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Investigation of Solid State Reaction in the Ternary Ti-Al-C, Cr-Al-C and V-Al-C Systems

Abstract- *The main goal of this work is to understanding the requirements to realize the synthesis of MAX phases in bulk form at high temperature. The phase stability of three different MAX phase systems Ti-Al-C,Cr-Al-C and V-Al-C has been investigated along this line. High purity powders were used as raw materials. They were mixed and then compacted under the pressure of 20 MPa. The compacted mixture was heated in an Ar atmosphere at a temperature range of (1000-1400) °C for (2-4) h. Finally, the sample was cooled down to room temperature. X-ray diffraction indicates that systems show a direct formation of MAX phase under these conditions. The SEM and optical microscopy results were used to confirm the structural features of the ternary phases and the less segregation or agglomeration. The results of sintering temperatures versus final density were discussed in terms of physical properties evaluation and hardness for indicate the mechanical properties. Finally, the differential scanning calorimetric results over the range of 25 to 650 ºC show that the reactions in all systems related directly to the Al melting point. It is obvious that the reactions in all these systems started at ~600 ºC that may support this attitude. It is expected to contribute towards a better basic understanding of this fascinating class of solids. Furthermore, we try to evaluate the here-proposed novel low temperature synthesis for other $M_{n+1}AX_n$ systems. This may release a new synthesis route for the mass production of materials with rather unique properties.*

Keywords-*Ternary system, solid-state reaction.*

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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

1. Ti_2AlC

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_2AlC MAX phases as shown in Figure 1 [3].

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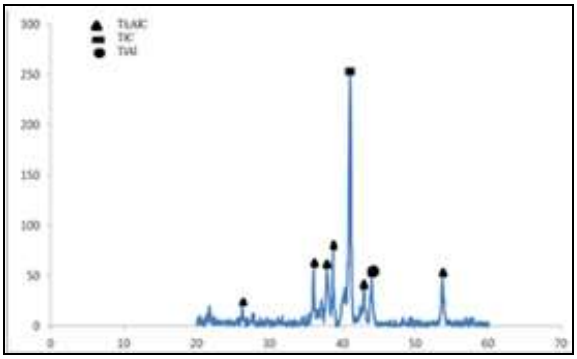

Figure 1: X-Ray diffraction pattern of Ti_2AlC [3]

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 was650°C as shown in Figure 4.

2. Ti_3AlC_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_3AlC_2 after compared with the Ti_3AlC_2 standard as shown in Figure 5. The phase analysis of Ti_3AlC_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_3AlC_2 (MAX phase as the formula Mn+1AXn, where n=2) in compared with the standard of Ti_3AlC_2. The formation of TiC phase because its stability phase [6].

