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Investigation of Solid State Reaction in the Nanolaminate – Carbides in the Ternary

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Abstract. The main goal of this work is to contribute towards the basic understanding required to realize synthesis the MAX phases in bulk 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 to indicating the mechanical properties. Finally, the differential scanning calorimetric results, over the range of 25 to 650 °C 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 °C which 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 Mn+1AX_n systems. This may release a new synthesis route for the mass production of materials with rather unique properties

Keywords: High purity powder, high temperature, Nanolaminate Carbides

1. Introduction

Over recent years, a new family of layered ceramics has attracted much interest due to their unique crystalline structure properties, such as high strength and modulus, machinability by both electrical discharge method and conventional cutting tools, good thermal and electrical conductivity and high melting point [1]. These nanolaminate carbides are hexagonal crystalline structure and complex ternary compounds can be given by the general formula Mn+1AX. Where M is a transition metal from the period table, A is an A Group element (mostly IIIA and IVA). And X is either carbon or nitrogen (1). Among this group of compounds, Ti₃AlC₂ and Ti₂AlC are two important materials which have been widely studied in the Ti–Al–C system (1). Ti₃AlC₂ exhibits some compressive plasticity abnormal room-temperature in contrast to normal brittle ternary ceramics. Ti₂AlC has also been reported to have high yield strength, significant plasticity at high temperatures, high electrical conductivity and excellent machinability (1). Another two interesting materials are Cr₂AlC and



V_2AlC . Cr_2AlC ternary carbide have been good properties which makes it a candidate for many high-temperature applications. Like metals, it is a good thermal and electrical conductor [2].

2. Experimental work

The experimental work includes two main steps:

1. The first step is the preparation of the samples that includes three systems with different molar ratio and different concentrations of (Ti-Al-C, Cr-Al-C and V-Al-C) base system by using powder metallurgy technique. The sample preparation includes:

- a Dispersion process.
- b Preparation and mixing of powders.
- c Compacting of powders, which include cold compaction.
- d Making the sintering process at different temperatures for each system under controlled atmosphere (Argon gas).

2. The second step is the characterization of samples including the following:-

- a X-ray Fluorescence (XRF).
- b X-ray Diffraction (XRD).
- c Scanning Electron and Optical Microscopic Observations (SEM).
- d Differential scanning calorimetric (DSC) and Microstructure Test (Optical Microscope Test).
- e Vickers micro hardness.
- f Density measurement.

Ti_2AlC : have been mixed (50%wt, 25%wt, 25%wt respectively). A mixer is used for 5 minutes to achieve pressing with 20 bar maximum pressure. Cylindrical steel die (made from tool steel) used in compacting process with upper and lower punch. Paraffin was used as a binder in this work at certain powder composition to provide strength to green compact. The furnace used for sintering process at 1300°C with rate 20 $^\circ\text{C}/\text{minute}$ and is held for four hours; finally, the cycle cools down slowly inside the furnace sample was held on heat-resistant plate in the furnace. The X-ray Diffraction test (XRD) is performed to obtain the MAX phase from the ternary system to form Ti_2AlC after compared with the Ti_2AlC standard as shown in Figure (1).

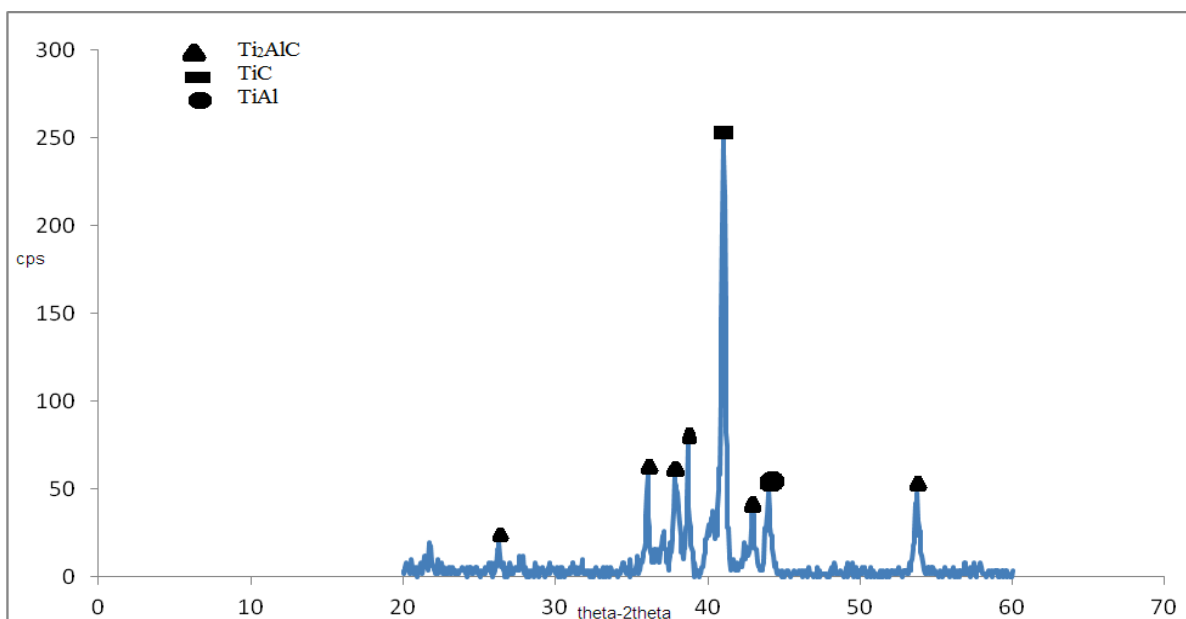


Figure 1. X-Ray diffraction test for Ti_2AlC sample with cold Compacted and Sintered at 1300°C for 4hr.

The SEM micrographs are observed that the samples were starting different grits from 600 and 800 grit to get smooth and scratch flat surface after ground by SiC emery paper. Then, these samples were cleaned with a smooth cloth as shown in figure (2). The pack scatter used to give an indication about the appearance of most phases in a different colour (4). Figure (2) shows at high temperature the large particle size approximately was the MAX phase due to its high atomic weight as shown down.

