Research on The Pore-Forming Mechanism of Porous Tial Intermetallics with (NH4)2CO3

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Abstract. Porous TiAl intermetallic compound is a material with excellent properties, which could be applied to various fields. However, the disadvantage of current porous TiAl intermetallics is that the permeate flux is low. In this paper, (NH4)2CO3 was selected as pore-forming agent to fabricate porous TiAl intermetallics by activation reactive sintering. After that, the effect of pore former (NH4)2CO3 content and pore-forming mechanism were investigated. The results indicated that the pore former (NH4)2CO3 is benefit for the formation of through-holes in porous TiAl intermetallics, and the Kirkendall partial diffusion effect has great influence on the pore formation.

1. Introduction

Porous metal materials with adjusting porosity could be widely applied in the separation, purification and different liquid components concentration of chemical, aerospace, pharmaceutical industry [1]. Chen et al [2] reported porous TiAl intermetallics were prepared with Ti and Al element powders as raw materials by Kirkendall partial diffusion-activation reaction sintering. At present, porous TiAl materials with controllable pore structure, excellent filtration performance, long service life has been basically achieved, and which can be applied in acid, alkali, and server environment for industrial processes. However, there are still some shortcomings with this material, such as small flux, low filtration efficiency.

In order to solve these problems, adding metal Mg [3], NaCl [4], polymer material [5], active yeast [6] as pore former and dealloying [7] to increase through-hole are the mainly methods. But these methods are difficult to remove residual substances, which may affect the performance of the material. In this work, (NH4)2CO3 was added as a good pore-forming agent. The reasons lied in the low price, wide source, low boiling point and easy volatilization. Therefore, a pore-forming agent (NH4)2CO3 was studied its influence on the porosity of the through-holes of porous TiAl intermetallics. Last but not least, the pore-forming mechanism from mathematical perspective was explored.

2. Experiment and methods

The raw materials were used in this experiment: Ti powder (- 200 ~ + 400 mesh, purity 99.7%), Al powder (- 325 mesh, purity 99.5%), ammonium carbonate (- 200 mesh, analytical grade). The Ti and Al element powders are mixed according to Ti-33wt % Al in a planetary ball mill for stirring 5 h with the ball to material ratio 5:1. Then, the same proportion (mass ratio 1%, 3%, 5%, 7%) of (NH4)2CO3 was added to the mixed powders. After the grinding, the mixed powders were subjected to press molding at a pressing pressure of 200 MPa. The green compact of a diameter of 32 mm and a
thickness of 2 mm was formed. Then it would be subjected to activation reaction sintering in a vacuum sintering furnace. The porosity was measured by bubble point method, and the gas permeability was measured by a dry film differential pressure flow measurement method.

3. Results and discussion

3.1. Sintering process
As is shown in Fig 1, there were four stages. The first temperature stage was to remove the water. The second stage was corresponding to the resoving of \((\text{NH}_4)_2\text{CO}_3\) with temperature of 200°C. The third stage was related to the diffusion of Ti and Al. For the last stage, the sample was kept for 120 min, it was related to the densification of Porous TiAl intermetallic compounds.

![Fig. 1 The sintering temperature as a function of sintering time.](image)

3.2. The effect of pore-forming agent content on the expansion behavior of porous material
In order to study the effect of the content of pore-forming agent on the expansion behavior of porous TiAl intermetallics, the table 1 was prepared.

| Space-holder | Amount (wt. %) | Radial Direction (%) | Axial Direction (%) | Volume Expansion (%) |
|--------------|----------------|----------------------|---------------------|----------------------|
|              | 0              | 10.22                | 10.51               | 34.25                |
| \((\text{NH}_4)_2\text{CO}_3\) | 1              | 11.11                | 10.08               | 35.90                |
|              | 3              | 12.15                | 10.37               | 38.82                |
|              | 5              | 13.78                | 10.51               | 43.07                |
|              | 7              | 14.98                | 10.66               | 46.30                |

As can be seen in the table, the axial expansion rate and volume expansion rate of the sample presented a linear growth trend with the increase of the content of pore-forming agent. To explore the quantitative relationship between volume expansion rate \(\alpha\) and the content of pore-forming agent \(w\), assuming that they meet the linear relation, that is:

\[
\alpha = kw + b
\]  

Linear fitting was performed on the data in the table to obtain:

\[
\alpha = 1.742w + 34.095, \ R^2=0.99825
\]
The determination coefficient was close to 1, indicating that the linear fitting degree was good.