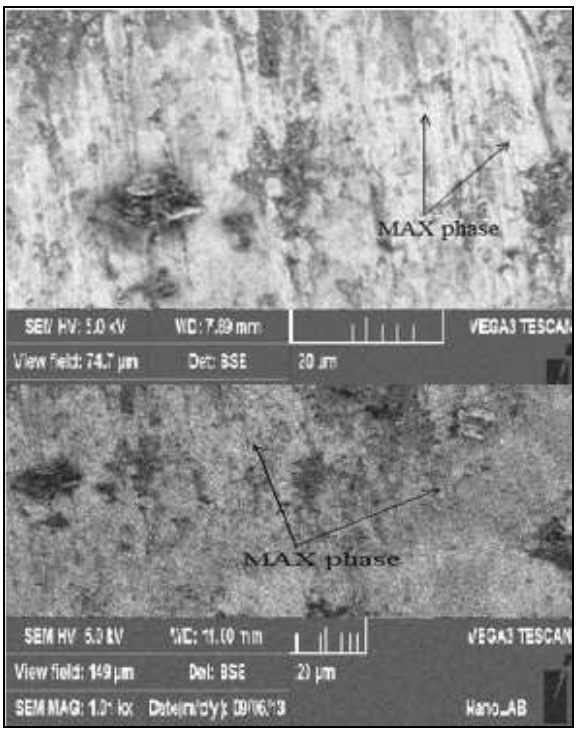

Figure 2: SEM for Sample Ti_2ALC cold pressed and sintered at 1400°C for 4hr

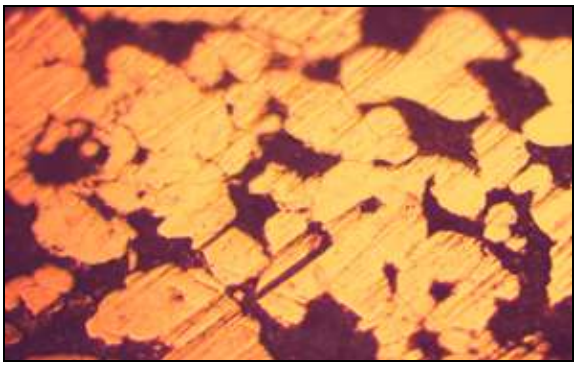

Figure 3: The optical microscopy of Ti_2ALC composition cold pressed and sintered at 1400◦C for 4hrs

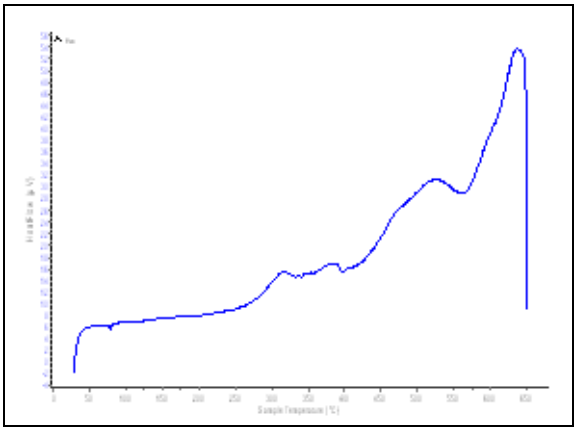

Figure 4: shows DSC of the sample of Ti_2AlC

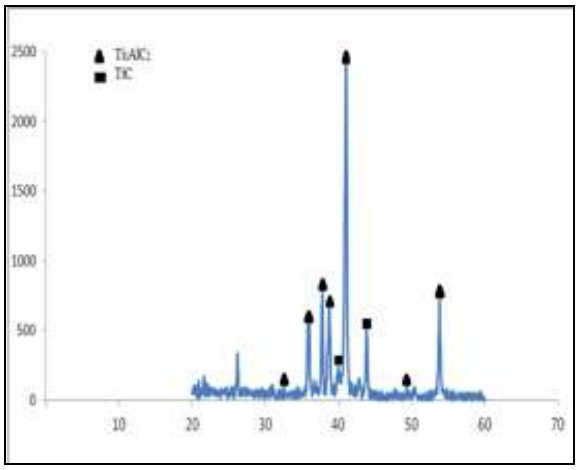

Figure 5: X-Ray diffraction pattern of Ti_3AlC_2

II. Cr-Al-C

The sample of Cr-Al-C is fallowed the same procedure but electrical press with 15 ton/cm^3 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 Cr_2AlC after compared with the Cr_2AlC 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.

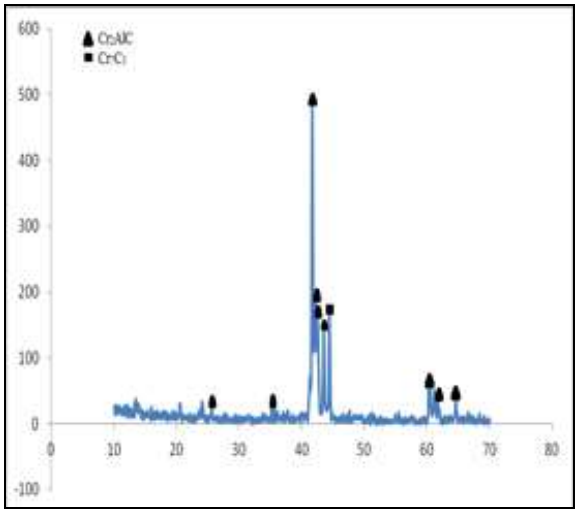

Figure 6: XRD diffraction pattern of Cr_2AlC [5]

