The Effect of Aluminum Concentration on The Phase Evolution of The Ternary Ceramics Of (Ti-Al-C) System

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ABSTRACT

In this work it has been tried to introduce this type of new materials as reproducible industrial materials and overtake some production obstacles by exploring on the direction of chemistry structure relation.

In this study composition was prepared from elemental powders (Titanium, Aluminum and carbon black) by using the powder metallurgy techniques, under different concentration due to the change in the Ti to Al concentration. The concentrations are (10% Al-80%Ti-10%C), (20%Al-70%Ti-10%C) and (30%Al-60%Ti-10%C).A compacted sample were formed in cold press using a 30ton followed by heat treatment started from (600˚C, 800˚C, 1200˚C and end in 1400˚C). The effect of Al concentration on phase evolution in the Ti-Al-C system has been investigated and the effects of cold pressing as well as heat treatment have been investigated. X-ray diffraction (XRD) and SEM technique we used for phase evolution. The density and porosity percentage were calculated using Archimedes method, also the micro hardness was measured under that different process.

The XRD, SEM data shows that, by increasing the Al concentration intermediate phases like TiAl3 and/or TiAl appear to be stable instead of the H phase. By raising the temperature, transformations accurse to produce both MAX phase structures in this system Ti2AlC and Ti3AlC2. This production pathway from the intermediate phase to ternary phase is suggested to be the more accepted, and it depends on atomic mobility. No evidence for the direct formation of MAX phases from elemental powders is found which may explain the need of high temperatures to produce such phases since the breaking of bonds is required for the intermediate phase. Finally, the use of pre-heating process decreases the temperature of formation of the MAX phases with the effect of the highest Al concentration.

Keywords: phase evolution, Ternary Carbide, MAX phase, Ti2AlC, Ti_3AlC_2

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تأثير تركيز الالمنيوم على تكوين الاطوار الكاربيدية الثلاثية لمنظومة ال السيراميكية (Ti-Al- C)

الخلاصــة

في هذا العمل تمت محاولة التعرف على هذه المواد الجديدة كمواد قابلة للتصنيع باستخدام مواد اولية مع الاخذ بنظر الاعتبار كل المعوقات التي تؤدي بالتفاعل الى هذه الأطوار النهائية. في هذه الدراسة تم تحضير عينات من التيتانيوم والالمنيوم النقي مع الكاربون الاسود بإستخدام تقنية الميتالورجيا مساحيق وبعدها وزعت العينات على اساس اختلاف التركيز بين الالمنيوم مع التيتانيوم لدراسة التأثير الحاصل من قبل الالمنيوم على ظهور الاطوار الكاربيدية لمنظومة (Ti-Al-C).

باستخدام التراكيز كالتالي: (30%Al- 60%Ti-10%C). العينات المظغوطة بالكبس البارد بمقدار 30 طنا الحقت بمعاملة حرارية بدرجات مختلفة بدأت من (1400˚C, 1200˚C, 800˚C, 600˚C,)وبهذا تم دراسة تأثير تغير نسبة الالمنيوم على سلوك الاطوار الناتجة من منظومة (Ti-Al-C) بدرجات حرارية مختلفة. علاوة على ذلك تم دراسة تأثير الكبس على البارد على هذه السبائك. وتحليل الاطوار بإستخدام جهاز الاشعة السينية (XRD) وكذلك تمت دراسة السطوح الناتجة بإستخدام المجهر الالكتروني الماسح(SEM). وقياس الكثافة والمسامية باستخدام طريقة ارخميدس مع قياس صلادة السطح.

أظهرت نتائج التحليل والتصوير المجهري انه بزيادة تركيز الالمنيوم يبدا الطور البيني بالظهور ويكون مستقرا في درجات الحرارة الواطئة بدلا من ظهور الطور الكاربيدي،وبزيادة درجة حرارة التلبيد يحدث التحول الذي يؤدي الى ظهور ما يسمى (Max Phase) او (H Phase) وبخاصة في كل من المنظومتان المنتجتان ل(Ti_2AlC) و (Ti_3AlC_2). هذا التحول من الطور البيني الى الطور الكاربيدي يعتمد على حركة الذرات ولا توجد اي اشارة الى ان التحول يكون مباشرا الى الطور الكاربيدي دون المرور بالطور البيني والذي يفسر ضرورة الحرارة العالية لإنتاج هذه المواد مع ضرورة وجود طاقة عالية لكسر الاواصر المتكونة بين الاطوار البينية للتحول الى الاطوار الكاربيدية الثلاثية النهائية.

