The influence of Al content on pore structures of porous Mo$_2$TiAlC$_2$ ceramics through powder metallurgy technique

Junsheng Yang, Yi Wen, Xide Li, Yiquan Fan, Haoran Zou, Chuo Zhang, Lieqiang Xiong and Yuzuo Liu
School of Mechanical Engineering, Wuhan Polytechnic University, Wuhan, PR China

**ABSTRACT**

Porous Mo$_2$TiAlC$_2$ ceramics with different Al content in nominal compositions were fabricated through powder metallurgy technique of Mo, Al, and C elemental powders and TiH$_2$ powders, which were carried out in vacuum environment. Systematic experimental results revealed that the pore structure of these Mo$_2$TiAlC$_2$ ceramics were affected by different Al content significantly. With ascending Al content changed from 0.9 to 1.3 mol, pore sizes and viscous permeability coefficients of these test specimen substantial reduce while volume demonstrated an ascending tendency, the phase is mainly Mo$_2$TiAlC$_2$, and the secondary phase Mo$_3$AlC$_2$ decreased with the increase of Al content, and the reason for deviation of molar mass was attributed to the volatilization of Al. When the Al content continues to rise to 1.7 mol, the pore structure parameters including pore sizes, viscous permeability coefficients, and porosities increased, and the impurity phase appeared. Besides, evolution of pore structure parameters in sintering stage and the pore-forming mechanism was explored. The present work is of momentous significance in the preparation of quaternary and multi-element porous MAX phases ceramics/alloys.

**1. Introduction**

Due to good thermal conductivity, low hardness, normal thermal expansion coefficient (TEC), high damage tolerance, and thermal shock resistance, the MAX phase of ternary layered compounds has attracted extensive attention of material scientists all over the world [1–4]. And MAX phases of ternary layered compounds have become an important candidate for industrial applications in new fields like aerospace.

The formula of MAX phases could be presented as M$_{n+1}$AX$_n$, where M is expressed as a transition metal, A pertains to an A group element, X refers to carbon or nitrogen, and $n = 1–6$ [5–9]. In the family of MAX phases, a sort of solid solutions of (M’, M’`)$_{n+1}$AX$_n$ attracted much attention of material workers. In this formula, the M site consists of two transition metal elements, and they possess multiple possible attributes of M$_{n+1}$AX$_n$ and M$_{n+1}$AX$_n$ triggering the interests of researchers. For example, Zou et al. [10] successful fabricated TiVAIC MAX phases through the method of powder metallurgy, and its corrosion resistance mechanical property was studied preliminary. Zheng et al. [11] synthesized (Ti$_{0.5}$Nb$_{0.5}$)$_3$AlC$_2$ MAX phases materials through reactive hot pressing technique. And the results revealed that this new compound has unique layered 514 phase. It is more important that n is proved to be extended to a wide range in n M$_{n+1}$AX$_n$ phases. Therefore, more new MAX phases are improved to discovery. Niu et al. [12] synthesized dense Mo$_2$TiAlC$_2$ ceramics with the way of spark plasma sintering (SPS), and the good oxidation resistance of dense Mo$_2$TiAlC$_2$ ceramics was confirmed simultaneously. Layered quaternary ceramic Mo$_2$TiAlC$_2$ is a new kind of MAX phases [13]. Of special another interest to this work are Mo-containing MXene phases, and MXene phase materials have broad application prospects in hydrogen evolution [14], hydrogen storage [15], CO$_2$ degradation [16], supercapacitors [17], and so on. Because of the lower etching difficulty when A is aluminum in MAX phase, it has been attracted with more and more attention owing to significant potential in etching Mo-containing MXene [18,19]. Therefore, it is significant for promoting preparation technology of Mo$_2$TiAlC$_2$ ceramics. Although the fabrication of dense Mo$_2$TiAlC$_2$ with the method of SPS has been reported by several materials workers [12,13], but there are rare manuscripts about preparing Mo$_2$TiAlC$_2$ ceramics by reactive synthesis technology and even less about preparation of porous Mo$_2$TiAlC$_2$ ceramics.

In this paper, porous Mo$_2$TiAlC$_2$ ceramics have been fabricated by using Mo, Al, graphite elements powers and TiH$_2$ powders as raw materials through powder metallurgy technique, and the purpose of pore structure regulation is achieved by changing the Al content. The pore structure evolution and phase transformation process of Mo–Ti–Al–C system effected by different Al content were clearly described. In addition, in the traditional reaction synthesis method, the rapid heating...
method was used to save time to obtain a simple production process. Not at all, the pore forming mechanism affected by different Al content and temperature was also investigated. The intention of this paper is to expand the application of Mo-based MAX materials and lay the foundation for subsequent exploration of their catalytic performance after etching.