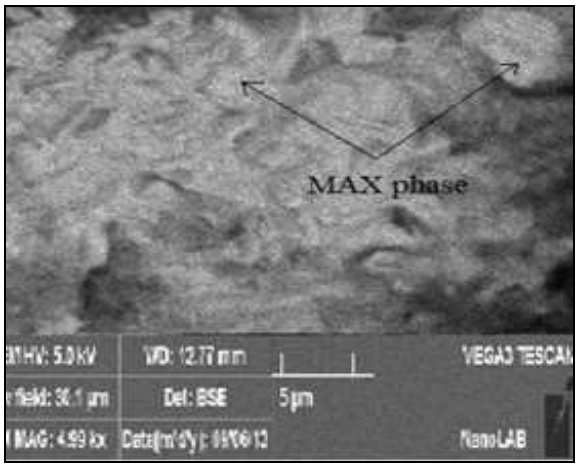

Figure 7: SEM for sample Cr_2AlC cold pressed and sintered at 1000°C for 2h

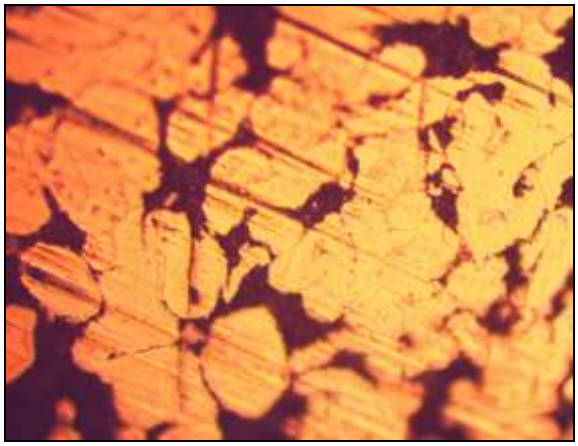

Figure 8: Optical microstructure of Sample Cr_2 ALC cold pressed and sintered at 1000◦C for 2 h

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 ~350ºC to ~450ºC. 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 ~650ºC. 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].

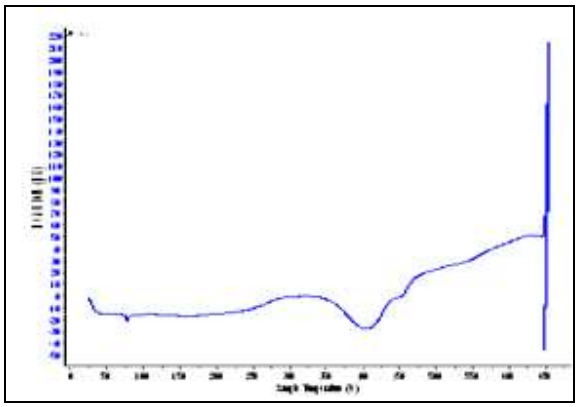

Figure 9: shows DSC of the sample of Cr_2AlC

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_2ALC system shows a direct formation of MAX phase under these conditions.

Figure 11 shows the microstructure results (SEM) of V_2AlC 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_2AlC) a great similarity can be found as compared with the signal obtained from the Ti_2AlC see Figure 13. Almost the same DSC signal was observed at ~260-320ºC. Furthermore, the final reactions were observed at the temperature range between ~580-640ºC. 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].

