1. Introduction

Over recent years, a new family of layered ceramics has attracted much interest due to their unique physical and mechanical properties. These materials show high melting point, good thermal and electrical conductivity, high strength and high modulus of elasticity beside the possibility to be machineable [1]. These ceramics are complex ternary compounds with a hexagonal crystalline structure. They can be represented by the general formula of $M_{n+1}AX_n$ where M is a transition metal element; A is an A Group element mostly from group IIIA and IVA in the periodic table and X is either carbon or nitrogen. Among this group of compounds $Ti_3AlC_2$ and $Ti_2AlC$ MAX phases are very much interesting materials, which have been widely studied in the Ti–Al–C system [1]. It has been revealed that $Ti_3AlC_2$ exhibits some abnormal room-temperature properties. Compressive plasticity in contrast to normal brittle ceramics. $Ti_2AlC$ has also been reported to have high electrical conductivity, excellent machinability, high yield strength, and significant plasticity at high temperatures [1]. Another two interesting compounds are $Cr_2AlC$ and $V_2AlC$ MAX phases. These layered ternary carbides have received considerable attention because of an unusual combination of good properties, which makes it a candidate for many high-temperature applications. For instance, $Cr_2AlC$ is like metals in one side where it has an excellent electrical and thermal conductor. On the other hand, it is like ceramics with the rest of properties [2].

2. Experimental

I. Ti-Al-C

I. $Ti_3AlC$

Ti-Al-C had been mixed as (50%wt, 25%wt, 25%wt respectively). The compound powders were pressing with 20 bar maximum pressure. Cylindrical steel die used in compacting process with upper and lower punch. Paraffin was used as a binder in this work at certain powder composition. The cold worked piece then sintered at 1300 °C with rate 20 °C /minute and was held for four hours. Finally, the cycle cool down to room temperature inside the furnace and sample was held on heat resistant plate inside the furnace to provide contamination. The X-ray Diffraction test (XRD) is performed to obtain the phase evolution from the ternary system to form different phases including $Ti_3AlC$ MAX phases as shown in Figure 1 [3].
Figure 1: X-Ray diffraction pattern of Ti$_2$AlC$_2$ [3]

The SEM micrographs are observed after the sample was prepared using SiC grinding paper. Different micro grits have been used starting with 600 and 800 mish. Flat and scratch free surface were finally polished with smooth cloth to get the final mirror surface as shown in Figure 2. The back scattered electrons show the differences in brightness, which may lead to indicate the appearance of most referred phases [4]. Figures 2 shows at high temperature the large particle size approximately was the MAX phase due to its high atomic weight as shown down. The obtained microstructure is also studied using optical microscope see figure 3. Magnification was about 1450 X where pores are almost the dark range. Differential Scanning Calorimeter (DSC) technique is widely used to examine the transformation temperatures as well as to obtain the energy of transformations [5]. This test conducted by taking (5-10) mg of each sample and testing at scan rate of 10 °C/min. The cooling agent used in DSC (in order to cool up to 50°C) was liquid nitrogen while maximum temperature was 650°C as shown in Figure 4.

2. Ti$_3$AlC$_2$

The same procedure applied to another type of Ti-Al-C but sintering temperature at 1450°C for 4 hours with rate 20 degree /minute. Ti-Al-C (3:1:2) after sintering the specimens are respectively mixed and pressed at 20 bar in vacuum furnace. Holding cooled in furnace to room temperature. The X-ray diffraction test (XRD) is performed to obtain the MAX phase from the ternary system to form Ti$_3$AlC$_2$ after compared with the Ti$_3$AlC$_2$ standard as shown in Figure 5. The phase analysis of Ti$_3$AlC$_2$ was carried out by X-ray diffraction (XRD) and produced due to sintering process can be seen in Figure 5. Almost of these peaks in Figure 5 indicated Ti$_3$AlC$_2$ (MAX phase as the formula Mn+1AXn, where n=2) in compared with the standard of Ti$_3$AlC$_2$. The formation of TiC phase because its stability phase [6].