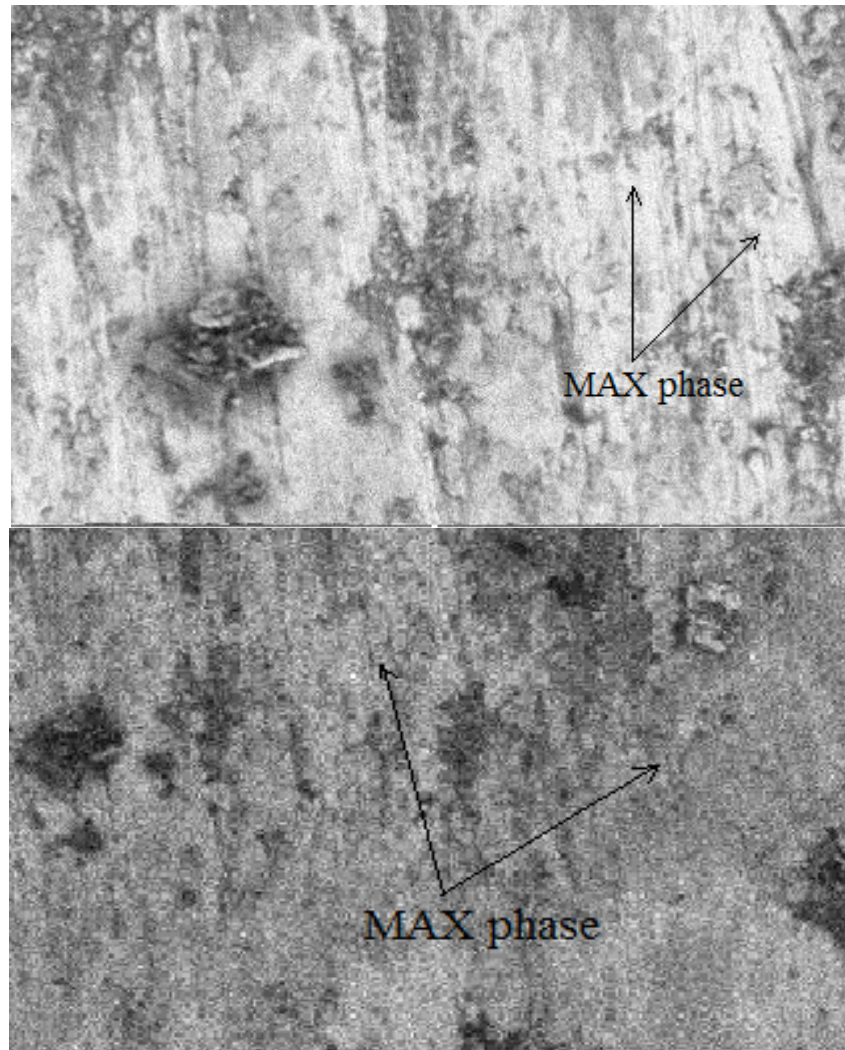


Figure 2. SEM and cold Compacted and Sintered at 1400°C for 4hr for Ti:Al:C sample=2:1:1 ratio for 2 shots.

The microstructure is also discovered by an optical microscope to see the phases existing and the grains. The optical microscope is shown in Figure (3). The magnifications were 1490 and the scale of 100 μ m. The porosity is always the dark regions.

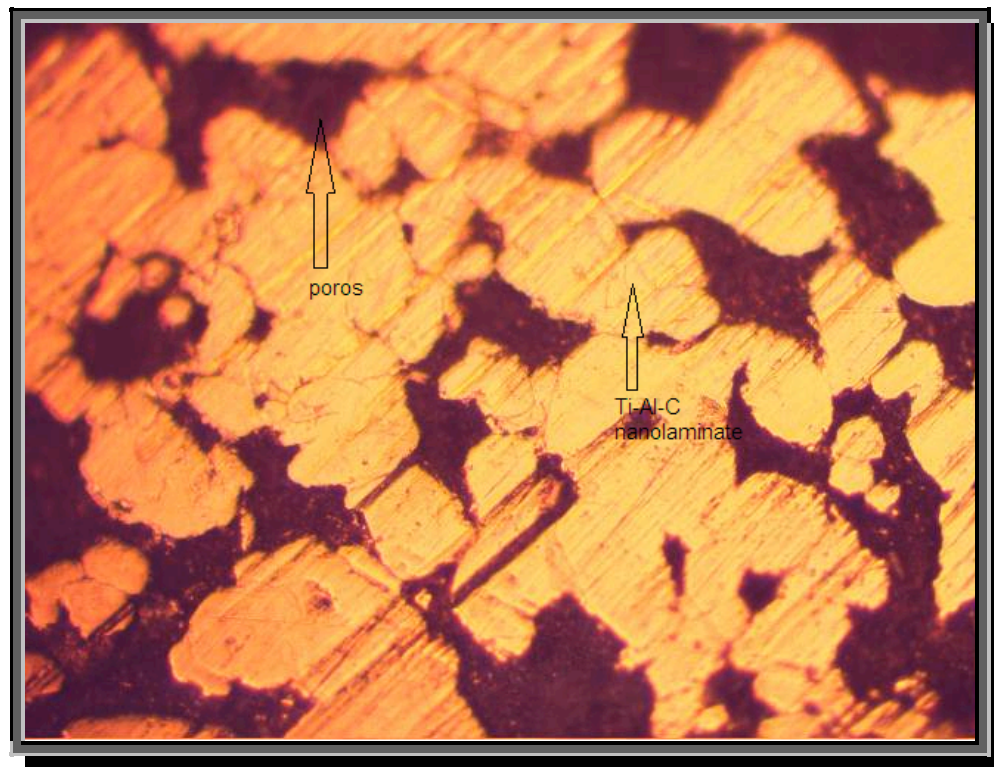


Figure 3. Ti:Al:C Sample of Optical Microstructure 2:1:1 ratio and Cold compacted and sintered at 1400°C for 4hrs with 145x.

The energy of transformations and the transformation temperatures of Ti-Al-C samples have been determined by Differential Scanning Calorimeter (DSC) is the most widely used technique (5). This test was conducted by taking (5-10) mg of each sample and testing at a scan rate of 10 °C/min. The cooling agent used in the DSC (in order to cool up to 50°C) was liquid nitrogen while maximum temperature was 700°C as shown in Figure (4).

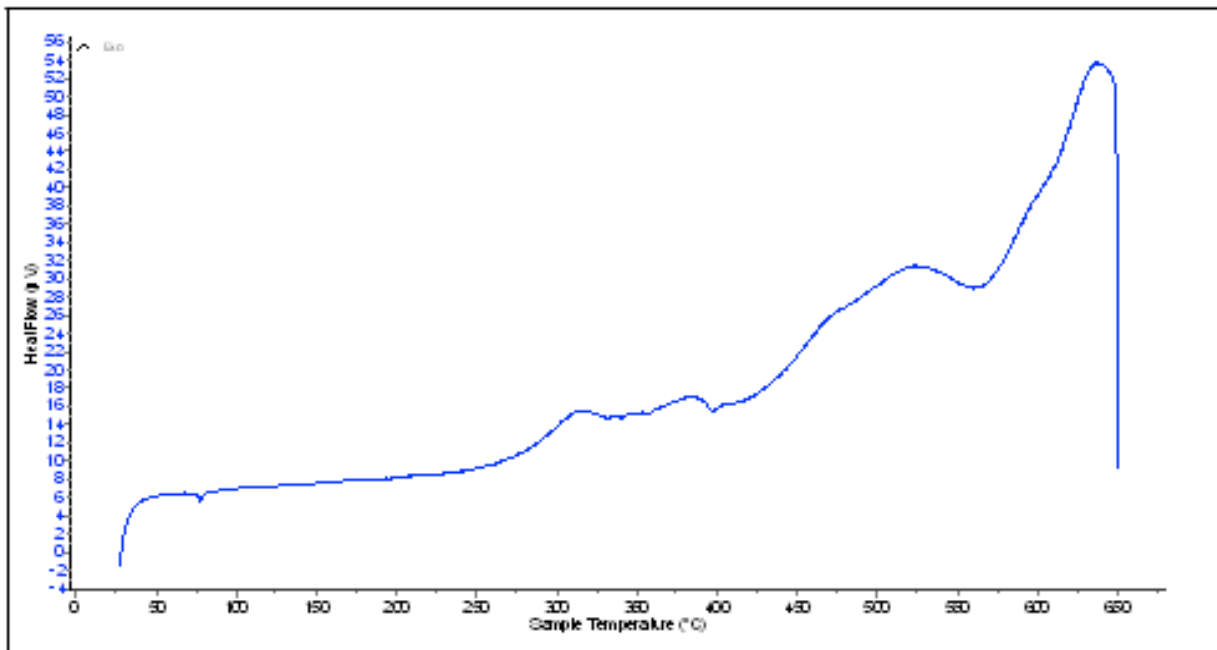


Figure 4. DSC of the Ti_2AlC sample

Ti_3AlC_2 : The same procedure applied to another sample of Ti-Al-C but sintering temperature at 1450°C for 4 hours with rate of 20 c/minute. Ti-Al-C (3:1:2) respectively mixed and pressed 20 bar in a vacuum furnace. The held time four hours and cooled in a furnace at room temperature. The (XRD) test X-ray Diffraction 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 observed in Figure (5).

