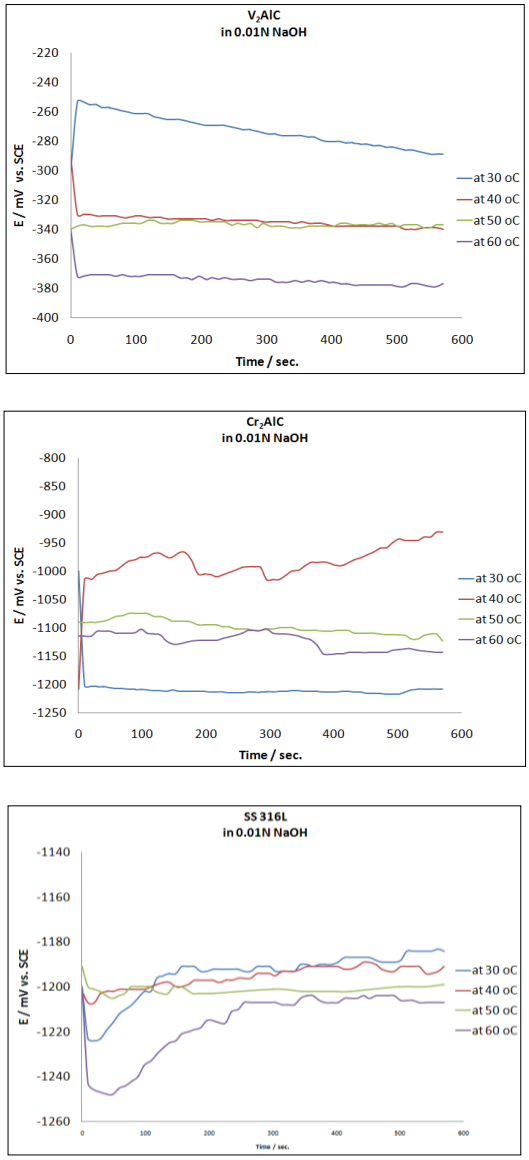


Fig. 3. Potential–time measurements of Materials in 0.01N NaOH at four temperatures.

Table 1,
Corrosion parameters for V_2AlC, Cr_2AlC and SS316L in 0.01N NaOH at four temperatures.

Material	*Temp. °C*	*$-E_{oc}$ mV*	*$-E_{corr}$ 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_2AlC	30	289	394.7	5.23	147.8	151.4	6.209
	40	340	431.0	5.50	86.4	183.2	4.635
	50	337	497.1	10.32	93.9	98.9	2.029
	60	377	473.5	11.45	130.5	364.8	3.645
Cr_2AlC	30	1209	1166.5	16.60	150.9	241.1	2.428
	40	931	975.3	18.47	267.6	266.5	3.139
	50	1123	1133.6	19.29	152.8	317.8	2.323
	60	1144	1191.8	31.26	106.2	164.1	0.896
SS 316L	30	1184	1183.5	37.81	91.0	134.7	0.624
	40	1191	1181.6	86.24	136.8	201.2	0.410
	50	1199	1187.8	99.89	154.5	234.2	0.405
	60	1207	1200.7	221.08	170.6	271.6	0.206

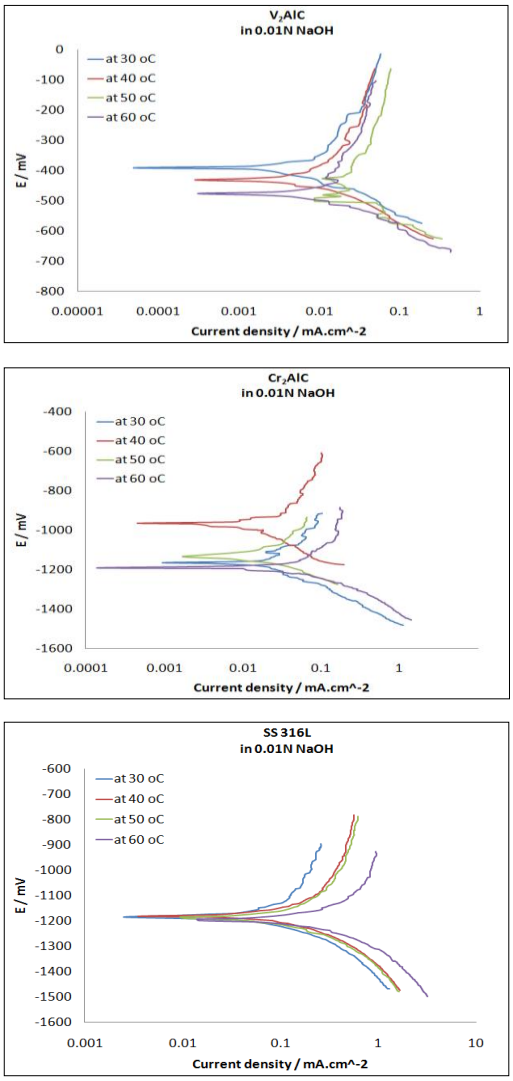


Fig. 4. Tafel plot of materials in 0.01N NaOH at four temperatures.