INTRODUCTION

The ternary ceramics (carbides or nitrides) are three-component systems that are similar to two-component systems except that there are four independent variables: pressure, temperature and the concentration of two components (which fix the third). If pressure is arbitrarily fixed, the presence of four phases gives rise to an invariant system. A complete graphical representation of ternary system is difficult, but the pressure is held constant, composition can be represented on an equilateral triangle and a temperature on a vertical ordinate to give an idea about the relations between these three elements [1] The phases of the Ti-Al-C system were introduced. First, the ternary phases in the system are described with focus on the MAX phases, the model materials in this research. Second, the binary phases are considered, which in one way or another play an important role for the properties in the bulk materials, thin films and coatings. [2] The phase diagram of the Ti-Al-C system is shown in figure (1).

The ternary carbides or nitrides with a Mn+1AXn chemistry where n = 1, 2, or 3, M is an early transition metal, A is an A-group element (mostly groups 13 and 14), and X is C or N represent a family of more than 60 members [3]. A host of metal called carbides are used in ceramic formulations; these include (TaC, TiC, Cr3C2, VC, Mo2C, B4C, WC, and ZrC).These metal carbide powders are produced by carbothermal reduction of the relevant metal oxide or reaction of the relevant metal with carbon in CO or an inert atmosphere [4].

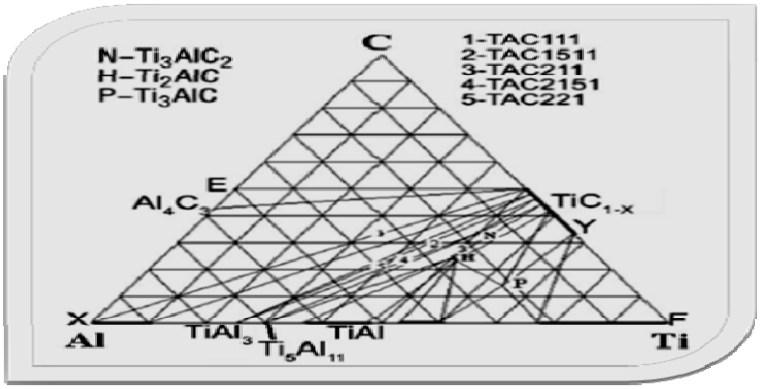

Figure (1): The (Ti-Al-C) System [1]

The stoichiometry can vary (n = 1, 2, or 3) leading to M2AX, M3AX2 or M4AX3 phases. The crystal structure of Ti2AlC and Ti3AlC2 is hexagonal with space group P63/mmc [5] as is illustrated in figure (2). The crystal structures contain TiC layers interleaved with single Al layers. The stacking sequence depends on the stoichiometry where Ti3AlC2 has one Al layer for every third TiC layer, and Ti2AlC, has one Al layer for every second TiC layer. The TiC is built up by Ti octahedrons connected in each edge with C atoms filling the octahedral sites. The TiC layers are twinned with the Al layers as the mirror plane. [6]

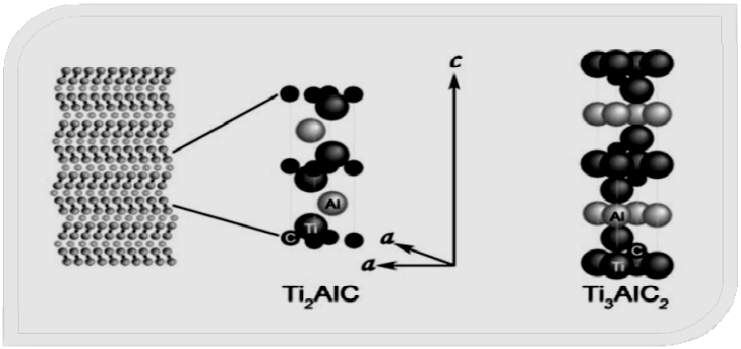

Figure (2): Crystal Structure of Ti_2AlC and Ti_3AlC_2 [7]