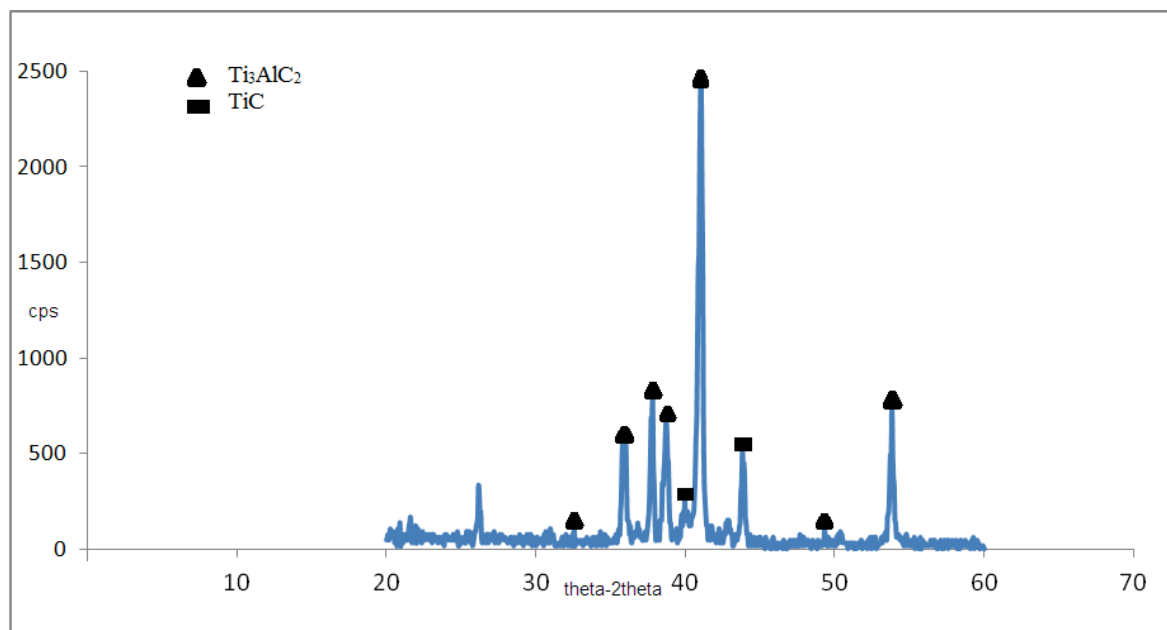


Figure 5. X-Ray diffraction test for a Ti_3AlC_2 pattern with Cold compacted and sintered at 1450°C for 4hrs.

The phase analysis of Ti_3AlC_2 was carried out by X-ray diffraction (XRD) and produced as a result of sintering process can be seen in figure (5). Most of these peaks in figure (5) indicated Ti_3AlC_2

(MAX phase as the formula $Mn+1AX_n$, where $n=2$) in compared with the standard of Ti_3AlC_2 . The formation of TiC phase because of its stability phase (6).

Cr-Al-C: The sample of Cr-Al-C followed the same procedure but electrical press with 15 ton/cm^3 in a vacuum furnace at temperature 1000°C and held 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) (7).

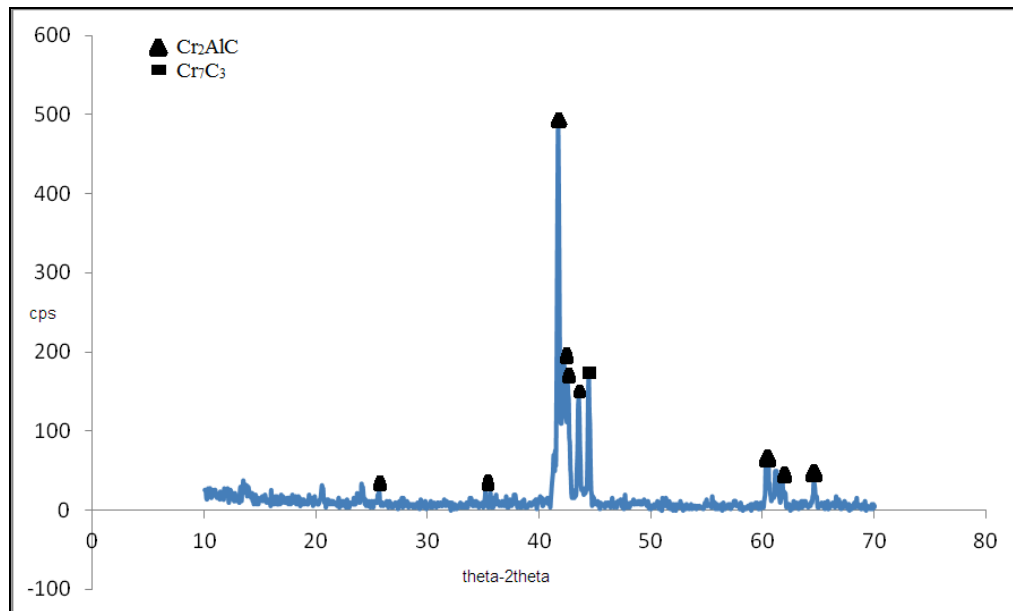
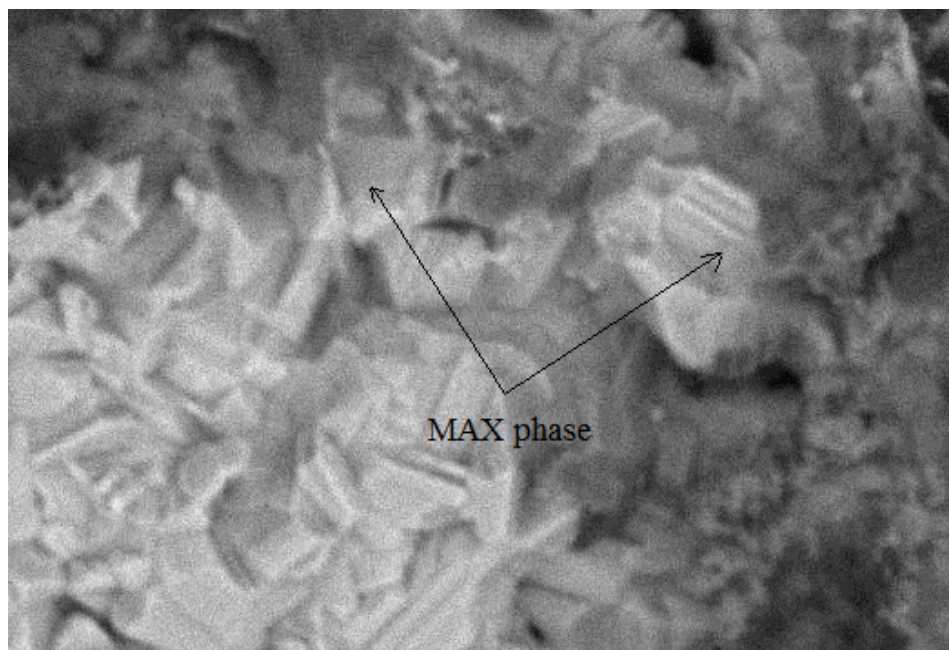


Figure 6. XRD Diffraction of Cr_2AlC pattern with Cold compacted and sintered at 1000°C for 2hrs.

Figures (7) shows at high temperature the large particle size approximately was the MAX phase due to its high atomic weight as shown down of The SEM micrographs of Cr_2AlC (8).