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, where can be seen that the polarization resistance values were for V_2AlC followed by Cr_2AlC and then for SS 316L.

The polarization resistance of MAX phase materials varied with increasing temperature due to variation of cathodic and anodic sites on the material surface, but at constant temperature the resistance of these materials more than for SS 316L, for example at 60°C, the polarization resistance of V_2AlC was 3.645 $\Omega.cm^2$, while for Cr_2AlC and SS 316L were 0.896 and 0.206 $\Omega.cm^2$ respectively.

Generally, the sequence of R_p take the order:

R_p $\Omega.cm^2$

V_2AlC > Cr_2AlC > SS 316L

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.

According to the results of corrosion current density, can be say that the highest corrosion rate was for SS 316L followed by Cr_2AlC. While V_2AlC has lowest corrosion rate.

The cyclic polarization of MAX phase materials shows no chance to pitting compared with SS 316L, which is recognized as a dangerous form of

corrosion, in tested media as shown in Figure (5). This means that V_2AlC and Cr_2AlC materials were exhibited a good resistance to corrosion in 0.01N NaOH solution at different temperatures in the range of 30 – 60°C.

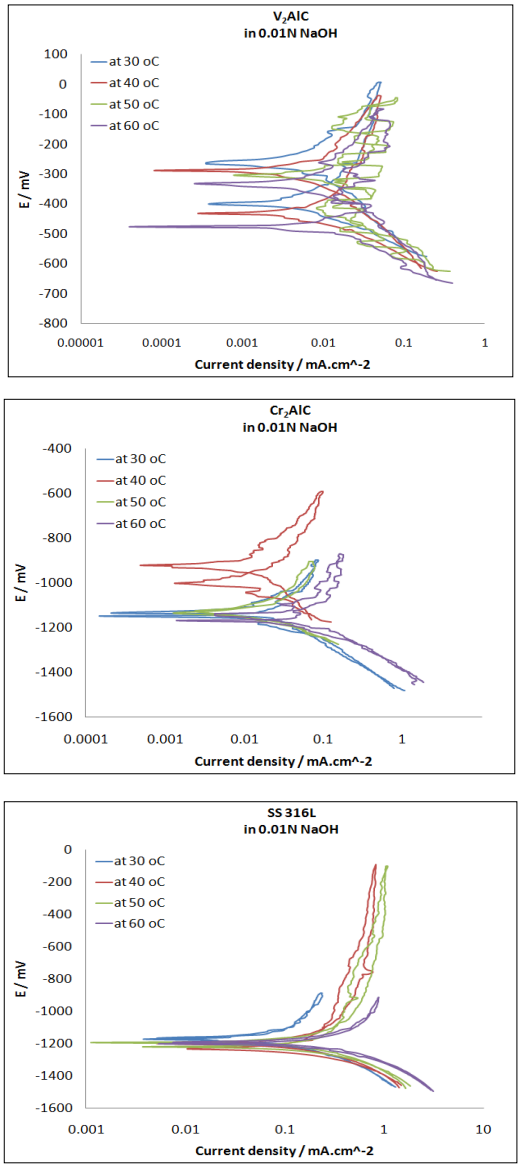


Fig. 5. Cyclic polarization of materials in 0.01N NaOH at four temperatures.

4. Conclusion

From the study of corrosion behavior for MAX phase materials can be concluded that these materials have good corrosion resistance in basic medium. This conclusion was confirmed through the potential – time measurements, polarization test and cyclic polarization due to homogenously structures and regular crystal in lattice of these ceramic materials. The corrosion parameters indicated that the E_{oc} and E_{corr} values were more negative for SS 316L followed by Cr_2AlC and then V_2AlC. The corrosion current density (or corrosion rate) take the order SS 316L > Cr_2AlC > V_2AlC. Polarization resistance values which calculated depending on Tafel slopes and current density indicated that the most resistance was for V_2AlC due to protective layer on its surface which is more stable than that formed on Cr_2AlC and SS 316L surfaces.

5. References

[1] Payer JH, Boyd WK, Dippold DG, Fisher WH. Materials Performance, NACE, May 1980.

[2] Hoar TP (Chairm.). Report of the Committee on Corrosion and Protection, London: Dept. of Trade and Industry, H.M. Stationary Office, 1971.

[3] Zhou Y. C., Wang X. H., Sun Z. M. and Chen S. Q. 2001, "Electronic and structural properties of the layered ternary carbide Ti3AlC2", J. Mater. Chem., 11, 2335–2339.

[4] Wang X.H. and Zhou Y.C. 2002, "Intermediate-temperature oxidation behavior of Ti2AlC in air", J. Mater. Res., Vol. 17, No. 11.

[5] Wang X.H., Zhou Y.C. 2002, "Microstructure and properties of Ti3AlC2 prepared by the solid–liquid reaction synthesis and simultaneous in-situ hot pressing process", Acta Materialia, 50, 3141–3149

[6] Zhimei Sun, Rajeev Ahuja and Sa Li, and Jochen M. Schneider 2003, "Structure and bulk modulus of M2AlC .MÄTi, V, and Cr", Appl. Phys. Lett., Vol. 83, No. 5.