The atomic binding character in the MAX phases has been shown to be a combination of metallic, ionic, and covalent. The covalent-ionic Ti-C bonds are comparable to the bonds in the binary TiC and are stronger than the metallic Ti-Al bonds present in the ternary structure. The relatively weak bonds between the TiC and Al layers in the basal planes contribute to an anisotropic character of the material leading to kink-band formation and delaminating along the basal planes upon deformation. [6] As seen in figure (3).

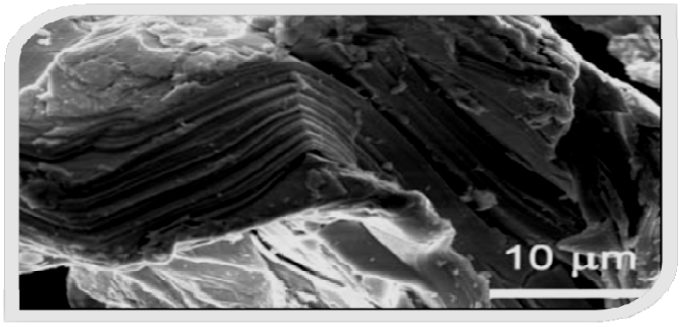

Figure (3): Structure of Ti2AlC [6]

Ti3AlC is an inverse perovskite structure with an Al cubic structure, Ti on its face-centered positions, and C on the body-centered position. It has shown to be difficult to synthesize pure Ti3AlC material thus most report about Ti3AlC as a precipitation. To this point no experimental data of its properties have been found. There are, however, simulations of its electronic structure and elastic properties. [8] TiC is among the hardest materials known. [6] It has also attracted attention because of its high melting point and wear resistance, It is widely used as protective coatings for cutting, molding and milling tools, coatings for ball-bearings and spray gun nozzles as well as for fusion-reactor applications.[6] TiC has a face-centered cubic close packed crystal structure, as shown in figure (4), and the space group is Fm3m.[9] TiC belongs to the group of interstitial carbides where carbon occupies the (interstitial) octahedral sites between the close packed Ti atoms. This structure is a building block in the Tin+1AlCn (n=1, 2) crystal structure. Interstitial carbides have partly ionic and covalent bonds, but with a metallic character that causes a relatively low electrical resistivity of 50 µcm, compared with Ti of 40 µcm. The strong ionic bonds between Ti and C are due to the great difference in electronegativity of 1.0. TiC exhibits Young's modulus of ~450 GPa, a melting point around 3000 °C, and a density of 4.9 g/cm3. The hardness is ~25 GPa, while for TiC thin films it can be as high as ~30 GPa depending on lattice defects. [10]

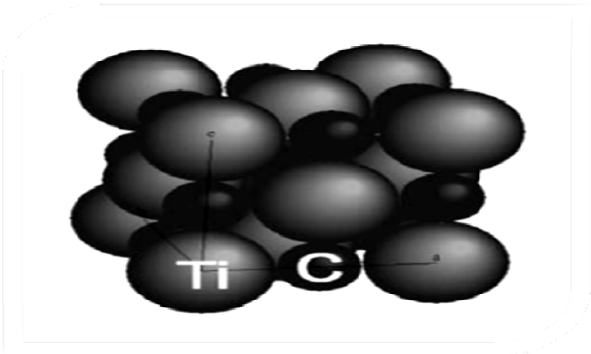

Figure (4): Crystal Structure of TiC with Interstitial C at the Octahedral Sites. [9]