2. Experimental materials and procedure

In the present work, powder mixtures of Mo (99.7% pure, particle size 38–74 μm), TiH₂ (99.6% pure, particle size 38–74 μm), Al (99.5% pure, particle size 38–74 μm), and graphite (99.8% pure, particle size 5–6 μm) were selected as the starting material. The raw powders were mixed by Mo:TiH₂:Al:C with atomic ratios of 2:1:X:2 (X is from 0.9 to 1.7 with an increment of 0.2). In addition, extra 5% stearic acid was added into the mixture as a binder for the shaping of green compact. The powders were mixed for 48 h in a polyurethane jar with zirconia balls used as the mixing balls at the ball/powder ratio of 10:1 (mass ratio). After that, the dried mixtures were cold-pressed into green compacts with the dimensions of Φ25 mm×H2 mm under the pressure of 160 MPa. And then the as-pressed discs were sintered in a vacuum furnace at the vacuum degree of 1.2 × 10⁻³ Pa. And the sintering processes is displayed in Figure 1, as can be seen, four holding platforms were presented. The first insulation platform is to initially remove impurities such as moisture in the vacuum furnace. As the second insulation platform is located at 620°C, below this temperature, stearic acid is decomposed and Al atoms are fully diffused through thermal diffusion. The third insulation platform corresponds to the formation of some intermetallic compounds and Mo and Ti carbides (including MoC and TiC, respectively) at 1000°C. The last insulation platform at 1500°C is the temperature required for the formation of the final phase of Mo₂TiAlC₂. The temperature rising speed surpass 10°C/min in heating-up period during the whole process in order to simplified preparation process. After sintering, it was placed in ultrasonic vibration for 3 h, and then placed in a 60°C vacuum drying oven for drying.

The phase constitution including different Al content and temperature was detected by X-Ray diffraction (XRD: Dmax 2500VB) at the scan rate of 4°/min and the step size of 0.02°. The pore morphology was characterized by scanning electron microscopy (SEM, FEI Nova Nano 230). The overall and open porosity was tested by the Archimedes’ method. Besides, before and after sintering, the volume expansion of the disc was tested by vernier caliper to check the volume expansion. The pore size and viscous permeability coefficients were measured by aperture measuring apparatus. The principle of pore size test is in accordance with the bubble point method [20].

3. Results and discussion

3.1. Synthesis and phases characterization

In order to explore the phase compositions of porous Mo₂TiAlC₂ and synthesize pure porous Mo₂TiAlC₂, the sintering samples were tested by XRD processed at different Al content. The XRD results of the acquired phases are exhibited in Figure 2. As illustrated, the discs were comprised of three phases constituents (including Mo₂TiAlC₂, AlMo₃, and Mo₂Al₂C). As the Al

![Figure 1](image-url)  
Figure 1. Sintering process diagram of porous ceramics.
content kept rising from 0.9 to 1.7 (atomic ratio), the peak intensities of AlMo$_3$ reduced gradually, and when Al content reached 1.3, the peak became almost disappeared and undetectable. As the aluminum content kept on rising to 1.7, the peak of AlMo$_3$ disappeared and the remaining peaks hardly changed. In the previous study of TiVAIC, Zou et al. [21] have also found that impurity peak strength reduced first and remained constant with ascending aluminum content posterior. The change of AlMo$_3$ peak intensities demonstrated that relatively pure Mo$_2$TiAlC$_2$ phase could be acquired at the 1.3 mol aluminum content. These XRD results showed that the pure porous Mo$_2$TiAlC$_2$ ceramics can be procured by regulating the Al content, and the porous ceramics were relatively pure as the aluminum content was 1.3 mol. When the Al content exceeded 1.3 mol, the impurity peaks of Al did not appear, and the reasonable explanation is that the excess Al volatilizes at high temperature.