[7] Jochen M. Schneidera,, Zhimei Suna, Raphael Mertensa, Fatih Uestela, and Rajeev Ahujac 2004, "Ab initio calculations and experimental determination of the structure of Cr2AlC", Solid State Communications 130, 445–449.

[8] 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. 2005, "Electrical transport, thermal transport,

and elastic properties of M2AlC (M=Ti, Cr, Nb, and V)", Physical Review B 72, 115-120.

[9] Yuri Khoptiar, Irena Gotman,w and Elazar Y. Gutmanas 2005, "Pressure-Assisted Combustion Synthesis of Dense Layered Ti3AlC2 and its Mechanical Properties", J.Am.Ceram.Soc.,88,28-33.

[10] Zhimei Sun, DenisMusic, Rajeev Ahuja and Jochen M Schneider 2005, "Ab initio study of M2AlN (M = Ti,V, Cr)", J. Phys.: Condens. Matter, 17, L15–L19.

[11] Wubian Tian, Peiling Wang, Guojun Zhang, Yanmei Kan, Yongxiang Li, and Dongsheng Yan 2006, "Synthesis and thermal and electrical properties of bulk Cr2AlC", Scripta Materialia, 54, 841-846.

[12] Wu-bian Tian, Pei-ling Wang, Guo-jun Zhang, Yan-mei Kan, and Yong-xiang Li 2007, "Mechanical Properties of Cr2AlC Ceramics", J. Am. Ceram. Soc., 90 [5] 1663–1666.

[13] Denis Music, Jens Emmerlich and Jochen M Schneider 2007 "Phase stability and elastic properties of Tan+1AlCn(n = 1–3) at high pressure and elevated temperature", J. Phys.: Condens. Matter, 19, 136207 (9pp)

[14] Yanchun Zhou, Fanling Meng, and Jie Zhang 2008, "New MAX-Phase Compounds in the V-Cr-Al-C System", J.Am.Ceram.Soc., 91(4) 1357–1360.

[15] Wubian Tian, Peiling Wang, Yanmei Kan, and Guojun Zhang 2008, "Oxidation behavior of Cr2AlC ceramics at 1100 and 1250oC", J Mater Sci., 43:2785–2791.

[16] Wubian Tian, ZhengMing Sun, and Hitoshi Hashimoto 2009, "Compressive deformation behavior of ternary compound Cr2AlC", J Mater Sci, 44:102–107.

[17] Zhou W.B, Mei B.C. and Zhu J.Q. 2009, "On the synthesis and properties of bulk ternary Cr2AlC ceramics",Materials Science-Poland,Vol.27,No.4/1.

[18] Chang-Sam Kim, Sung Ik Hwang, Jung-Soo Ha, Seung-Min Kang and Deock-Soo Cheong 2010, "Synthesis of a Cr2AlC-Ti2AlC ternary carbide", Journal of Ceramic Processing Research. Vol. 11, No. 1, pp. 82-85.

[19] ASM Handbook Volume 13, 1992. Corrosion. Materials Park, Ohio, USA: ASM International. For an easier read: Jones LW: Corrosion and Water Technology for Petroleum Producers. Tulsa, Oklahoma.

[20] Robert G., John R. and David W. 2003, "Electrochemical techniques in corrosion science and engineering", by Marcel Dekker, Inc.

السلوك التآكلي للمواد V_2AlC و Cr_2AlC بالمقارنة مع الفولاذ المقاوم للصدأ في هيدروكسيد الصوديوم عند اربع درجات حرارية

رنا عفيف عنائي* احمد محمد الغبان رسل فاضل فالح*****

*،**،***قسم هندسة المواد / الجامعة التكنولوجية

*البريد الالكتروني: Dr.rana_afif@yahoo.com

** البريد الالكتروني: ahmed_gaban@yahoo.com

*** البريد الالكتروني: russulfadhelfaleh@gmail.com

الخلاصة

يتضمن هذا البحث تصنيع مواد الطور MAX التي تُعد من المواد الجديدة المميزة بانتظام في الشبكة البلورية باستخدام ميتالورجيا المساحيق، وتم دراسة السلوك التآكلي لهذه المواد باستخدام المجهاد الساكن لتقدير متغيرات التأكل والمقارنة مع المادة الاكثر مقاومة والممثلة بالفولاذ المقاوم للصدأ 316L. اجريتْ جميع التجارب في وسط قاعدي من هيدروكسيد الصوديوم بتركيز ٠.٠١ نورمالية وعند اربع درجات حرارية ضمن المدى ٣٠ – ٦٠ درجة مئوية. وقد بينتْ نتائج مقاومة الاستقطاب المحسوبة بمعاولة ستيرن- جيري بان المواد المحضرة تمتلك مقاومة افضل من الفولاذ المقاوم للصدأ . كما ان الاستقطاب الحلقي اكد مقاومية هذه المواد مقارنة مع الفولاذ المقاوم للصدأ من خلال عدم ظهور الحلقة الهستيرية.