Ti-Al alloys have a combination of properties such as low density of ~4 g/cm3, good creep resistance and high strength. This has made them interesting as structural materials at high temperature, which is useful within the aerospace and automotive industry. [10] According to the phase diagram, the different Ti-Al intermetallic phases range from Ti-rich (Ti3Al) via TiAl to Al-rich (Al3Ti) phases. Ti3Al has a hexagonal crystal structure while both TiAl and Al3Ti have a face-centered cubic crystal structure. [11] The properties of Ti-Al such as electrical resistivity and creep resistance depend on its microstructure as well as composition. For instance, Ti-Al thin films have a lower friction coefficient and a lower hardness with increasing Al content. At high temperatures Ti-Al forms Ti- and Al-oxides. The formation of oxides is complex and depends on phase composition, temperature, and content or vapor pressure concentration. Higher Al content (>50 at %) or introduction of other metals such as Cu or Cr will improve the oxidation resistance. In some researches, Ti-Al alloys act as binding phases in HVOF-sprayed Ti2AlC coatings and are thus also of importance for the density and adhesion of the coatings. [12]

The MAX phase were studies by **N.V. Tzenov and M. W. Barsoum**.[13] In 2000,they have synthesized Polycrystalline bulk samples of Ti3Al1.1C1.8 that have been fabricated by reactively hot isostatically pressing a mixture of titanium, graphite, and Al4C3 powders at a pressure of 70 MPa and temperature of 1400°C for 16 hr. The hot isostatically pressed samples are predominantly single phase (containing; 4 vol. % Al2O3), fully dense, and have a grain size of; 25 μm. This carbide is similar to Ti3SiC2, with which it is isostructural, and has an unusual combination of properties.

Y. Zou, et al. [14] in 2008 have rapidly synthesized Ti3AlC2 by pulse discharge sintering Ti/Al/C (molar ratio 3:1.1:1.8) powder mixtures in a temperature range of 1200–1400°C. The fully dense and single-phase Ti3AlC2 was obtained at sintering temperature 1250–1350°C for 15 min and at 1300°C for 15-60min the typical microstructure of polycrystalline bulk Ti3AlC2 consists of plate-like grains, and the grain size can be adjusted by choosing sintering temperature and time. The intermediate phases of AlTi3, AlTi, Ti3AlC and Ti2AlC were found during the reactive sintering process and the mechanisms for the Ti3AlC2 phase formation were proposed.

A. Hendaoui, et al. [15] In 2010 have synthesized the ternary MAX phase compounds from Ti, Al and C elemental powders, by using an alternative route called (Mechanically Activated Self-propagating High temperature Synthesis) MASHS. This original process combines a short duration ball milling (MA) of reactants (Ti, Al, C) with a self-sustaining combustion (SHS).

Experimental Work:

Titanium (99% pure, ↓75-↓88μm, GRINM, Beijing, P. R. China), Aluminum (99% pure, ↓75-↓88μm, Fushun Al Factory, P. R. China) and carbon black (GRINM, Beijing, P. R. China) were used as raw materials. Typically, the powder mixtures were dispersed with ethanol in a ball mill type (BAIRD & TATLOCK) for 60min at 150(Rpm) level of speed for each sample, see table (1 and 2). The homogeneous powder obtained was dried at 120°C for 1 hour, and the agglomeration mixture was then cold pressed into cylindrical bars with dimensions of 5cm in height and 10 mm in diameter. The heat treatment were done at different temperatures, under controlled atmosphere (argon gas) to impede the samples oxidation with a stable sintering process at heating rate 10˚ C/min started from (600 ˚C-800˚C -1200˚Cand end at

1400˚C) for 3 hours. The phase formation was identified by Shimadzu X-ray diffractmeter (type XRD- 6000/7000), and microstructures of the products were analyzed by SEM type (VEGA3 TESCAN). The SEM and optical microstructure samples are observed after the sample is ground by SiC emery paper with different grits starting from 600,800,1200 grit to get flat and scratch free surface. Finally, these samples are polished with smooth cloth. The etching solution for SEM test and optical microscope test are listed in table (3).

Table (1): The Powder Type, average Particle Size and Purity

Elemental powder	Particles size"D"(sieving) (mm)	Purity%
Ti	↓75-↓88μm	99.9
Al	↓75-↓88μm	99.9

Table (2): The Powder composition

concentration	System1	System2	System3
%	(80%Ti-10%Al-10%C)	(70%Ti-20%Al-10%C)	(60%Ti-30%Al-10%C)

Table (3): Etching solution of SEM and Optical Microscope Test

Type of test	Solution composition
Scanning electron microscope test	Conductive Carbon[16]
Optical microscope test	100 ml water and 1–3ml HF 2–6ml HNO_3 (Kroll′s reagent) for 15sec[16]

Results and Discussions:

The formation of the intermediate phases at 600°C and the formation of MAX phases related with the phase intensity of the peaks in XRD to give information about the effect of concentration on the phase evolution in all steps.