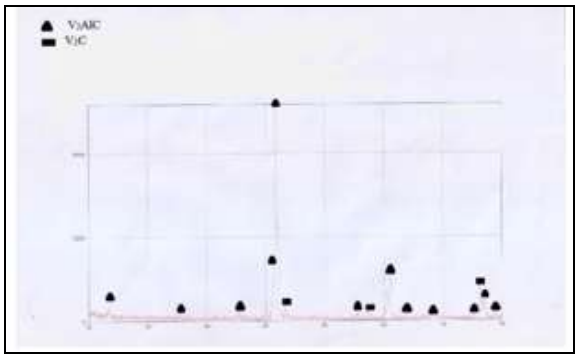

Figure 10:X-ray diffraction pattern of V_2AlC

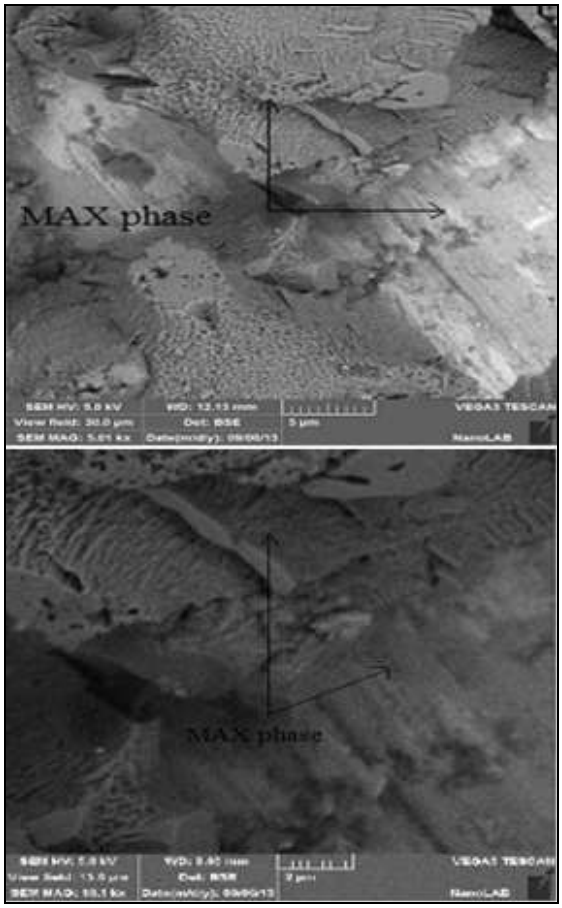

Figure 11: SEM for Sample V_2ALC cold pressed and sintered at 1300 °C for 3hrs

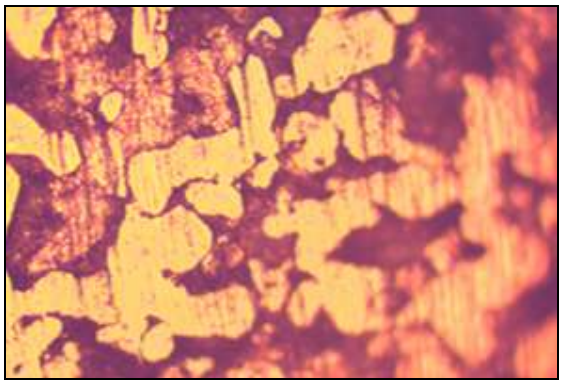

Figure 12: The microstructure of V:Al:C 2:1:1 sample cold pressed and sintered at 1300°C for 2h

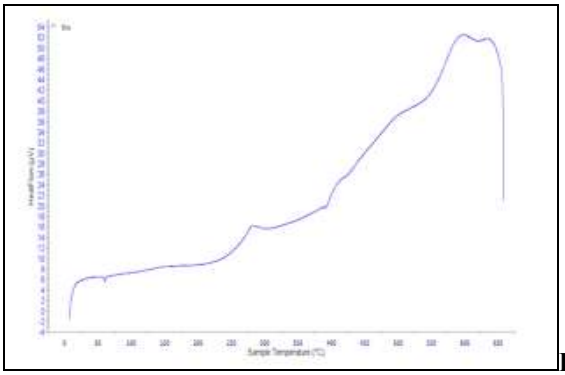

Figure 13: DSC of the sample of V_2AlC

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:

Density % = [(Ws –Wd)/(Ws –Wn)] *100 …(1)[11].

Where:

Wd= the weight of dry sample.

Ws= the weight of saturated samples.

Wn= the weight of immersed sample.

Figure 14 shows the density measurements of Ti_2AlC sample where the linear increasing of the density starts at 1200◦C to 1400◦C because the probability formation of MAX phase. At 1400◦C starts decrease with increasing the temperature that the probability disintegration was event.

Figure 15 show the density behavior with the sintering temperature of Cr_2AlC sample. It shows that there is linear relation from 1200◦C to 1350◦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◦C due to the formation of MAX phase. After that the density of sample is decreased with increasing the temperature at 1450◦C due to probably the disintegration

Figure 16 shows that the density is fixed to 1200◦C because probably the density of the inter phase was equal the density of the final phase.

After that the density of the sa1350◦C and fixed at 1450◦C.

