EFFECT OF FABRICATION PARAMETERS ON SYNTHESIS OF Ti_2AlC AND Ti_3AlC_2 MAX PHASES BY MASHS

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Abstract: *Mechanically Activated Self-propagating High temperature Synthesis (MASHS) is the method which is used to promote self-propagating synthesis by increasing activity of reactants and increase the purity of products. In this study Ti_2AlC and Ti_3AlC_2 max phases were synthesized by using mechanically activated self-propagating high temperature synthesis (MASHS) and samples reactivity and phase structure of samples was studied. This process was performed by combination of short duration ball milling (MA) of reactants (Ti, Al and C as raw materials) and self-propagating high temperature synthesis (SHS) by microwave or furnace. Mixtures of Ti/Al/C by mole ratio of 2:1:1 and 3:1:2 were milled for 2h., then exothermic reaction was initiated in microwave or high temperature furnace and their reaction behavior and structure have been investigated by DTA and XRD. Results revealed that it's possible to fabricate these materials by MASHS method but purity of them depends on type of reaction condition. DTA and XRD analyses proved that increasing of soaking time did not improve purity of compounds and some impurities such as TiC would be formed in non-optimized reaction routes.*

Keywords: *MAX phases , MASHS, Ti_2ALC, Ti_3AlC_2, XRD*

1. INTRODUCTION

Max phase are new generation of materials which is the main topic of many researches in recent years. These materials have been introduced by Drexel university researchers as structural materials which have special two dimensional layer structures and because of this structure attain unique properties [1, 2]. The intermetallic MAX phases are ternary carbides and nitrides with the general formula Mn+1AXn (MAX) with n = 1-3, where M is an early transition metal, A is an A-group (mostly IIIA and IVA periodic elements) and X is either carbon or nitrogen. It is known that in the Al–Ti–C ternary system (named TAC ceramics), there are three MAX phase named as Ti_2AlC, Ti_3AlC_2 and Ti_4AlC_3. Previous studies revealed that Ti_3AlC_2 and Ti_2AlC combines a unique combination of metals and ceramics properties, including low density, high elastic modulus, easy machinability, excellent thermal shock resistance and damage tolerance, high mechanical strength, good plasticity, good oxidation and creep resistant and high electrical and thermal conductivity which lead them to use as high-temperature structural and functional material [3,4]. Also it's found that between these three max phases Ti_3AlC_2 has very good mechanical properties and Ti_2AlC has highest melting point, making them so interesting material in high temperature applications [5].

Ti_2AlC have been fabricated initially by heat treatment of mixed titanium, carbon and aluminum in quartz tube subjected vacuum during 150 hours in 1000 °C [6, 7]. Ti_3AlC_2 was fabricated for the first time by cold compaction of Ti, TiAl, Al_4C_3 and C in 1300 °C in H_2 atmosphere for 20hours.[8-14] After synthesis of these max phases, bodies of them was fabricated by HP and HIP [6, 14]. Until now many methods for synthesis of powders[6-14] and fabrication of bulk materials by HP[9], HIP[15], SPS [16], CS [13, 14], SHS [4, 8, 10, 17], pressure less sintering [5, 18] and by reaction sintering [6,11] have been reported but except SHS, most of them are so expensive and time consumable. The main disadvantage of SHS is lower reaction rate in some conditions (e.g. oxidation layer on raw materials) and low purity of compounds. Then in recent years mechanical activation was proposed before SHS in order to overcome these disadvantages. In this article mechanically activation of raw materials followed by self-propagating high temperature synthesis was studied for fabrication of Ti_3AlC_2 and Ti_2AlC and their formation and phase structure was investigated.