X-ray diffraction tests are done for all samples before and after the sintering processes. Figures (5) to (8) shows the diffraction patterns obtained for all samples. The phases that developed as a result of sintering could be detected. The phases are produced as a result of sintering process is analyzed by computer analyzer program named International Center for Diffraction Data (ICDD) and by (EXCELL) program.

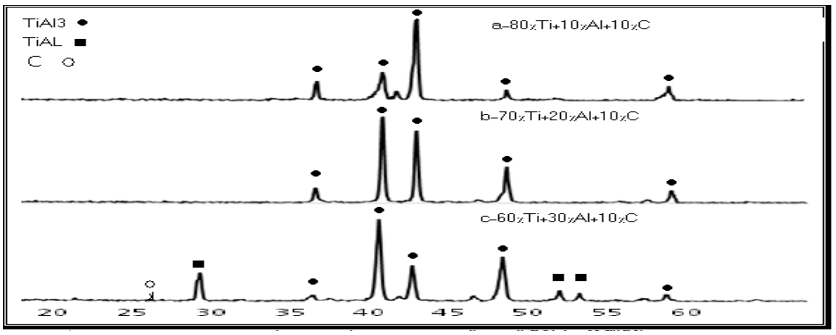

Figure (5): XRD Patterns of Samples Pressed at 30 ton and Sintered at 600°C for 3 hrs.

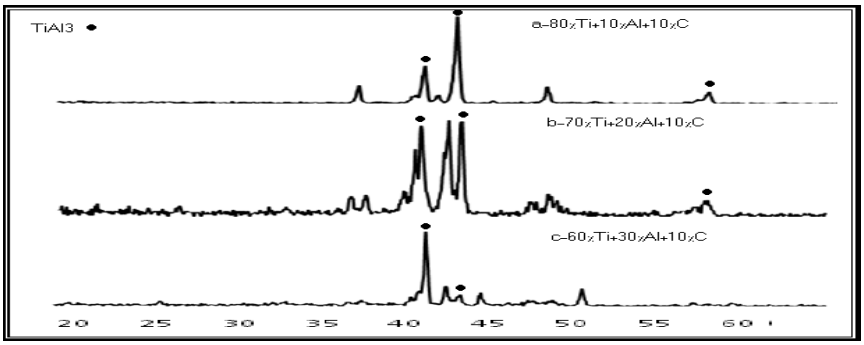

Figure (6): XRD Patterns of Samples Pressed at 30 ton and Sintered at 800°C for 3 hrs.

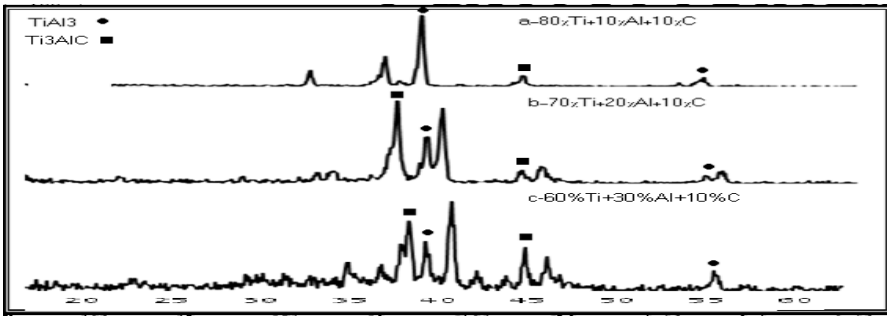

Figure (7): XRD Patterns of Samples Pressed at 30 ton and Sintered at 1200°C for 3 hrs.