Figure 2: SEM for Sample Ti$_2$ALC cold pressed and sintered at 1400°C for 4hr

Figure 3: The optical microscopy of Ti$_2$ALC composition cold pressed and sintered at 1400°C for 4hrs

Figure 4: shows DSC of the sample of Ti$_2$ALC
II. Cr-Al-C
The sample of Cr-Al-C is followed the same procedure but electrical press with 15 ton/cm² has been used and sintering has been used in vacuum furnace at temperature 1000°C for two hours. The X-ray Diffraction test (XRD) is performed to obtain the MAX phase from the ternary system to form Cr₂AlC after compared with the Cr₂AlC standard as shown in Figure 6 and 7 [7].
Optical microscope micrographs are shown in Figure 8 where pores are mostly a dark region. Microstructure figure shows that there is a high percentage of porosity and the phase appears with a high amount of porosity due to the cold compaction and the time of sintering process.

DSC test shows clearly that the overall reaction occurred at the investigated temperature range is completely endothermic as shown in Figure 9. One DSC signal is observed at the range from ~350°C to ~450°C. Furthermore, this signal seems to be a combination of two signals, which may refer to different reactions of two steps. No further signals are observed with increasing temperatures up to ~650°C. This may indicate the stability of the transformed phase at the previous range. It is also expected that the reaction with Aluminum is the key to let this reaction occur at this system. Hence, aluminum diffusivity may play in important role to start and continue the reaction in all these systems [9].
High purity powders were used as raw materials. Powders were mixed and then compacted under the pressure of 20 MPa. The compacted mixture was heated in an Ar atmosphere at a temperature of 1300 °C for 2 h. Finally, the sample was cooled down to room temperature. X-ray diffraction in Figure 10 indicates that the V$_2$AlC system shows a direct formation of MAX phase under these conditions.

Figure 11 shows the microstructure results (SEM) of V$_2$AlC sample.

At high temperature, the large particle size approximately was the MAX phase due to its high atomic weight as shown above. The microscopic pictures shown in Figure 12 represent also pores, which are almost the dark regions beside the bright regions.

In this system (V$_2$AlC) a great similarity can be found as compared with the signal obtained from the Ti$_2$AlC see Figure 13. Almost the same DSC signal was observed at ~260-320°C. Furthermore, the final reactions were observed at the temperature range between ~580-640°C. This may also indicate the primary and secondary reaction levels. All reactions for this system including exothermic response at this temperature range. It should be noted that according to the low temperature melting point of Al, it is expected to be the first diffused atoms source to form V-Al binary system [10].
3. Density Test

Archimedes method has been used to measure the density percentage of each sample. The method leads to measure the weight of dry samples first, and then the weight after immersion sample in water for 24 hours. Finally the weight is measured the samples during placed in water. The below Formula was used to get the final density of each sample:

\[
\text{Density \%} = \left(\frac{W_s - W_d}{W_s - W_n}\right) \times 100 \quad (1)
\]

Where:

- \(W_d\) = the weight of dry sample.
- \(W_s\) = the weight of saturated samples.
- \(W_n\) = the weight of immersed sample.

Figure 14 shows the density measurements of \(\text{Ti}_2\text{AlC}\) sample where the linear increasing of the density starts at 1200\(^\circ\)C to 1400\(^\circ\)C because the probability formation of MAX phase. At 1400\(^\circ\)C starts decrease with increasing the temperature that the probability disintegration was event. Figure 15 show the density behavior with the sintering temperature of \(\text{Cr}_2\text{AlC}\) sample. It shows that there is linear relation from 1200\(^\circ\)C to 1350\(^\circ\)C because probably, the density of the interphase was equal the density of the final phase and begin to increase with increasing the temperature beyond 1350\(^\circ\)C due to the formation of MAX phase. After that the density of sample is decreased with increasing the temperature at 1450\(^\circ\)C due to probably the disintegration.