2. EXPERIMENTAL PROCEDURE

Titanium (>99% purity, particle size>50nm, Merck Company), Aluminum (>99% purity, particle size between100 to 200 µm, Fluka company) and carbon (>99.9% purity, particle size >50 µm, Fluka company) powders were used as raw material. Powders were mixed based on below stoichiometric ratios of reactions (1) and (2) for synthesis of Ti_3AlC_2 and Ti_2AlC respectively:

$$3Ti + Al + 2C \rightarrow Ti3AlC2 \quad (1)$$

$$2Ti + Al + C \rightarrow Ti2AlC \quad (2)$$

These mixtures poured in cup (125 ml) with BPR of 2:1 and were activated by planetary ball mill for 2hours and 250 round/min. rotating speed. Balls were made from alumina and activation was done under four atmosphere Argon pressure. After mixing, separation of mixed powders from ball was done under glove box. Then activated powders were compressed at 50 MPa and 12 mm diameter dies and 10 mm height green samples were fabricated. SHS reactions were done in 900 watt microwave (LG-MP9488S) and inert gas furnace. Samples were embedded in activated carbon bed during reaction in microwave. Samples hold in microwave for about 5 minutes. Heat treatment in furnace were done by heating samples up to 1500°C with heating rate of 10 °C/min and hold at the maximum temperature for 2 and 6 hours. Because of non-protective atmosphere of furnace, samples that heat treated in the furnace were encapsulated by quartz tube for oxidation protection. One of these capsulated samples is shown in figure1. Reaction behavior of was analyzed by Differential thermal analysis (DTA) (NETZSCH STA 409 PC/PG) up to 1500 °C in an inert atmosphere. Mixture of powders was studied by DTA after activation by planetary ball mill. Crystal structure was studied by XRD (Philips Xpert). Identification of phases from XRD were done by phillips Xpert program, ICDD database (cards No. 04-001-6044 and 29-0092 for Ti_2AlC) and 00-052-0875 for Ti_3AlC_2) and some references.[9]

Fig. 1. Encapsulated sample by quartz before reaction in the furnace

3. RESULTS AND DISCUSSION

DTA of 2Ti/Al/C and 3Ti/Al/2C activated powders were done and results are shown in Fig. (2) and (3). Figures clearly show two samples reaction behavior were same. Based on fig. (1) 3Ti/Al/2C mixture has an endothermic peak around of 660-670 °C which is related to Al melting and formation of Ti-Al alloy. A sharp exothermic peak reveals near 700 °C and belongs to reaction between Ti and C and formation of TiC. Then around 1400-1450 °C another sharp exothermic peak exposes which the strongest peak and related to formation of Ti_3AlC_2. DTA curve of 2Ti/Al/C shows that this mixture melts and reacts as same as 3Ti/Al/2C but comparing two curves shows that the intensity of exothermic reaction of 2Ti/Al/C is lower than 3Ti/Al/2C mixture. According to previous studding [9, 19], reaction between Ti and C is extremely exothermic and these two material have great tendency to react with each other. Thus because molar ratio of C and Ti in 3Ti/Al/2C is more than molar ratio of C and Ti in Ti/Al/2C powders, intensity of reaction increases and therefore the Exothermic peaks at 700 °C will be expand and become sharp. On the other hand in 2Ti/Al/C powders reaction starts and ends at wide temperature ranges but in 3Ti/Al/2C powder mixture reaction occurs in narrow ranges then control of reaction kinetics is so much easier in

2Ti/Al/C powders and producing of Ti_2AlC is simpler and easier than Ti_3AlC_2. This results is consistent with other studies. [9]

XRD patterns of reacted samples in microwave are shown in figures (4) and (5). Based on this diagrams three principal phases Ti_2AlC, TiC and Ti_3AlC_2 exists in the samples after reaction in microwave. Important peaks of three phases were collected and written in table (1). According to this table and ICDD Standard patterns, XRD characteristic peaks for these three material is very close, so it`s too hard to identify the phases, even each phases has sole diffraction peak. Then for Ti_2AlC formation the important and specific peak must reveals at $2\Theta=13°$ and related to {002} planes. For TiC formation the