### 3.2. Effect of Al content on volume change

In the sintering process, the porosity of porous materials would change, which was accompanied by the change of material volume. So, it is of great significance to understand the change law of the volume of porous Mo$_2$TiAlC$_2$ ceramics with the increase of Al content after sintering. The volumes and dimension expansion ratios of porous Mo$_2$TiAlC$_2$ ceramics are displayed in Figure 3. As depicted in this figure, the volumes and axial, radial expansion ratios were presented to increase with the progressive increase of Al content (the axial, radial, and volume expansion ratios were obtained by dividing unsintered green compact). As the aluminum content varied in the range of 0.9 –1.7 mol at 0.2 mol interval, volume expansion ratios and axial direction parameter presented the same growth trend, and they increased first rapidly and then slowly. The radial expansion was growing at a very small rate. With ascending amount of aluminum (from 0.9 to 1.3) at 0.2 mol intervals, the volume expansion rapidly grew from 31.84 to 38.77%. After that, as aluminum content proceeded to increase to 1.7 mol, the rate of volume expansion lingering increased to 39.32%. When the Al content was lower than 1.3, the volume expansion could be attributed to the formation of porous Mo$_2$ TiAlC$_2$ ceramics, and Al elements diffused to other elements to form compounds, and pores are formed in situ. As Al content exceeded 1.3, excess aluminum becomes metallic liquid when the sintering temperature rises above its melting point, and the liquid phase surface tension of the metallic liquids caused the sintered grain shrinkage [22]. In addition, excess Al was evaporated as a part of pore-forming agent at high temperature, which would increase the volume.
of porous ceramics [23]. Due to the existence of these two factors, the volume of porous ceramics increased slowly with more Al. Excessive Al would have a great effect in the total porosity and open porosity of porous Mo$_2$TiAlC$_2$ ceramics, which would be discussed in Section 3.4. The unobvious change of radial expansion could be attributed to the influence of gravity.

In the previous study about porous alloys, Jiang et al. [24] obtained the relationship between volume expansion radio and porosity of porous materials according to the mass conservation of green compacts before and after sintering. The relationship among volume and porosity could be described by the mathematical expression

$$
\rho_0 V_0 (1 - \theta_0) = \rho V (1 - \theta_p - \theta_c)
$$

(1)

where $\theta_0$ is the overall porosity of initial mesopore in green compacts and $\theta_p, \theta_c$ are the open porosity after the sintering and the closed porosity in the compacts after sintering; $\rho_0$ and $\rho$ are the theoretical densities of the compact before and after sintering. $V_0$ and $V$ are the volumes before and after sintering, and the relationship among them is

![Figure 3](image1.png)

**Figure 3.** The expansion of volume, axial, and radial of the samples after the final sintering in different Al content.

![Figure 4](image2.png)

**Figure 4.** The relationship between the volume expansion ratio and the open porosity obtained by practical observation and theoretical calculation.
\[ V = V_0(1 + \alpha) \]  

where \( \alpha \) is the volume expansion ratio. So, the expression between open porosity \( \theta_p \) and volume expansion ratio \( \alpha \) can be finally derived as

\[ \theta_p = -\frac{\rho_0(1 - \theta_0)}{\rho} \frac{1}{1 + \alpha} (1 - \theta_e) \]  

As can be seen, there was a strict linear relationship between open porosity and \((1 + \alpha)^{-1} \) (Figure 4), and the linear equation was obtained by linear regression:

\[ y = -166.855x + 163.157 \]  

\[ R^2 = 0.9859 \]

The coefficient of determination \( R^2 \) was very close to 1, which means that there is a close relationship between the open porosity and the rate of volume expansion. And the larger rate of the volume expansion is, the higher the opening porosity is.

### 3.3. Characterization of pore structure parameters of sintered samples

Pore structure parameters are well known to play a vital role in porous materials including porous ceramics. As result, this work was necessary to carry out to explore the impacts of different aluminum content on porous Mo\(_2\)TiAlC\(_3\) ceramic pore structures parameters. In this paper, different pore structures involved porosity (open porosity and overall porosity), pore sizes (including maximum pore size and average pore size), and viscous permeability coefficient, and the variation track with the increased aluminum content was systematically investigated.

The impacts of progressive increasing aluminum content on porosities (including overall porosity and open porosity) of porous Mo\(_2\)TiAlC\(_3\) ceramic are displayed in Figure 5a. As demonstrated, the overall and open porosities showed almost the similarly growth trend, first rose and almost kept stable later. When aluminum content gradually varied in the range of 0.9–1.3 mol, the overall porosity rose from 40.82\% to 46.71\%, and open porosity grew from 36.87\% to 42.94\%. As the aluminum content kept on rising continuously to 1.7, the overall porosity rose slowly to 47.02\%, and open porosity grow slowly to 43.69\%. And the specific reasons would be carefully analyzed in the section of pores formation mechanism.