Figure 16 shows that the density is fixed to 1200\(^\circ\)C because probably the density of the inter phase was equal the density of the final phase. After that the density of sample is decreased with increasing the temperature (from 1500 to 1450) \(^\circ\)C because of probably of disintegration.
II. Mechanical properties/Microhardness test

The hardness of investigated samples has been measured using Vickers microhardness type (TP µP-A, HV- 1000) [11]. The average of about 7 points was adopted. A 1 Kg load has been used for each sample. Figure 17 shows the results of the hardness values for the Ti2AlC compositional sample.

It can be seen that micro hardness is increased by increasing the temperature till 1300°C and fixed (linear) with little increasing at temperature until 1400 °C. After that, it is decreased from 1400 ° C. Finally, until 1500°C during sintering process the final value of micro hardness of Ti2AlC compound is 460 HV as shown in Figure 17.

After that the micro hardness was increased with increased the temperature until1400°C. Finally, it was decreased until 1500°C. The final value of microhardness of Cr2AlC was 300 HV as shown in Figure 18.

The micro hardness exhibits approximately linear behavior across the sintering temperatures of V2AlC with little decreasing at (1200 -1300)°C except above 1450°C it is decreased with the temperature. The final value of micro hardness of V2AlC was 360 HV as shown in Figure 19.

According to other researches, the final value of micro hardness in this research has been small because low sintering time, which slows. The phase formation and its crystallization at 100%.

4. Results

MAX phases are combinations of an early transition metal M, an element from the A groups, usually IIIA and IVA in the periodic table, and element X, which is either carbon and nitrogen within the formula of M_{n+1}AX_n, where n is 1, 2 or
Three groups are formed depending on the starting composition. The goal is to use the powder technique to produce the MAX phases with a very simple pathway for the first time. Three different systems had been chosen which are Ti:Al:C, Cr:Al:C and V:Al:C in order to find out which of them is easy to be formed. The syntheses of Ti$_2$AlC, Ti$_3$AlC$_2$, V$_2$AlC and Cr$_2$AlC MAX Phase compounds were found to be possible using different stoichiometric ratios of the above elemental powders. In all cases, the solid-state reaction was found to be responsible to provide such phases with a significant amount of other products. Here, a significant partial melting during the synthesis was noticed which may provide such phases with a significant amount of other products. Figure 20: The combination of three types of MAX phases.

III. Cr$_2$AlC
The XRD pattern of the samples cold-pressed at 1000 °C for 2 h is shown in Figure 6. The load was 15 ton/cm$^2$. It is found that the phase of sintered sample consisted of the Cr$_2$AlC phase, as the major crystalline phase. As the first stage, a stoichiometric composition Cr$_2$AlC was tried for synthesis of the phase. The results showed that the sintered sample contained Cr$_2$AlC (MAX Phase).

IV. V$_2$AlC
X-Ray diffraction was carried out after heating powder in the temperature 1300 °C for 2 h. The XRD data shown in Figure 10 indicate that the almost phase is V$_2$AlC after compared with the standard of the V$_2$AlC.

5. Conclusions
From the Investigation of solid-state reaction in the ternary Ti:Al:C, Cr:Al:C and V:Al:C system, the following conclusions can be drawn.
1-The synthesis route of three different ternary carbides system of Ti:Al:C, Cr:Al:C, and V:Al:C were investigated.
2-Pure elemental powders have been used to construct an accepted quantity of these new materials via powder technology techniques with a very simplified way.
3-Different tools have been used to examine and qualified the structure, topography, kinetics, and some physical and mechanical properties of the final products.
4-The results show the possibility of using the cold pressing to produce the so called MAX phases.
5-XRD, SEM, and optical microscopy results confirm the formation of MAX phases.
The DSC results give some information about the A element (Aluminum) contribution on the phase formation.

It is contributed towards the basic understanding required to tailor and modify these ternary systems.

References