Finally, the density is decreased with decreasing the temperature (from 1500 to 1450) ◦C because of probably of disintegration.

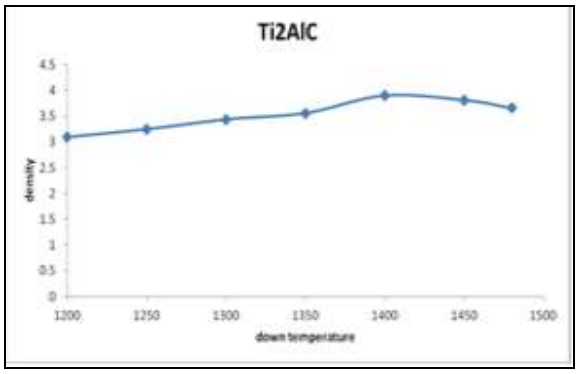

Figure 14: shows variation of density of the sample of Ti_2AlC sintered at different temperatures

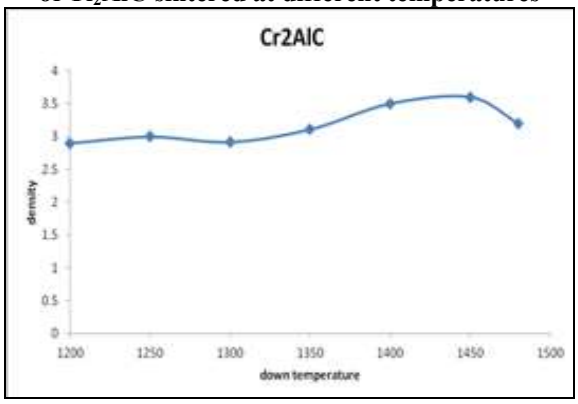

Figure 15: shows variation density of the sample of Cr_2AlC sintered at different temperatures

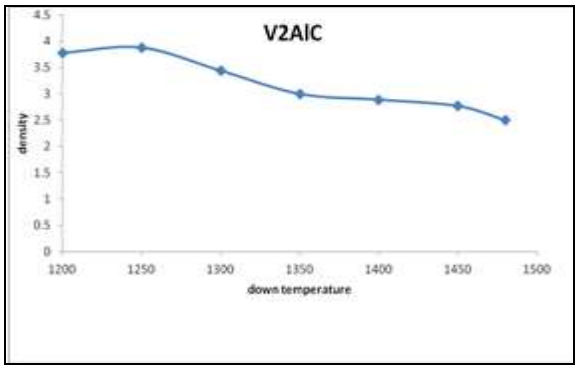

Figure 16: shows variation density of V_2AlC sintered at different temperatures

Note there are factors have affected the density of these samples such as degree of interaction, compressed method and crystal structure.

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 Ti_2AlC 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 Ti_2AlC 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 Cr_2AlC was 300 HV as shown in Figure 18.

The micro hardness exhibits approximately linear behavior across the sintering temperatures of V_2AlC with little decreasing at (1200 -1300)˚C except above 1450˚C .it is decreased with the temperature .The final value of micro hardness of V_2ALC 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%.

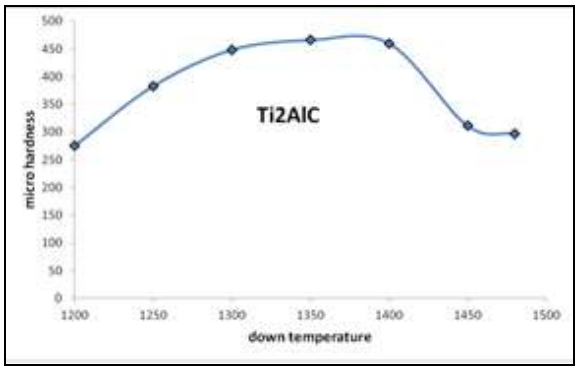

Figure 17: variation of hardness values of the Ti_2AlC composition sintered at different temperatures