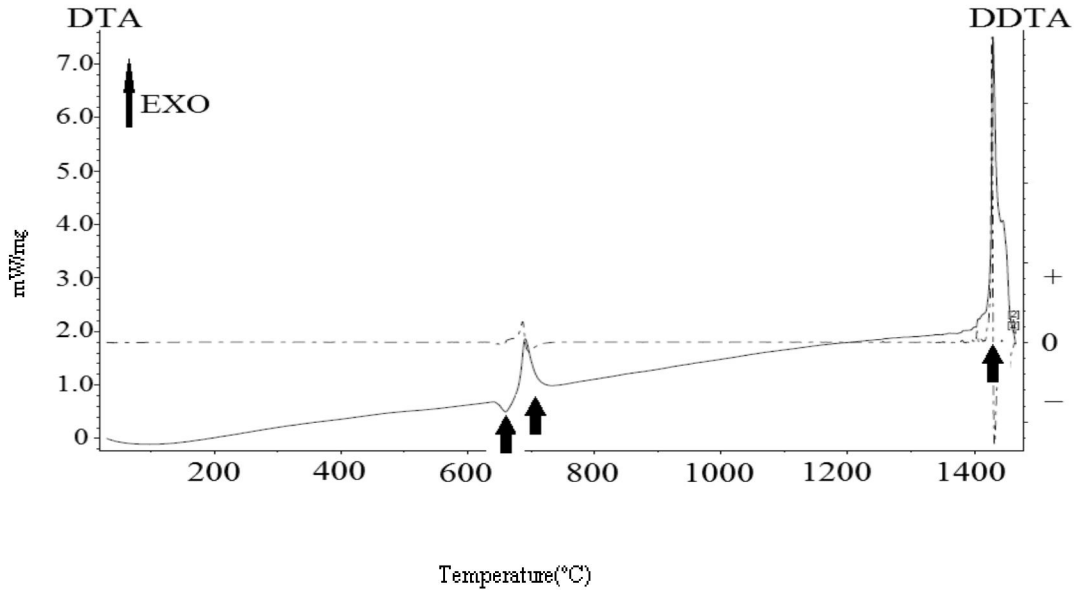

Fig. 2. DTA and DDTA curves of activated $3Ti/Al/_2C$ powders (dashed line is DDTA (DTA first derivative)

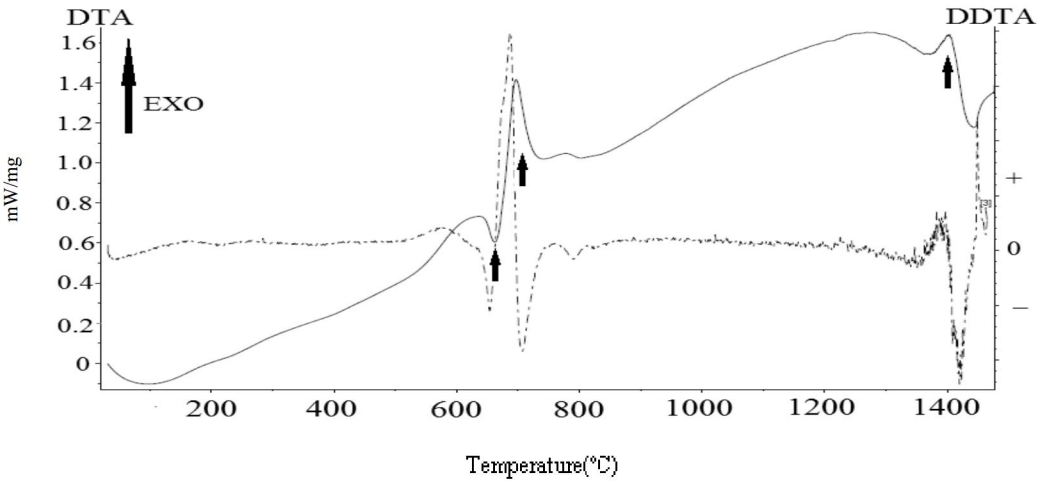

Fig. 3. DTA and DDTA curves of activated 2Ti/Al/C powders(dashed line is DDTA (DTA first derivative)