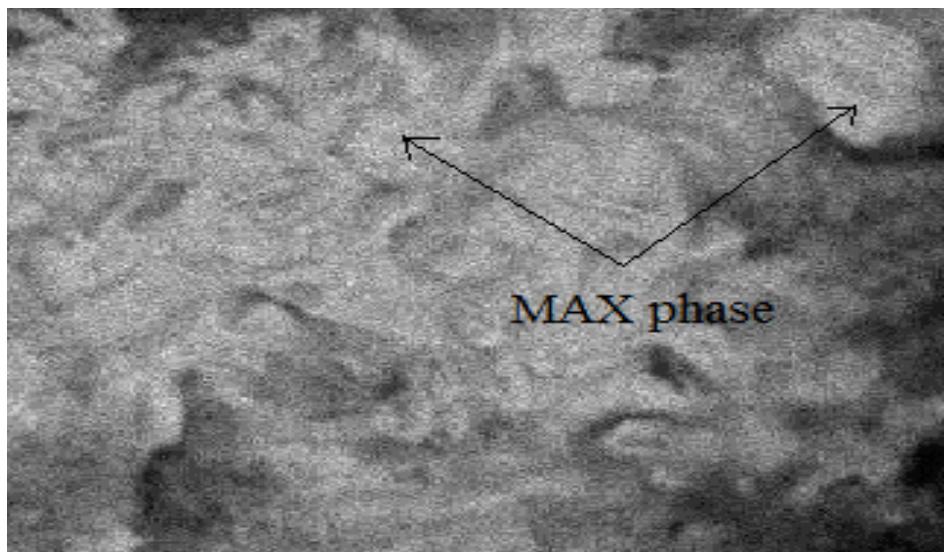


Figure 7. Cr:Al:C Sample 2:1:1 of SEM(Sintered at 1000°C for 2hrs and Cold Compacted) for 2 shots.

Optical microscope micrograph is observed in figure (8). The pores are mostly the dark regions. 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.

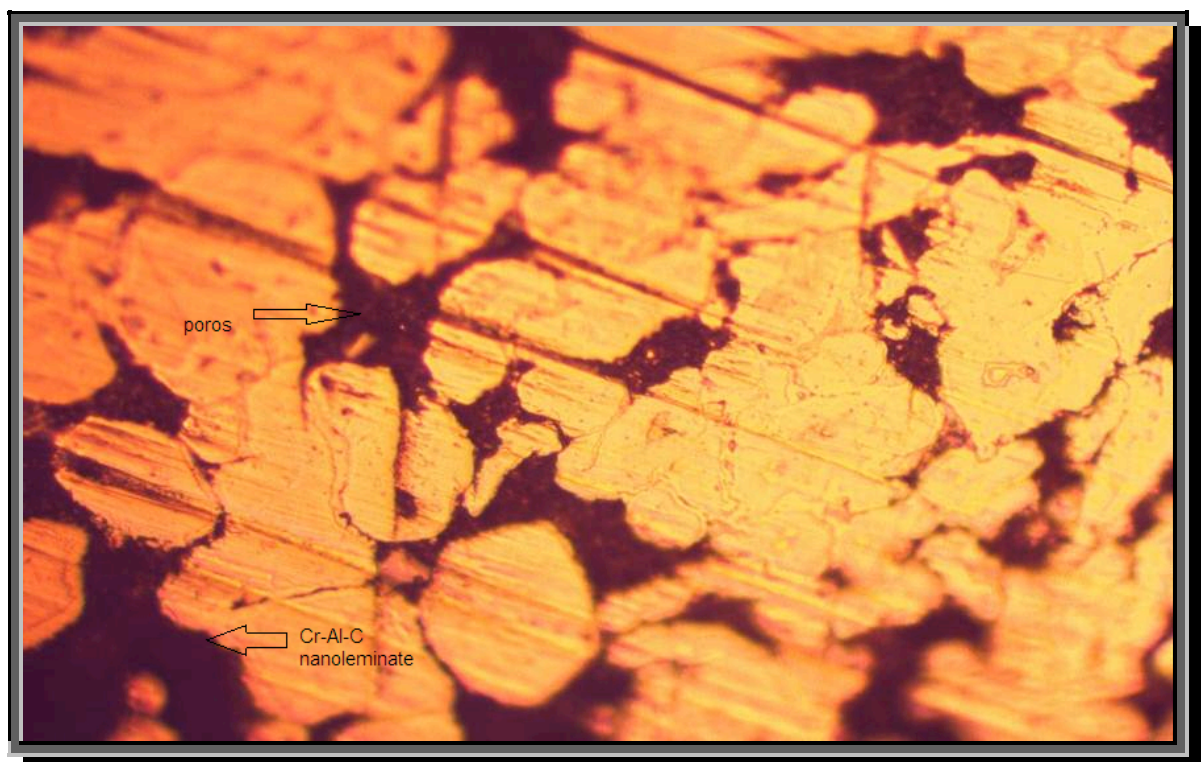


Figure 8. Cr:Al:C Sample of Optical Microstructure(2:1:1 sintered at 1000°C for 2 hrs with 80x and cold compacted).

This system shows clearly that the overall reaction occurs at the investigated temperature range is completely endothermic by DSC test as shown in figure (9). One DSC signal is observed at

the range from $\sim 350^{\circ}\text{C}$ to $\sim 450^{\circ}\text{C}$. 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 $\sim 650^{\circ}\text{C}$. This may indicate the stability of the transformed phase at the previous range. It is also expected that the reaction with Aluminium is the key to let this reaction occur at this system. Hence, Aluminium diffusivity may play an important role to start and continue the reaction in all these systems (9).

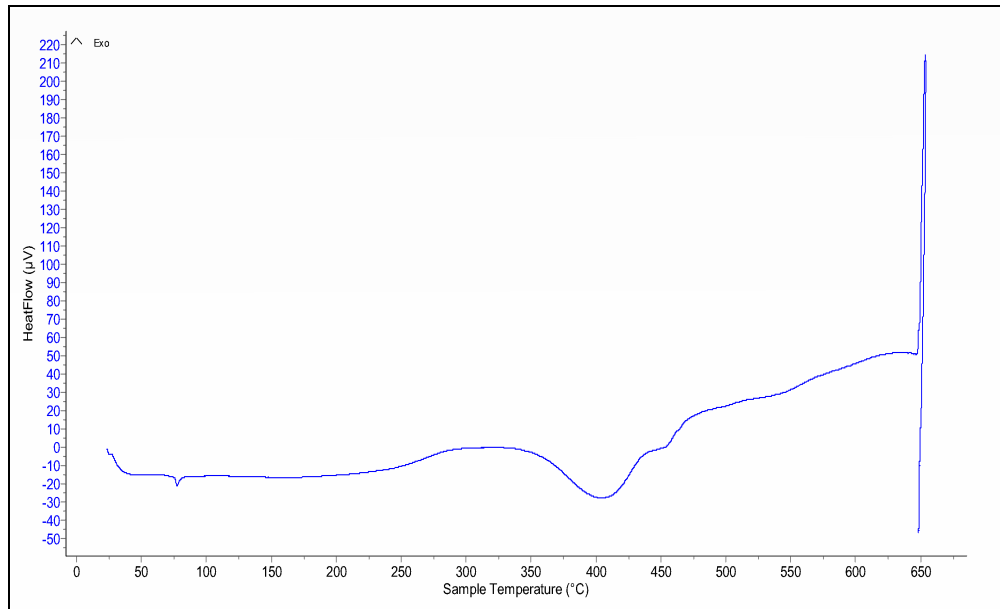


Figure 9. DSC of the Cr_2AlC sample.

High purity powders can be used as base materials. Usually, it mixed and then compacted at a pressure of 20 MPa. The compacted mixture was heated in an Ar atmosphere at a temperature of 1300°C for 2 h. In the end, the sample was leaving cool down at room temperature. X-ray diffraction in figure (10) indicates that the V-Al-C system shows a direct formation of MAX phase under these conditions.