Figure 5b shows the curves of the pressure drop on volume flow tested by using different specimens in discrepant aluminum content, and it was observed that the relationship between volume flow and pressure drop was obviously linear. The calculated viscous permeability coefficient can be obtained by Darcy’s law [25], and Darcy’s law is described as follows:

\[ Q = \frac{\phi_v A \eta e}{\eta} \Delta p \]  

where \( Q \) refers to the volume flow rate, \( A \) represents the area of testing cross-sectional (2.83 × 10\(^{-4}\) m\(^2\)), \( e \) is the thickness of the specimen, \( \eta \) is the dynamic viscosity of the fluid (N\(_2\), \( \eta = 1.766 \times 10^5\) Pa·s at 25°C), and \( \Delta p \) refers to the pressure drop from the entrance to the exit of the sample. So, the viscous permeability coefficient was obtained through the slope of curve between the volume flow rate and pressure drop, and the results were exhibited in Figure 5c. The viscous permeability coefficient showed a trend of decreasing first and then increasing with ascending aluminum content. When aluminum content was 1.3 mol, the value of viscous permeability coefficient reached the lowest, and it was 2.11 μm\(^2\).

Figure 6 showed the maximum pore size and average pore size of the porous Mo\(_2\)TiAlC\(_3\) samples changed with variable Al content. As can be seen, pore size had the same variation trend with viscous permeability coefficient notably. When the Al content varied in the range of 0.9–1.3 mol, average and maximum pore sizes reduced pronounced during this stage. Whereas, with the aluminum content increased continuously to 1.7, the pore size ascended.

### 3.4. Exploration on pore formation mechanism

According to phase transformation in the sintering process of the sample and the various factors affecting the pore formation before and after comprehensive sintering, the reasons for the evolution of pore structure in the reaction-sintered porous Mo\(_2\)TiAlC\(_3\) ceramics are attributed to mesopores produced by powder pressing, volatilization of molding agent, and Kirkendall effect. The specific causes will be discussed carefully below.

1. **Mesopores produced by powder pressing**

   In the pressing process of powder, because the pressure cannot press it into completely dense, there are interstitial pores between powder particles in green compact disc. During the pressing process of Mo, TiH\(_2\), Al, and C powders, fine pores exist between the powder particles in the green compacts by adjusting the press pressure. The pore size and porosity are mainly controlled by the particle size, shape, and pressing pressure of the powder. The effect of pressing pressure on the mesopores is essentially realized by the influence of pressing process on the plastic deformation of powder particles and the mesopores, which has a direct impact on the maximum pore size of the material.

2. **Volatilization of molding agent**
In this paper, a small amount of stearic acid was added to the mixed powders used as molding agent in the pressing stage. When the temperature in vacuum furnace exceeded the melting point of stearic acid (232°C), stearic acid volatilized. Some pores were formed at the original position of stearic acid. In addition, the volatilization of Al at high temperature would also form part of the pores [21].

(3) **Pores formed by Kirkendall effect**

The pores formed during sintering due to atomic migration, binding, and phase transition could be attributed to the Kirkendall effect [26]. It was noted that both overall and open porosity were opposite to that of pore structure parameters, which manifested that phase transformation is an important factor leading to the evolution of pore structure parameters.

With the objective of further inquiring into the phase transformation process on different sintering stage of porous Mo$_2$TiAlC$_2$ ceramics, porous Mo$_2$ TiAl$_{1.3}$C$_2$ ceramics were selected to explore the pore structure-forming process. The sintering was processed at the temperatures of 700, 1100, 1500°C (in Figure 2), and the holding time was 2 h. The XRD results of the acquired phases of 700 and 1100°C are shown in Figure 7. As illustrated, at ~700°C, only element powders and some intermediate Ti–Al compounds were detected. As preparing porous Ti$_3$AlC$_2$ ceramics, Yang et al. [27] found that TiC was easier to form than Ti–Al intermetallic compound because the Gibbs free enthalpy of TiC generation is remarkably lower. This indicated that the first substance formed in the reaction is supposed to be TiC. However, the situation does not apply well in this paper obviously. We believed that the reasons due to the faster reaction rate and the larger wetting angle of Ti and liquid state Al. In previous study of Ti$_3$AlC$_2$, Li et al. [28] have declared that liquid state Al reacts with solid state Ti to form Ti–Al intermediate compounds as the temperature exceeds 660°C. So, the chemical reaction equations below 700°C could be expressed as [21,28]

\[
\text{TiH}_2 \rightarrow \text{Ti} + \text{H}_2 \tag{7}
\]

\[
\text{Ti} + \text{Al} \rightarrow \text{TiAl} \tag{8}
\]

\[
2\text{Ti} + \text{Al} \rightarrow \text{Ti}_2\text{Al} \tag{9}
\]

A few years ago, Jiang et al. [29] have reported a method for fabricating Ti–Al micro/nanosized porous alloys by using elemental powders with different particle sizes based on Kirkendall effect. Their view was that pore formation was caused by the difference in diffusion rates of Ti and Al during heating. As Ti and Al react to form Ti–Al compounds, the net movement and consumption of Al elements will lead to numerous pores. Near the original position of the Al atom. And the higher Al content, the larger pore size. However, when Al content exceeds a certain amount, the pore size remained almost unchanged. In this paper, this is verified by the slow growth of porosity and pore size.
when the aluminum content exceeded 1.3 mol. More importantly, we believe that the diffusion of atoms at high temperature is not the main factor leading to pore formation in this paper.