important and specific peak must reveals at 2Θ=35.9° and related to {111} planes. Ti_3AlC_2 formation the important and specific peaks must reveals at 2Θ=9°, 2Θ=56.6° and 2Θ=74.2°. [9] Unfortunately some previous Iranian reports didn't consider these complexities and relate their results to formation of Ti_3AlC_2.[8] Based on fig. 4 in the Microwave reaction between 2Ti/Al/C activated powder mixture, Ti_2AlC will form as a major phase but small amount of TiC also will reveals in the sample. On the other hand, fig. 5 reveals during microwave reaction, Ti_3AlC_2 will not form completely. The peaks in the XRD diagram of Fig. 5 is extracted by expert program and it can be seen in table (1).

Based on table (2), characteristic peaks of Ti_3AlC_2 wouldn't revealed well in table only a tiny peaks of Ti_3AlC_2 in 2θ=9.5° (may be in nano

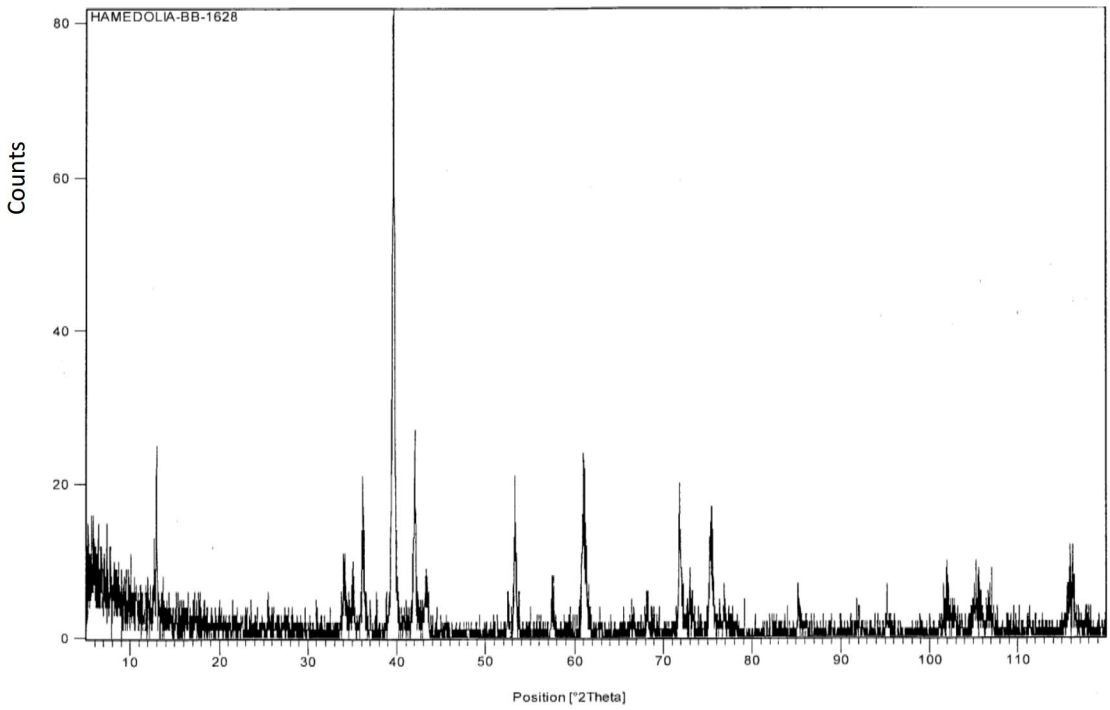

Fig. 4. XRD diagram of Activated and reacted Samples in microwave of 2Ti/Al/C powder mixture