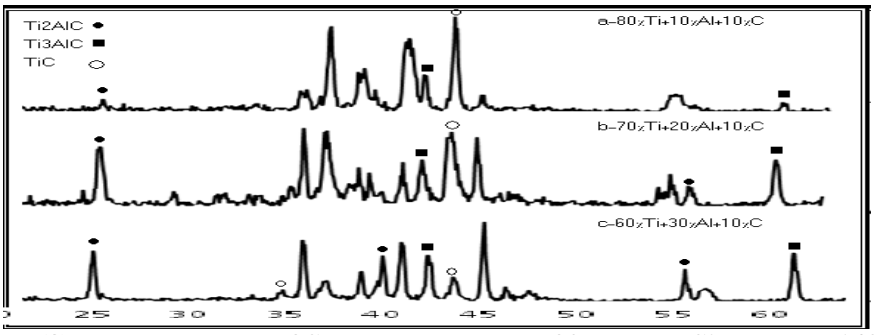

Figure (8): XRD Patterns of Samples Pressed at 30 ton and Sintered at 1400°C for 3 hrs.

As seen in figure (5), the phase development shows that at 600˚C the TiAl3 and TiAl intermediate phases are presented. The Al concentration has affected the crystallography (peak sharpness) of both phases. A small amount of non reacted Ti has been also found in some samples. Figure (6) shows the increasing of the sintering temperature TiAl3 papers to be the dominate phase. The perviskite structure of Ti3AlC tends to appear in a little amount with the rest of TiAl3. Figure (7) shows the structure of Ti3AlC (perviskite structure) which appear to be more dominated especially with decreasing the Ti concentration. Figure (8) shows the appearance of Ti2AlC and Ti3AlC and some TiC is also presented. [17][18]

By studying the effect of Al concentration during different temperatures started from 600C˚ other phase appear when the Al concentration increase due to the high Al percentage as shown in figure (5) and figure (6) some of rest Al melt at 800C˚ and the TiAl3 was the dominated phase, by increasing firing temperature and Al concentration, the perviskite structure appears due to sufficient energy and temperature to start the reaction, see fig. (7), in fig. (8). When the Al concentration increase some TiC was present with the other MAX phases, this caused by the formation of the intermediate phases to final phases [19]. Finally, the phase evolution is shown that by increasing the firing temperature at that soaking time, the ternary carbides start to be more stable (i.e at high temperature) instead of intermediate phases that are the most stable at low temperatures.

Microstructures of Ti-Al-C sample fired at 1400°C for 3hr. prepared at different concentration have been taken using scanning electron microscope. The microstructure reveals that the samples has consist of three phases or mainly two phases in which max phase appear in the high temperature with some samples.

As shown in figures (9-10 and 11). Back scatter detector is used for SEM test. The back scatter shows the different in color which may give an indication about the appearance of most phases.

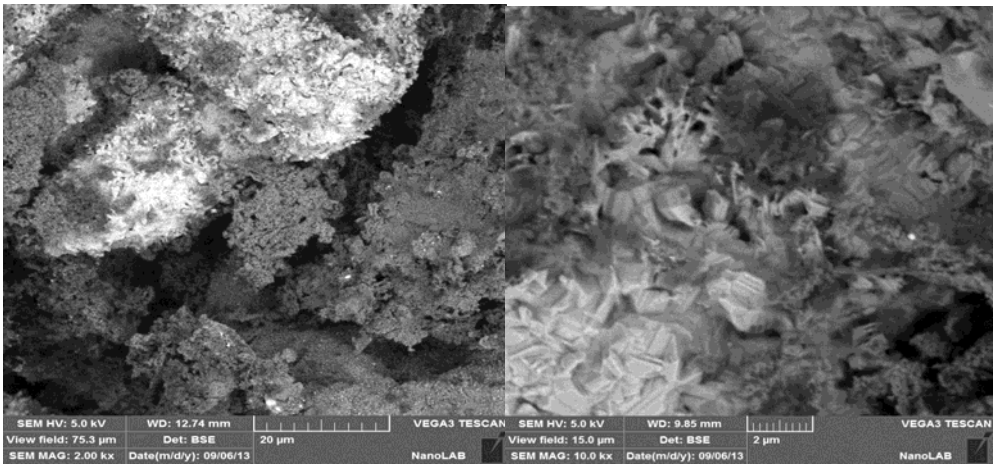

Figure (11): SEM for Sample 60%Ti+30%Al+10%C Cold Compacted and fired at 1400˚C for 3hrs.

