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 °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 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<sub>n+1</sub>A<sub>n</sub>C systems. This may release a new synthesis route for the mass production of materials with rather unique properties.

Keywords- Ternary system, solid-state reaction.

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<sub>n+1</sub>A<sub>n</sub>X<sub>n</sub> 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<sub>2</sub>A<sub>1</sub>C and Ti<sub>2</sub>A<sub>1</sub>C 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<sub>2</sub>A<sub>1</sub>C<sub>2</sub> exhibits some abnormal room-temperature properties. Compressive plasticity in contrast to normal brittle ceramics. Ti<sub>2</sub>A<sub>1</sub>C 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<sub>2</sub>A<sub>1</sub>C and V<sub>2</sub>A<sub>1</sub>C 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<sub>2</sub>A<sub>1</sub>C 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<sub>2</sub>A<sub>1</sub>C

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<sub>2</sub>A<sub>1</sub>C MAX phases as shown in Figure 1 [3].
Figure 1: X-Ray diffraction pattern of Ti$_2$AlC [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 pors 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 V₂AlC system shows a direct formation of MAX phase under these conditions.  

Figure 11 shows the microstructure results (SEM) of V₂AlC 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 (V₂AlC) a great similarity can be found as compared with the signal obtained from the Ti₂AlC 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].
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 V2AlC

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:

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

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 Ti2AlC 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 Cr2AlC 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 sample is decreased with the temperature (from 1500 to 1450) °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 Ti$_2$AlC 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$_2$AlC compound is 460 HV as shown in Figure 17. After that the micro hardness was increased with increased the temperature until 1400°C. Finally, it was decreased until 1500°C. The final value of microhardness of Cr$_2$AlC was 300 HV as shown in Figure 18. The micro hardness exhibits approximately linear behavior across the sintering temperatures of V$_2$AlC 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$_2$AlC 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 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$_2$AlC, Ti$_3$AlC, V$_2$AlC and Cr$_2$AlC 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$_2$AlC
Combustion synthesis of Ti$_2$AlC was observed. X-ray diffraction analysis shows that the combustion-synthesized product consists of Ti$_2$AlC (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$_2$AlC, 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$_2$AlC product is by solid state of Ti–Al–C system.

II. Ti$_3$AlC$_2$
Combustion syntheses of Ti$_3$AlC$_2$ ternary compound resulted from elemental powders, no melting was visible in these samples. X-ray analysis showed that the single-phase Ti$_3$AlC$_2$ product could be obtained (Figure 5). Ti$_3$AlC$_2$ has been found to be homogeneous at 1350°C and syntheses described herein were conducted assuming 3:1:2.

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.
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.

References

[1] Z. LIN, Y. Zhou and M. LI, J. Material Science Technology, Vol. 23, 2007.
[2] M.W. Barsoum, “Program of Solid State Chemical,” 28, 201, 2000.
[3] J.Y. Wang, Y.C. Zhou, Z.J. Lin, F.L. Meng and F. Li, Applications Physical Lett., P 86, 2005.
[4] V. Gauthier-Brumet, T. Cabioc’ H.P. Chartier “Reaction synthesis of layered ternary Ti$_2$AlC ceramic,” Journal of the European Ceramic Society, 29,187–194, 2009.
[5] A.M. Hasan “On the stability of MAX phase thin film,” RWTH Aachen University, 2011.
[6] Y. Zou, Z. Sun,”Low temperature synthesis of single-phase Ti3AlC through reactive sintering Ti/Al/C powders,” Materials Science and Engineering, A 473 90–95, 2008.
[7] Z. Lin, Y. Zhou, M. Li, J. Wang, Metallkd, 96, 291-29, 2005.
[8] Z.J. Lin, Y.C. Zhou, S. Li M, J.Y. Wang. Metall., “On the synthesis and properties of bulk ternary Cr2AlC ceramics,” 6, 291, 2005.
[9] J.C. Schuster, H. Nowotny, C.J. Vaccaro., “Solid State Chemical, “ 32, 213, 1980.
[10] Schneider, Jochen M, “Thermal stability of MAX-Phase, Sputtering,” RWTH Aachen college, 2013.
[11] R.A. Hussein, “Preparation and Characterization of NiTi Shape Memory Alloys,” MSc thesis, University of Technology, Materials Engineering Department, 2011.
[12] M.W. Barsoum, T. El-Raghy, American Scientist, 89, p 334-343, 2001.