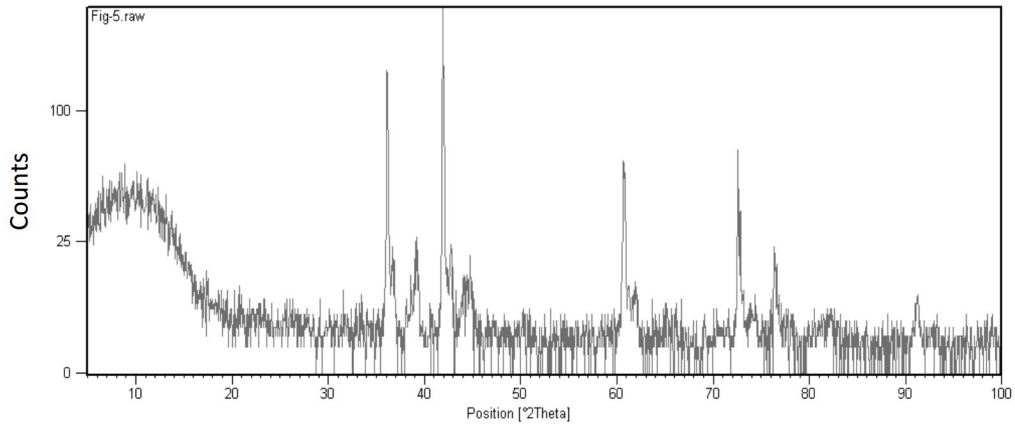

Fig. 5. XRD diagram of Activated and reacted Samples in microwave of 3Ti/Al/2C powder mixture

Table 1. Characteristic peaks of Ti_3AlC_2 , Ti_2AlC and TiC phases[9]

Ti_3AlC_2		TiAlC		TiC	
2Θ	I/I_o	2Θ	I/I_o	2Θ	I/I_o
9.5	**26.5**	13.0	39	35.9	78
34.1	20	34.0	19	41.7	100
36.8	7.6	39.6	100	60.5	60
38.9	20	39.8	18	72.4	30
41.9	28.1	53.3	14	76.2	17
48.6	7.8	61.0	14		
56.6	11.6	72.1	9		
60.3	23.6	75.3	11		
70.6	11.2				
74.2	18.2				
74.6	8.5				

crystalline form) and 2θ=39° have been seen, on the other hand, Ti_2AlC and TiC peaks reveals in this sample.

The XRD diagrams of 3Ti/Al/2C samples which are reacted in the furnace for 2 and 6 hours have been seen in figures (6) and (7) respectively. Their important peaks also calculated by xpert program and are shown in tables (3) and (4). Based on these figures and tables, in samples that heated in furnace in 1500 °C for 2hr, Ti_3AlC_2 phases have been formed but some TiC impurity phase also reveals in sample (a characteristic peak at 35°). By increasing soaking time, intersting transformation happens and all of max phases will transform to TiC(Fig. (7) and table (4)). This transformation reported in some previous studies [14, 20]but different from other finding [9]. Zohu et al. [9] found that if soaking

Table 2. Important peaks from XRD result of 3Ti/Al/2C Reaction in furnace (Calculated and formatted by Xpert Program)

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [°]	Rel. Int. [%]
36.1405	132.88	0.1968	2.48541	83.15
39.1674	19.26	0.3936	2.30003	12.05
41.9469	159.80	0.1968	2.15383	100.00
42.7516	16.89	0.2952	2.11514	10.57
60.7215	60.57	0.2460	1.52526	37.91
72.6002	54.22	0.1476	1.30222	33.93
76.4511	13.69	0.3600	1.24491	8.57

Table 3. Important peaks from XRD result of 3Ti/Al/2C after reaction in 1500 °C furnace for 2 hours (Calculated and formatted by Xpert Program)