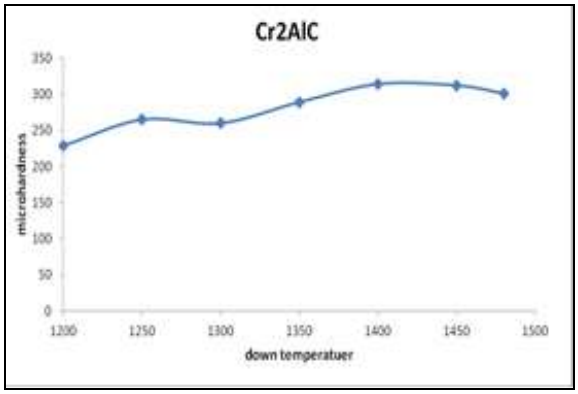

Figure 18: Shows those micro hardness values of Cr_2ALC are increased with increasing Temperature until 1250◦C

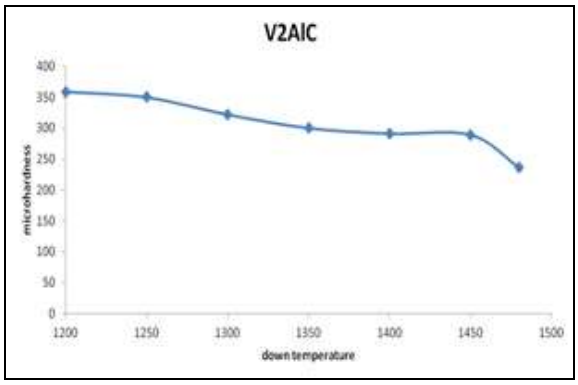

Figure 19: variation of hardness values of theV_2AlC composition sintered at different temperatures

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

3 Figure 20. 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_2AlC, Ti_3AlC_2, V_2AlC and Cr_2AlC 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 be provide the compound phase of MAX phases at may be low temperatures. Formation of these phases may be attributed to the very high reactivity of powders involved and generation of combustion temperatures during melting of low temperature melting elements. Ti_3AlC, Ti_2AlC, V_2AlC and Cr_2AlC compose in the solid state. Powder X-ray diffraction (XRD) showed that using this way of processing it was possible to obtain nearly single-phase (MAX phase) powders of all ternary carbides in three systems [5].

I. Ti_2AlC

Combustion synthesis of Ti_2AlC was observed. X-ray diffraction analysis shows that the combustion-synthesized product consists of Ti_2AlC (Figure 1). In this case, the peaks were detected single phase (MAX phase). The existence of this phase can be caused by carbon enough of Ti_2AlC, which has been found to be homogeneous at 1300 °C. We consider these preliminary results to be very encouraging; however, it seems that obtaining single-phase Ti_2AlC product is by solid state of Ti–Al–C system.

II. Ti_3AlC_2

Combustion syntheses of Ti_3AlC2 ternary compound resulted from elemental powders, no melting was visible in these samples. X-ray analysis showed that the single-phase Ti_3AlC_2 product could be obtained (Figure 5). Ti_3AlC2 has been found to be homogeneous at 1350°C and syntheses described herein were conducted assuming 3:1:2.

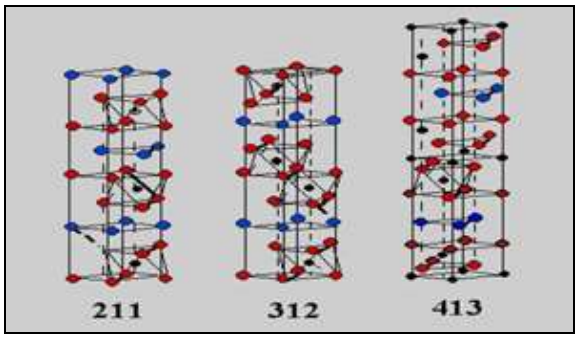

Figure 20: The combination of three types of MAX phases

III. Cr_2AlC

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^3. It is found that the phase of sintered sample consisted of the Cr_2AlC phase, as the major crystalline phase. As the first stage, a stoichiometric composition Cr_2AlC was tried for synthesis of the phase .The results showed that the sintered sample contained Cr_2AlC (MAX Phase).

IV. V_2AlC

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_2AlC after compared with the standard of the V_2AlC.

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.

6-The DSC results give some information about the A element (Aluminum) contribution on the phase formation.
7-It is contributed towards the basic understanding required to tailor and modify these ternary systems.

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