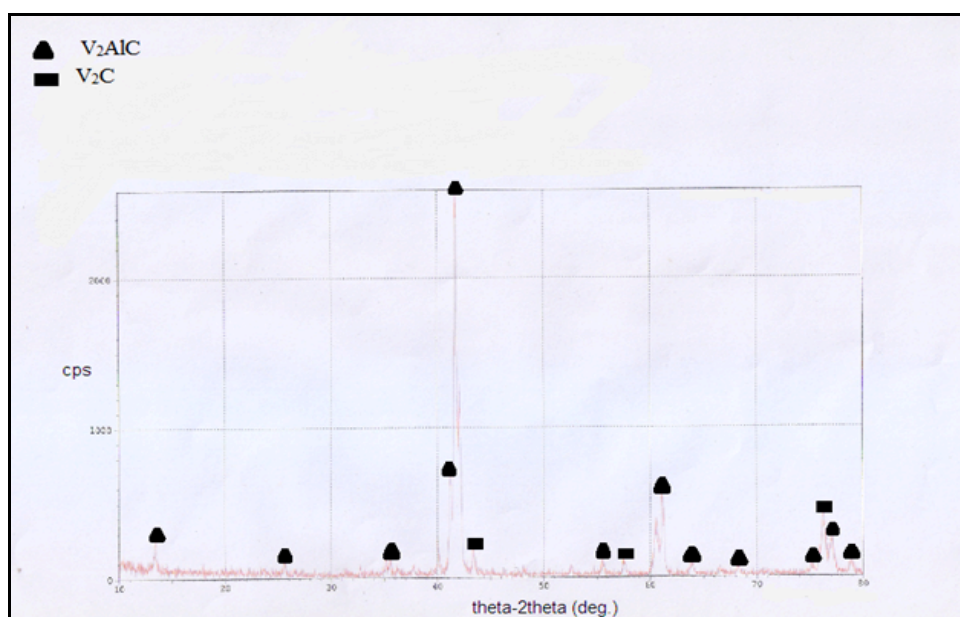


Figure 10. X-ray diffraction of V_2AlC pattern with Cold compacted and sintered at 1300°C for 2hrs.

At last, MAX phase of V_2AlC obtained after analysis peaks in figure (10) by comparing with the peaks standard of V_2AlC (5). The formation of V_2C phase because its stability phase Figures (11) show the microstructure results (SEM) of V_2AlC sample

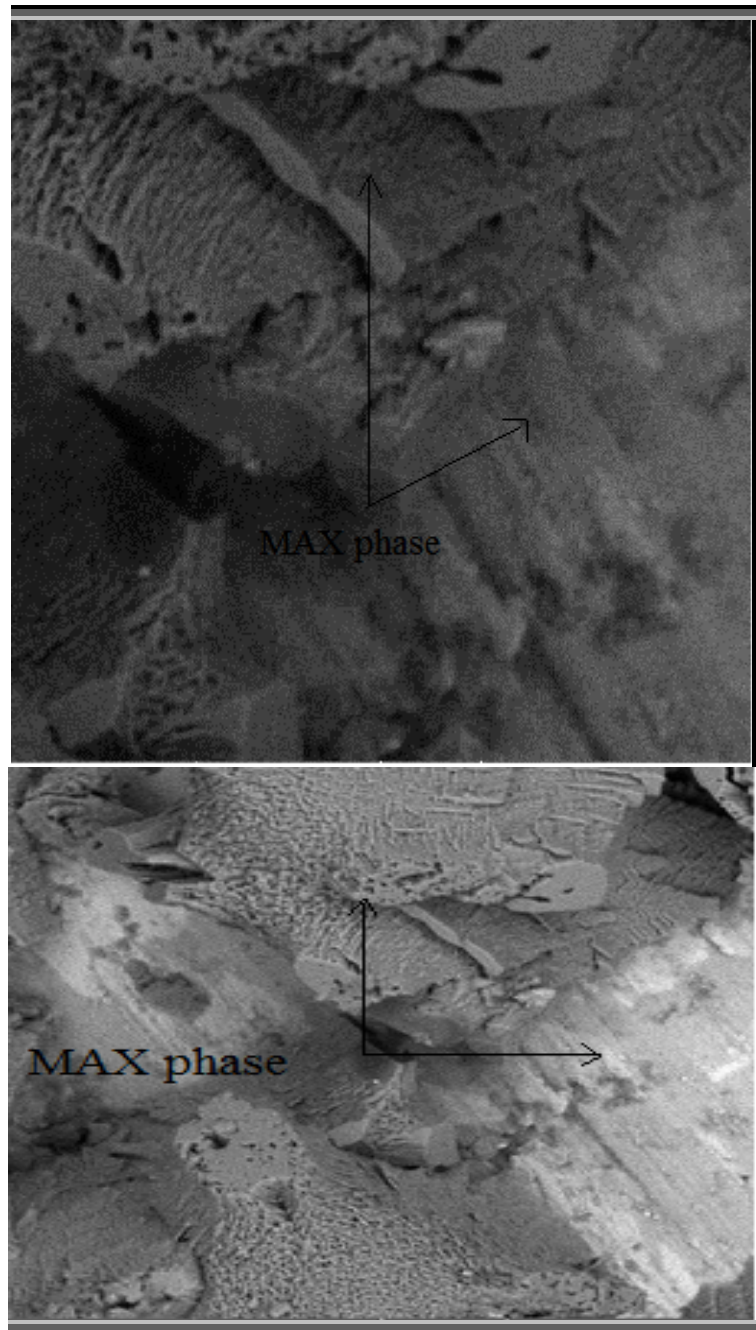


Figure 11. V: Al: C Sample of SEM (2:1:1 ratio sintered at 1300°C for 3hrs and Cold Compacted).

At high temperature, the large particle size approximately was the MAX phase due to its high atomic weight as shown above. The optical microscope micrograph is observed in figure (12). The porosity is mostly the dark regions.

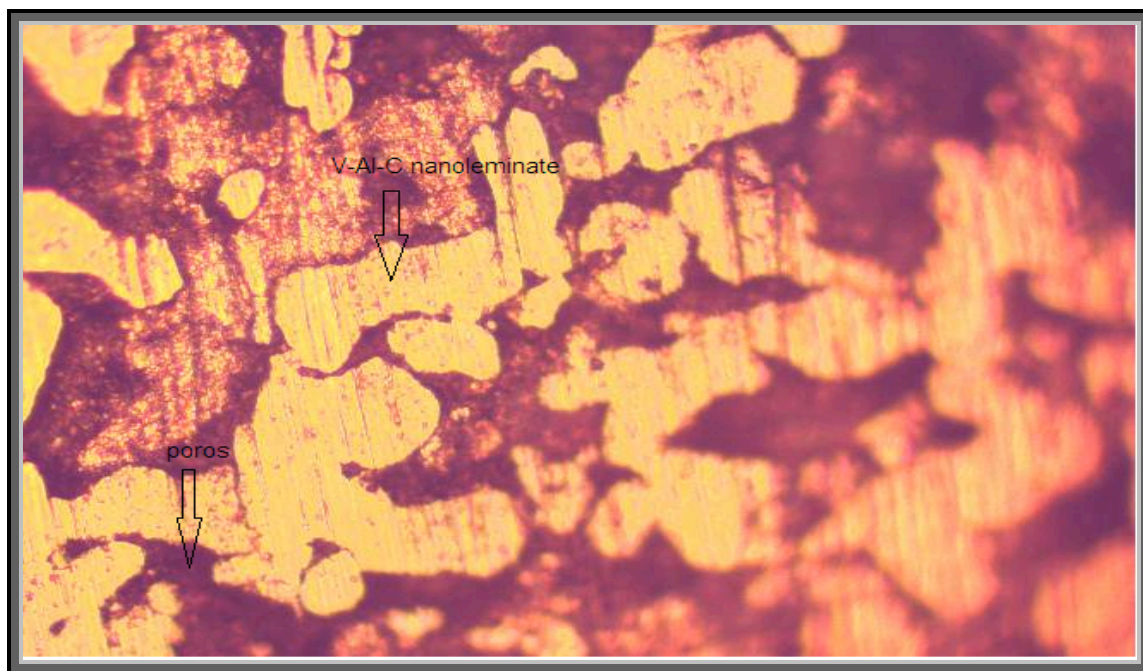


Figure 12. V: Al: C Sample of Optical Microstructure (2:1:1ratio Sintered at 1300°C for 2hrs with 145x and Cold compacted)

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 - $320^\circ C$. Furthermore, the final reactions were observed at the temperature range between ~ 580 - $640^\circ C$. This may also indicate the primary and secondary reaction levels. All reactions for this system including an 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).