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [°]	Rel. Int. [%]
25.7409	45.51	0.2952	3.46101	29.96
35.2884	69.91	0.1968	2.54345	46.02
37.7267	48.32	0.3936	2.38448	31.81
39.7515	35.18	0.1968	2.26757	23.16
41.0382	42.51	0.2952	2.19940	27.99
42.8327	151.90	0.2952	2.11132	100.00
43.5090	86.13	0.1968	2.08006	56.70
52.6583	17.43	0.2952	1.73818	11.47
57.6679	27.98	0.2952	1.59854	18.42
61.5270	30.61	0.2952	1.50721	20.15
66.6204	60.76	0.2460	1.40381	40.00
68.3870	47.18	0.2952	1.37179	31.06
73.6491	25.65	0.4920	1.28624	16.89
77.1691	6.53	0.5904	1.23612	4.30
88.8345	6.71	0.5904	1.10152	4.42
95.4015	11.80	0.7200	1.04145	7.77

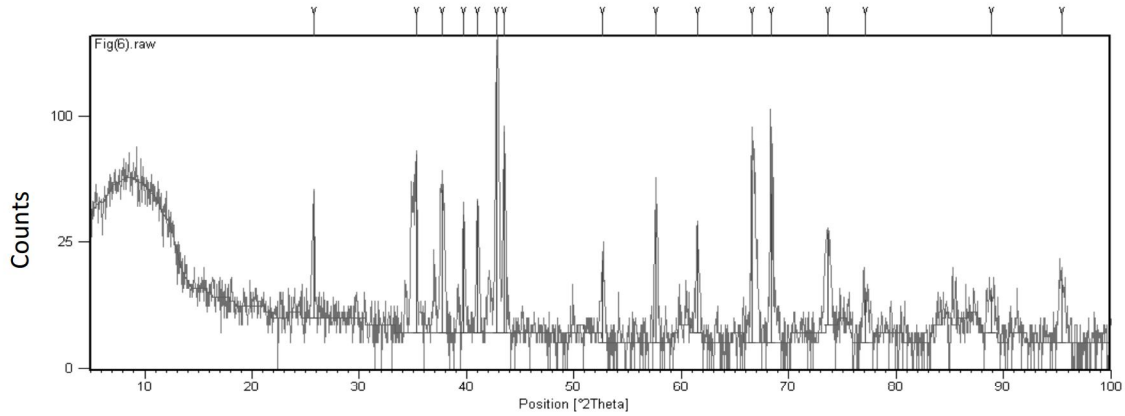

Fig. 6. XRD diagram of Activated and reacted 3Ti/Al/2C Samples in Inert gas furnace at 1500°C for 2 Hours

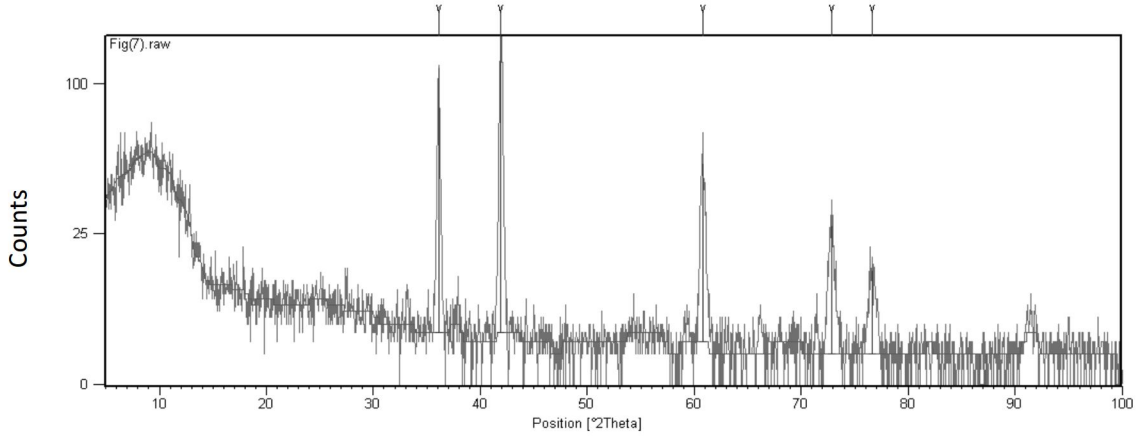

Fig. 7. XRD diagram of Activated and reacted 3Ti/Al/2C Samples in Inert gas furnace at 1500 °C for 6 Hours