When the temperature achieved 1100°C, the diffraction peak intensity of Ti2AlC enhanced much and the TiAl phase was not detected, whereas the diffraction peak intensity of Mo2C proceeded to reinforcing to be the main phase, and some TiC were generated additionally. The chemical reaction equations between 700 and 1100°C could be expressed as

\[
2\text{Mo} + \text{C} \rightarrow \text{Mo}_2\text{C} \quad (10)
\]
When the temperature increases to the range of 700–1100°C, Mo and remaining Ti atoms contact the C particle interface and begin to react to form carbide covering the basic surface. The thin carbide layers contained Mo₂C, TiC, and Ti₂AlC. Meanwhile, the remaining Mo and Al continued to react to form AlMo₃. When Mo and Ti atoms were consumed completely, a large number of carbides were generated and pores were restructured, the microstructure of porous ceramics changed, which could be proved by Figure 8. Therefore, comparing Figure 8a and Figure 8b, the pore size was observed to become larger and the pore distribution became more uniform gradually.

When further increasing temperature to be final of 1500°C, some intermediate phases of impurity peaks such as TiC, Mo₂C, and Ti₂AlC disappeared, and Mo₂TiAlC₂ could be examined. Therefore, the final generation phase of Mo₂TiAlC₂ possibly reacted by intermediate phases Mo₂C, Ti₂AlC, and AlMo₃. So, based on the above analysis, the reaction between 1100 and 1500°C could be expressed by the following chemical formula [12]:

\[
2\text{Mo} + \text{C} \rightarrow \text{Mo}_2\text{C} \tag{14}
\]

\[
\text{Al} + 3\text{Mo} \rightarrow \text{AlMo}_3 \tag{15}
\]

\[
\text{TiAl} + \text{TiC} \rightarrow \text{Ti}_2\text{AlC} \tag{16}
\]

\[
\text{Mo}_2\text{C} + 2\text{AlMo}_3 + \text{Ti}_2\text{AlC} + \text{TiAl} + \text{TiC} + 5\text{C} \\
\rightarrow 4\text{Mo}_2\text{TiAlC}_2 \tag{17}
\]

In this sintering stage, diffusion and reaction of carbides and various intermetallic compounds brought about a sharp expansion of volume. However, these substances aggregate and react together to increase their own volume, resulting in pore compression. This observation explained why pore size and viscous

![Figure 8. SEM image of the as-fabricated sample with different sintering temperature for holding 2 h: (a) 700°C; (b) 1100°C.](image)

![Figure 9. Reaction pathway of porous Mo₂TiAlC₂ ceramics in different Al content.](image)
3.5. Characterization of surface topography

The SEM pictorial of these specimen with ascending Al content (from 0.9 to 1.7) in 1500°C was exhibited in Figure 10. As can be seen, the pore distribution of the final products was uniform, and the pore size decreased first and grow with raising Al content subsequently, which was consistent with the changes in the pore size and viscous permeability coefficient we have measured. In addition, the typical layered structure was observed in this diagram, which indicates that porous MAX Mo2 TiAlC2 ceramics were successfully prepared [30].

4. Conclusion

In this paper, porous Mo2TiAlC2 materials with Al content gradually rising from 0.9 to 1.7 (molar ratio), with 0.2 discrepancies, were successfully manufactured using TiH2 powders, Mo, Al, and C elements power as raw materials through powder metallurgy technique. The work may provide reference meanings to reveal the influence mechanism of different aluminum content on the fundamental research of porous Mo2TiAlC2 ceramics. By increasing the Al content, the pore structure parameters including pore sizes and viscous permeability coefficient, the pore structure parameters decrease first and then rise. The volume first grows rapidly and then slowly. Results of pore formation mechanism revealed that pores were formed by mesopores, which were produced by powder pressing, volatilization of molding agent, and Kirkendall effect.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

The financial support of this project was provided by Outstanding youth fund of Wuhan Polytechnic University (Grant No. 2018J05) and Youth Natural Science Fund of China (Grant No. 51704221).

Potential interest competition

The authors have confirmed that they have no potential competing financial interests or internal personal connections that could have occurred to interference the work reported in this paper.

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