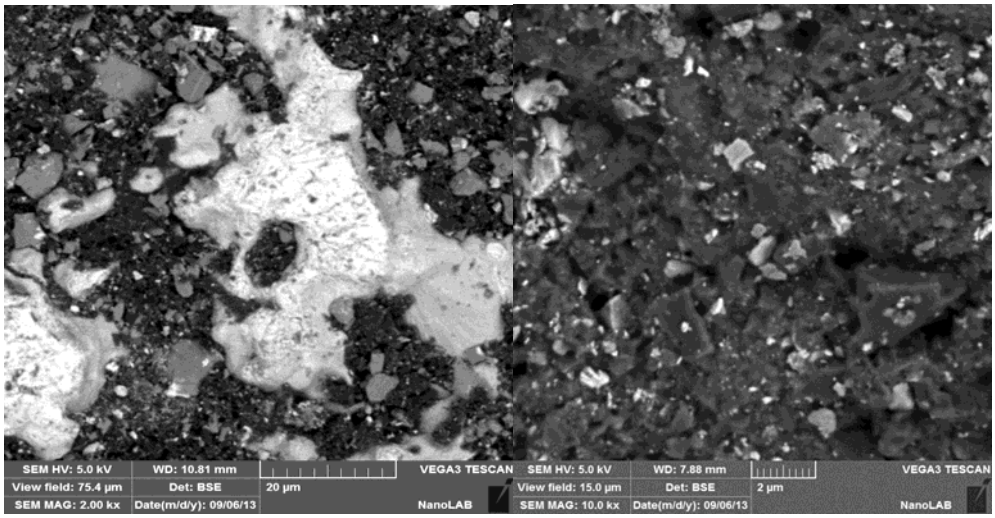

Figure (10):SEM for Sample 70%Ti+20%Al+10%C Cold Compacted and fired at 1400˚C for 3hrs.

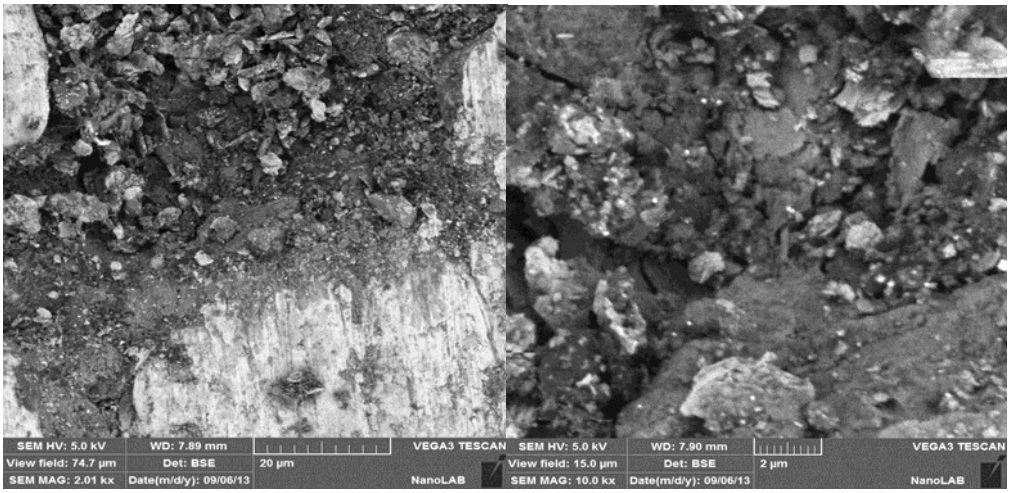

Figure (9): SEM for Sample 80%Ti+10%Al+10%C Cold Compacted and fired at 1400˚C for 3hrs

Where figure (9) shows the existence of three different phases and the MAX phase which due to its atomic weight. Figure (10) shows two different phases, while in figure (11) MAX phase appear but without mention which phase it is. By comparison with the XRD result for their sample we could defined the phase is Ti2AlC.
The result of tight optical microscope is shown in figures (12, 13 and 14).