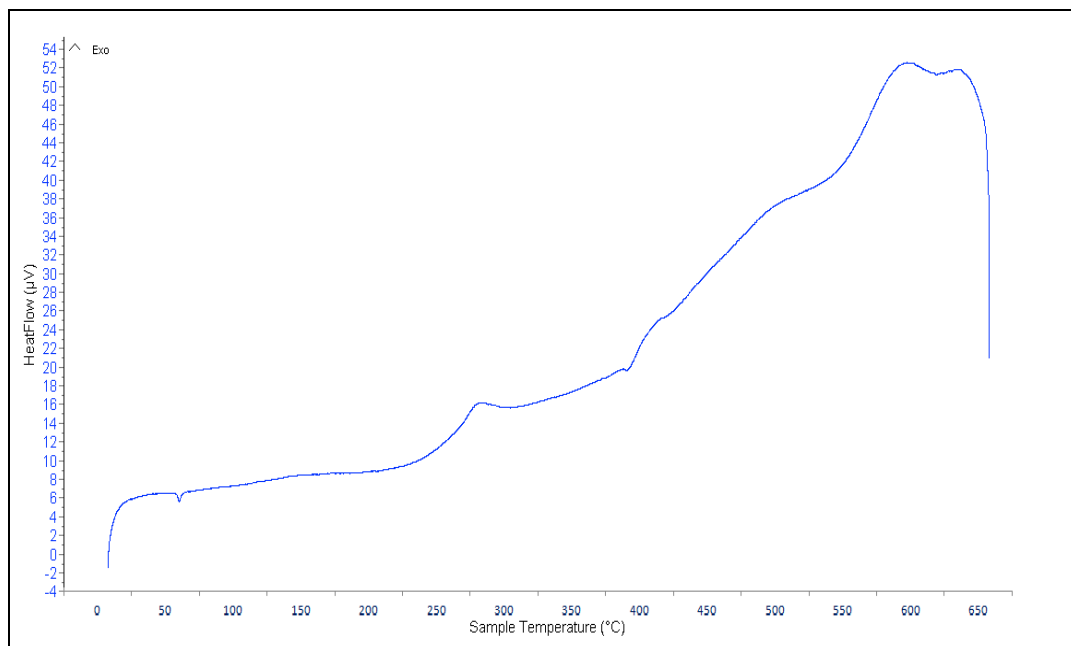


Figure 13. DSC of the V_2AlC sample.

3. Mechanical properties

3.1. Density test

The density percentage was measured by using method is Archimedes base. This is measuring the weight of dry samples, then the samples are immersed in water for 24 hours, and then weight the samples after cleaning their surface with a cloth after immersed, and at the end, we weight the samples while they are put it in the basket and immersed in water again.

The density is measured by this formula [11]:

$$\text{Density\%} = [(W_r - W_d)/(W_r - W_i)] * 100 \quad (3.1)$$

Where:

W_r = weight of saturated samples.

W_i = weight of the immersed sample

W_d = weight of dry sample

The figure (14) show Ti_2AlC sample density that the linear increase of the density starts at 1200°C to 1400°C because of the probability formation of MAX phase. At 1400°C starts to decrease with increasing the temperature that the probability disintegration was an event.

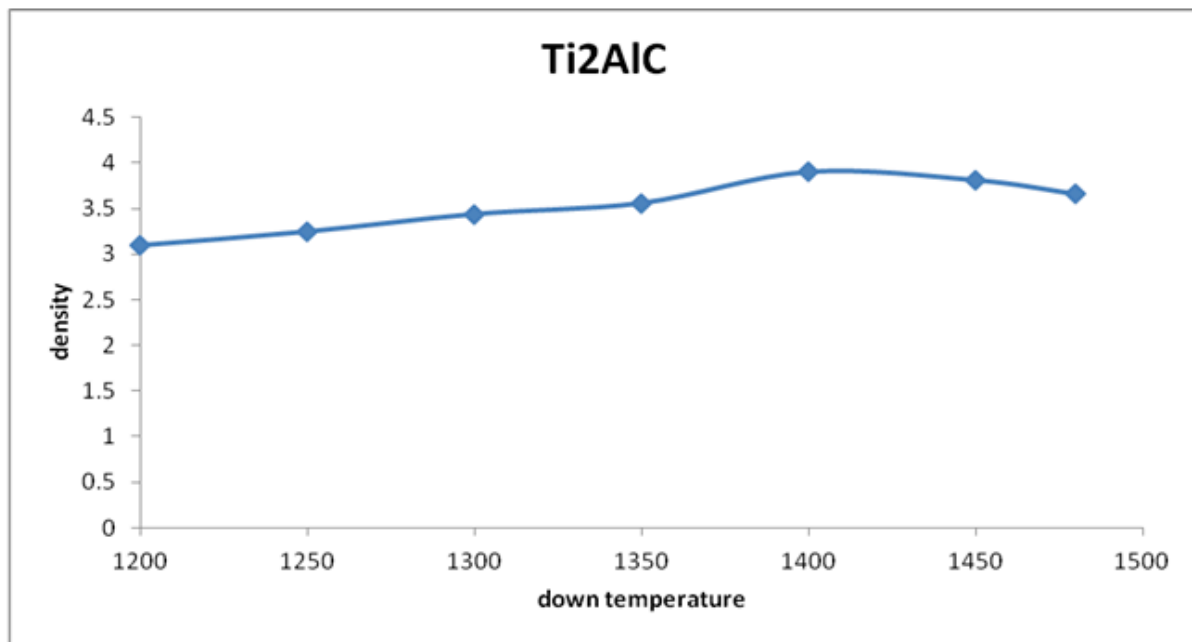


Figure 14. Density of the Ti_2AlC sample.

Figure (15) show the density behaviour and the temperature of Cr_2AlC sample. This figure shows that the density behaviour with the temperature was linear at 1200°C to 1350°C because the probability density of the interphase was equal the density of the final phase and begin to increase with increasing the temperature at 1350°C due to the formation of MAX phase. After that, the density of sample decreases with increasing the temperature at 1450°C due to the probability of disintegration.

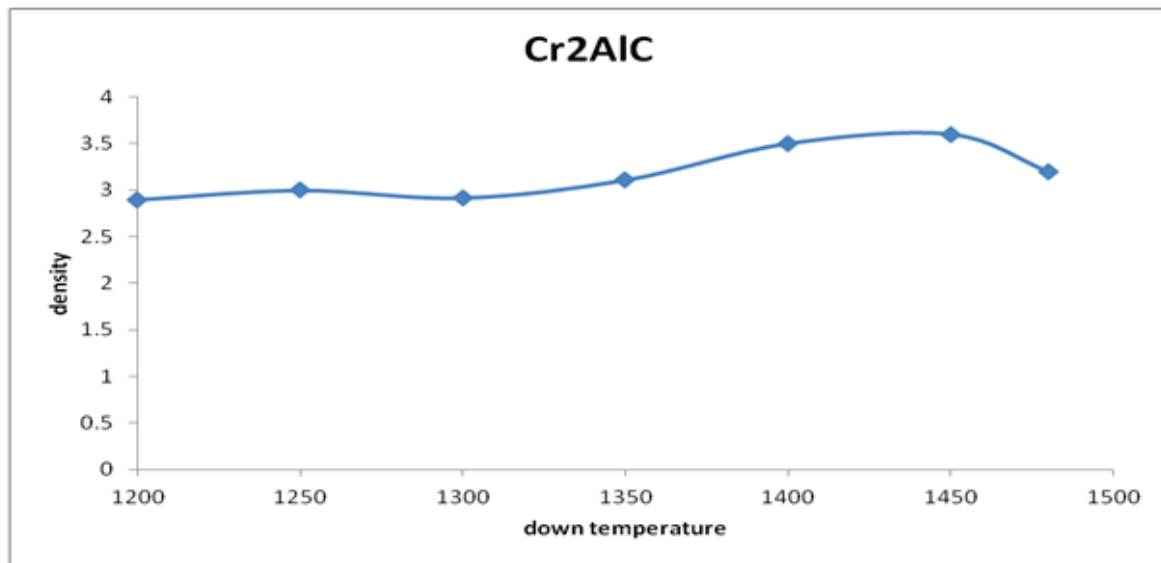


Figure 15. Density of the Cr₂Al sample.