Table 4. Important peaks from XRD result of 3Ti/Al/2C after Reaction in furnace for 6 hours (Calculated and formatted by Xpert Program)

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [?]	Rel. Int. [%]
36.1092	108.42	0.3444	2.48749	81.54
41.9209	132.97	0.2952	2.15510	100.00
60.8027	52.26	0.5904	1.52342	39.30
72.8188	27.17	0.5904	1.29885	20.43
76.6529	13.54	0.9600	1.24214	10.18

time increase, intensity of Ti_2AlC peak will be decrease and intensity of Ti_3AlC_2 will be increased. It means that transformation of Ti_2AlC to Ti_3AlC_2 which is different from our findings. Ge et al. [14] found that transformation of Ti_3AlC_2 to TiC may be related to Aluminum vaporization.Based on their result at higher temperature vapor pressure of Aluminum become higher, this may be lead to evaporation of aluminum from Ti_3AlC_2 compound and convert it to TiC. For complete transformation, heat treatment must be long enough to vaporize all aluminum.

In order to find what was happened in our

experiments, it is necessary to show the relationship between lattices unites of three TiC, Ti_2AlC and Ti_3AlC_2 phases. As it is seen in figure (7), in Ti_2AlC, all close packed layers are separated from each other by a layer of Ti_6C octahedra. In other word, if any Al layers do not exist, all of Ti_6C octahedron attach directly to each other and form TiC. If each two Ti_6C layer separated by a layer of Al, it forms Ti_3AlC_2 and if each layer of Ti_6C separated by one layer of Al, it forms Ti_2AlC. [9] Then Aluminum vaporization or Aluminum deficiency will contribute to these transformations. Also, if thermodynamic and kinetic factors of reaction considered [21], Although TiC is very stable in high temperature, formation of TiC from Ti and C is an exothermic reaction and Ti-C bond is so strong but in lower temperatures formation of Ti_6C is easier while it is hard for octahedra Ti_6C layers to attach each other and form TiC because lower distances between C atoms results biggest repulsion, so TiC needs high temperature to nucleate and growth. Then in lower temperatures and in the presence of Aluminum fabrication of Ti_3AlC_2 and/or Ti_2AlC would be preferred by the structure.

When the powder mixture of Ti-Al-C react, this mixture will expand from up to down. First, Aluminum melts then it diffuses to cavities between Titanium and Carbon powders and reaction starts between Aluminum and Titanium and then Carbon. By increasing the reaction temperature, reaction will begin between Ti and C directly by saturation- precipitation mechanism. Initially carbon atoms solves in Ti-Al melt, when Ti-Al melt supersaturated from carbon, nucleation of TiC begin and start to propagate. Finally ultimate product is TiC-Al and any ternary phases did not form. Since Based on previous reports[14], stable temperature range for formation of Ti_3AlC_2 is narrow band and this compound almost forms during cooling where there is enough time and proper temperature exists and of course TiC have not been formed in the sample before.

4. CONCLUSIONS

1. Fabrication of Ti_2AlC max phase is feasible by microwave method and minor TiC impurities will form during this process but fabrication of Ti_3AlC_2 max phase is no feasible by microwave method and most of sample will transform to $TiAlC_2$ and TiC.
2. Fabrication of Ti_3AlC_2 max phase is possible by heating 3Ti/Al/2C activated mixture by furnace but it will form in short holding time (2 Hours) at 1500 °C. Long time heating (6 hours) of 3Ti/Al/2C powder mixture at 1500 °C will transform the entire sample to TiC. This may be related to Aluminum vaporization or growth kinetics of TiC from Aluminum-Titanium melts.

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