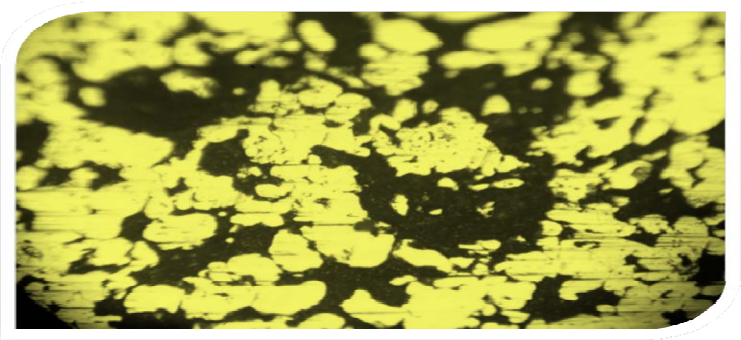

Figure (12) polarized microstructure of 80%Ti+30%Al+10%C Cold Compacted and fired at 1400˚C for 3hrs.

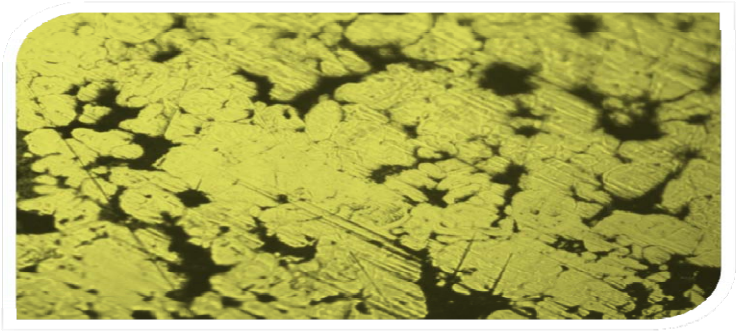

Figure (13) polarized microstructure of 70%Ti+20%Al+10%C Cold Compacted and fired at 1400˚C for 3hrs.

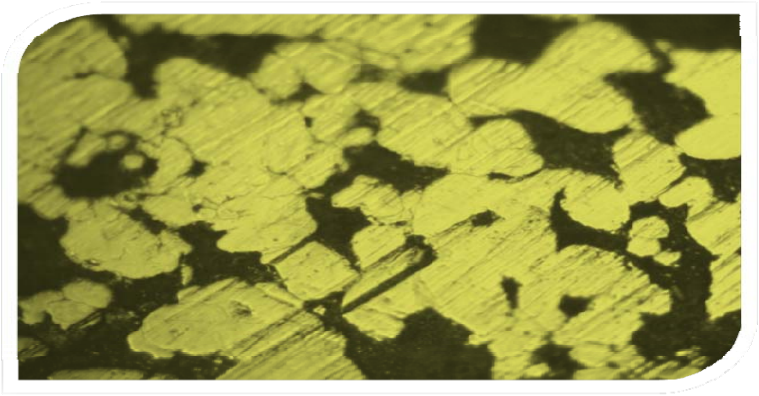

Figure (14) polarized microstructure of 60%Ti+30%Al+10%C Cold Compacted and fired at 1400˚C for 3hrs.

These figures shows that there is a high percentage of porosity and the phase appear with a high amount of porosity due to the cold compaction and the time of fired process.

CONCLUSIONS

From studying the effect of Aluminum on phase evolution of Ti-Al-C ternary system, the following conclusions can be drawn:

1- Aluminum has played a very important role on the formation of the intermediate phases and the ternary carbides.

2- By increasing the Aluminum concentration in the range of the 20% and 30% from the Al, intermediate phases tend to be more stable especially at low sintering temperature 600°C.

3- The difference in concentration give a fine result in determining and exacting the final phase appearance such as in the Ti_2AlC and Ti_3AlC_2 products with the highest percentage of Al in the system.

4- By increasing firing temperature with Al concentration the MAX phase, show more domination than the lower Al concentration due to the delaminating of intermediate phases such as TiAl and react with the rest of elemental powders to produce the ternary carbides.

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