Figure 16 shows that the density percentage fixes to 1200°C because the probability density of the interphase was equal to the density of the final phase. After that the density of the samples decreased from 1250°C to 1350°C and fixed at 1450°C. Finally, the density decreases with decreasing the temperature (from 1500 to 1450) °C because of the probability disintegration.

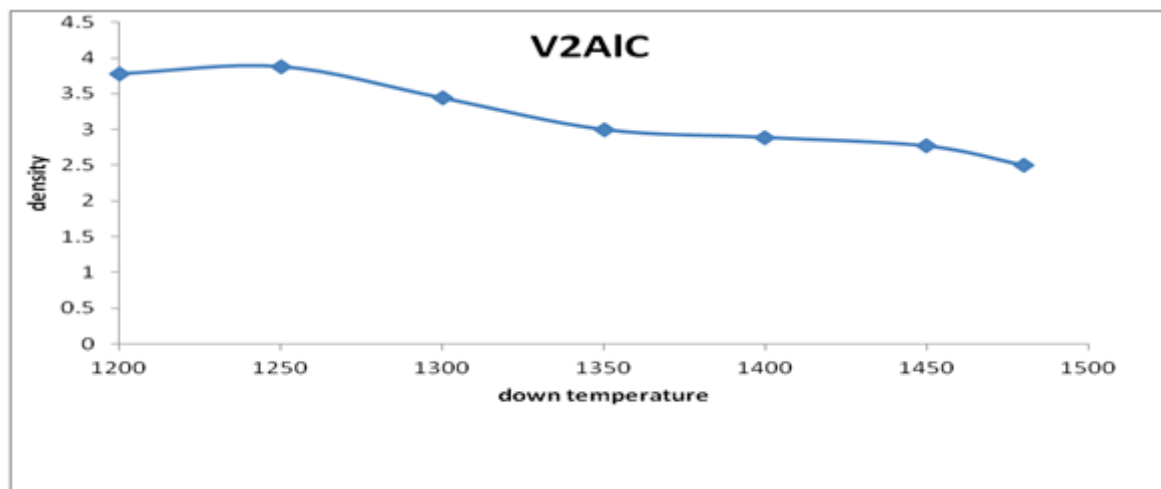


Figure 16. Density of the V₂AlC sample.

Note: - there are factors have been affected by the density of these samples such as Degree of interaction, compressed method and crystal structure.

3.2 Micro hardness Test

The hardness of these alloys can be given by using Vickers microhardness tester type (TP μ-, HV= 1000) which is placed then wear Laboratory (11). The located of 7 readings was taken for samples with a radius of 5mm and height of 4mm. All values of hardness are taken at a load of 1000 grams. The hardness values of the Ti₂AlC sample obtained are represented graphically in Figure (17)

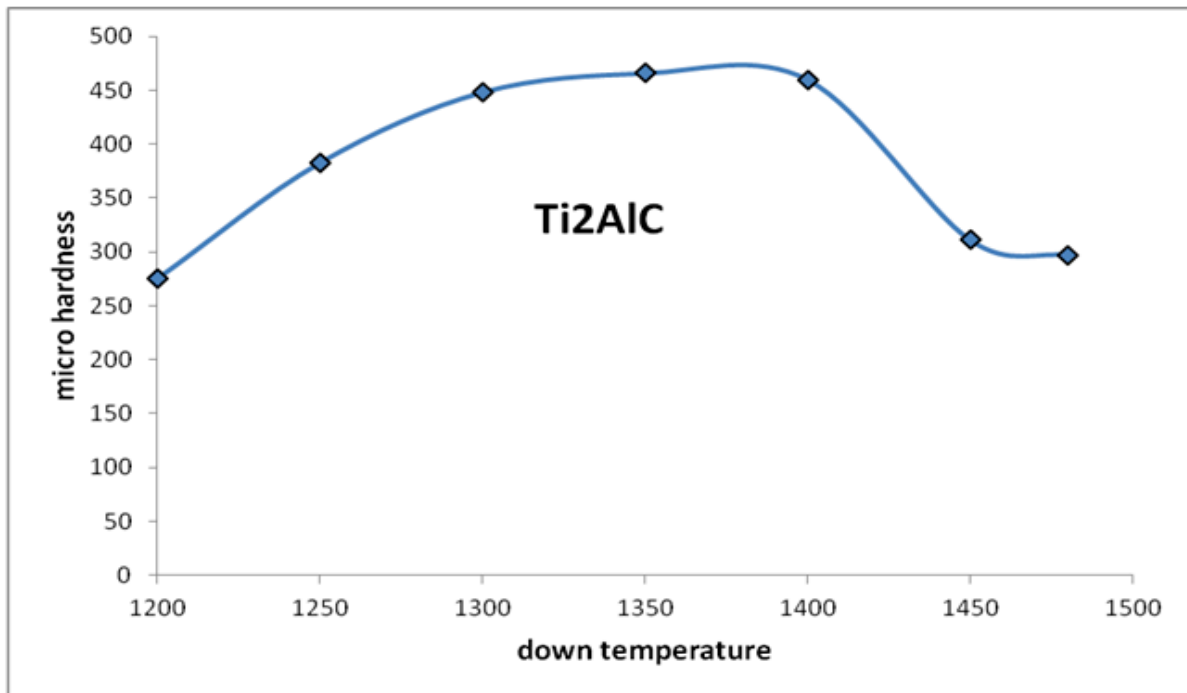


Figure 17. Density of the Vr_2AlC sample.

We can see that the measurement microhardness increases by increasing the Temperature until 1300°C and the microhardness fixed (linear) with little increased in microhardness until 1400°C. After that it decreased from 1400°C until 1480°C. Finally, the microhardness fixed until 1500°C during the sintering process. The final value of microhardness of Ti_2AlC was 460 Hv as shown above figure.

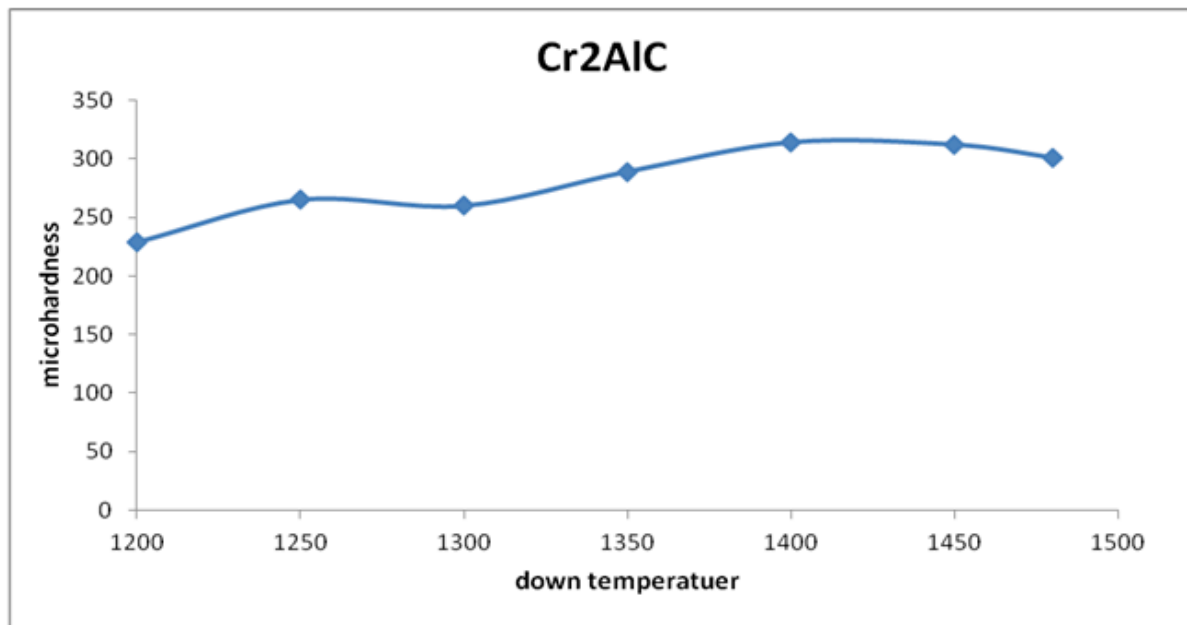


Figure 18. hardness values of the Cr_2AlC sample.

Figure (18) shows that measurement microhardness value of Cr_2AlC . The microhardness increased with increased temperature at 1250°C and fixed between (1250-1300) °C. After that the microhardness was increased with increased the temperature until 1400°C. Finally the microhardness

decreased until 1500°C. The final value of microhardness of Cr_2AlC was 300 Hv as shown above Figure

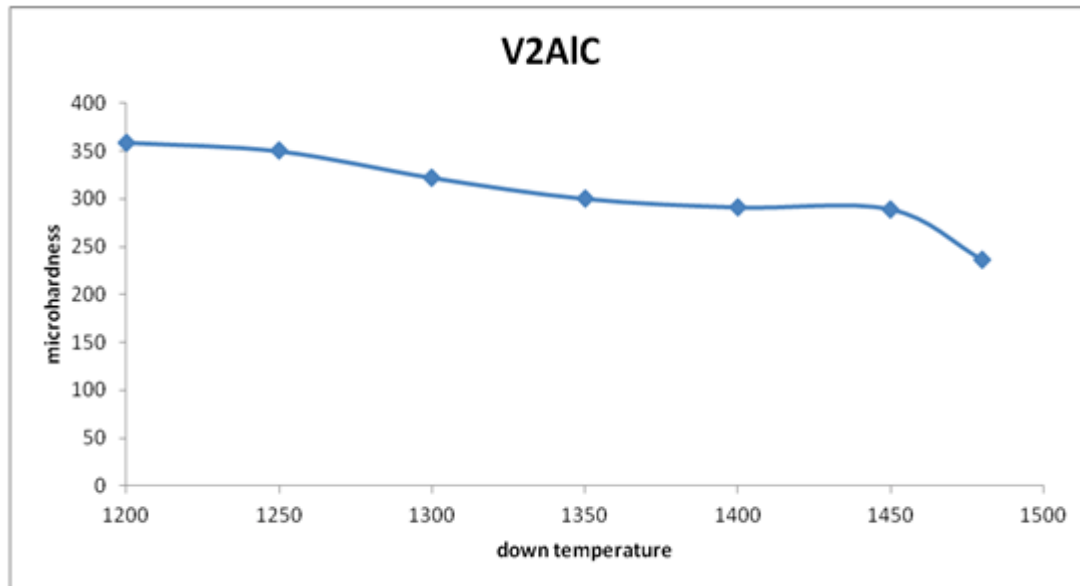


Figure 19. Microhardness values of the Cr_2AlC sample.

The microhardness exhibits approximately linear behaviour across the temperature of V_2AlC with little decreased at (1200 -1300) °C except above 1450°C the microhardness decreased with the temperature increased. The final value of microhardness of V_2AlC was 360 Hv as shown above figure. According to another research, the final value of micro hardness in this research was little because low sintering time which slows the phase to form and it's crystallizing at 100%.

4. Results and discussion

From the periodic table, the transition metal M (red). Groups, usually IIIA and IVA (blue), and a third element, X, which is either nitrogen or carbon (black), are made up MAX phase as the composition Mn+1AX_n , where n is 1, 2 or 3. The types of materials properties to give naturally form into three groups, centred by the number of the M, A and X atoms of the elements in each molecule; Then, there are three groups as 211, 312 and 413 materials [12, 13].

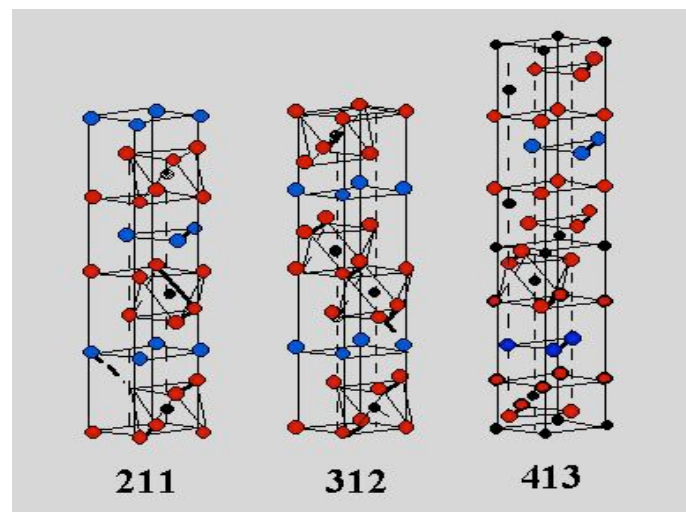


Figure 20. Classification of MAX phase [211,312,413]

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 V-Al-C, Ti-Al-C, and Cr-Al-C in order to find out which of them is easy to be formed. Combustion syntheses of Ti_2AlC , Ti_3AlC_2 , V_2AlC and Cr_2AlC compounds were discovered using different weight ratios of elemental V, Ti, Al, Cr, and C powders. In these methods, the reactions discovered to be extremely violent with a significant amount of reactants being the exit of the graphite boat. The structure products have been nonhomogeneous in their colour and morphology. Then, during the synthesis, a significant partial melting was noticed. The combustion was difficult to process and very hard. These phases may be classified into the very high reactivity of powders involved and generation of combustion temperatures well in excess of 1500°C depended to the combustion. High temperatures in detail can be causing any decomposition of desired in these systems. This system indicates that Ti_3AlC , Ti_2AlC , V_2AlC and Cr_2AlC compose in the solid state. The powder X-ray diffraction (XRD) estimated that using this method it was possible to get nearly single-phase (MAX phase) powders of all nanolaminate carbides in three systems(5).

Ti_2AlC

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

Ti_3AlC_2

Combustion syntheses of Ti_3AlC_2 ternary compound resulted from powder metallurgy. the single-phase Ti_3AlC_2 product could be obtained that show no melting was visible in this samples-ray analysis. (See Fig. 5). Ti_3AlC_2 has been found to be homogeneous at 1350°C and product gave herein were conducted as group 3:1:2.

Cr_2AlC

The XRD pattern of the samples cold-pressed at 1000°C for 2 h is shown in Fig. (6). the pressing was $15\text{ ton}\cdot\text{cm}^3$. The major crystalline phase which the phase of the sintered sample consisted of the Cr_2AlC phase. Initially, the composition Cr_2AlC was tried to form of the phase. MAX Phase showed that the sintered sample contained Cr_2AlC .

V_2AlC

After heating powder in the temperature 1300°C for 2 h, was applied. X-Ray diffraction data indicate that the almost phase is V_2AlC after compared with the standard of the V_2AlC shown in Figure (10).

5. Conclusion

From studying of the Investigation of solid state reaction in the nanolaminate Cr-Al-C, Ti-Al-C and V-Al-C system, the following conclusions can be drawn:-

- 1 The synthesis route of three different ternary carbides system of Cr-Al-C, Ti-Al-C, and V-Al-C were investigated.
- 2 Pure elemental powders have been used to construct an acceptable 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 (Aluminium) 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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