3.3. Effect of pore former content on porosity
Table 2 was the pore structural parameters with different pore former amount. As it indicated, when the pore former content was 0%, the porosity of the porous TiAl intermetallic was 42.4%. The content of (NH₄)₂CO₃ in the pore former was gradually increased, and the porosity of the porous material was gradually increased. But the growth rate was very slow. When the amount of the pore former (NH₄)₂CO₃ was 7%, the porosity reached a maximum of 49.9%. Analysing these data, the results illustrated that the pore former (NH₄)₂CO₃ had a limited effect on the increasing of porosity.

Table 2. The pore structural parameters with different pore former amount (NH₄)₂CO₃

| Space-holder | Amount (wt. %) | Overall porosity (%) | Permeability (m³·m⁻²·kpa⁻¹·h⁻¹) |
|--------------|---------------|----------------------|----------------------------------|
| 0            | 0%            | 42.4                 | 155.5                            |
| 1%           | 43.7          | 198.9                |
| (NH₄)₂CO₃    | 3%            | 45.5                 | 223.2                            |
|              | 5%            | 48.2                 | 246.8                            |
|              | 7%            | 49.9                 | 307.3                            |

It could be observed that when the pore former content was 0%, the gas permeability of the porous TiAl intermetallic was 155.5 m³·m⁻²·kpa⁻¹·h⁻¹, and the air permeability increased with the content of the pore former. Basically, the growth rate was multiplied, and the growth rate was obvious. When the content of the pore-forming agent reached 7%, the gas permeability of the porous TiAl intermetallic reached a maximum of 307.3 m³·m⁻²·kpa⁻¹·h⁻¹ simultaneously. The effect of the pore-forming agent on the porosity was not obvious, but the effect on the gas permeability was larger than that of overall porosity. It can be concluded that the increasing of the (NH₄)₂CO₃ content of the pore-forming agent contributed to the formation of through-holes between porous TiAl intermetallics.

3.4. Influencing factors of pore formation in TiAl intermetallic compounds
Porosity of the porous TiAl intermetallics was caused by four kinds of factors: (1) the volume expansion during the sintering process; (2) the mespore between powders and powder in the green compact; (3) the pore former in the original position after volatilization at a high temperature; (4) the Kirkendall's partial diffusion effect. According to the equation of mass conservation before and after sintering (the pore-forming agent was not included due to volatilization), the formula could be illustrated as:

\[ \rho_0 V_0 (1 - \theta_m - \theta_v) = \rho (1 + \alpha) V_0 (1 - \theta_s) \]  

(3)

Where, \( \rho_0 \) and \( \rho \) represent the theoretical density of the green and sintered porous samples, g/cm³; \( \theta_m \) symbolize the porosity of the interstitial pores in the green body; \( \theta_v \) depict the porosity occupied by the pore former; \( V_0 \) describe the green volume; \( \theta_s \) was the total void radio, and \( \alpha \) express sintering the volume expansion ratio of the sample.

Then the pore former porosity \( \theta_s \) caused by (NH₄)₂CO₃ could be expressed as:

\[ \theta_s = 1 - \theta_m - \frac{\rho}{\rho_0} (1 + \alpha)(1 - \theta_v) \]  

(4)
As we all know, the pore former porosity \( \theta_s \) is positive relevant to the amount of pore forming agent. So, the formula (2) can be conducted as follows:

\[
\theta_s = K_w w = 1 - \theta_m - \frac{\rho}{\rho_0} (1 + \alpha)(1 - \theta_v)
\] (5)

Where, \( K_w \) was the proportionality factor of pore forming agent.

In order to further verify the relationship between the pore \( \theta_s \) caused by the pore former and other parameters, the amount of pore forming agent \( W \) and the mapping were performed in Figure. 1.

Then fitting data and the resulting straight-line formula was:

\[
y = 1.459 - 1.908x \quad R^2 = 0.9899
\] (6)

The value of \( R^2 \) is 0.9899 close to 1, indicating that the experimental data is reliable with no large deviation. In order to obtain the effecting of the pore former content on the pores of the porous TiAl intermetallics, whose value was represented by \( K_w \). Combining equation \( \frac{1}{1+\alpha} \) with \( (1-\theta_v) \) linear fit to obtain a slope of 1.147, or \( \rho_0 \lambda (1-\theta_m - \theta_s) \). Diagramming of Equation 5 and Figure 2, the pore-forming coefficient \( K_w \) of the pore-forming agent was found to be 0.60. Jiang et al. \[10\] synthesized porous TiAl intermetallics by activation reaction sintering technique. The results indicated that the pore parameters were ratio to the Al amount.

Since the composition ratio of the porous TiAl intermetallics used in this experiment was Ti-33wt.% Al, and the Kirkendall reaction perforation coefficient can be conducted as 0.92. According to Fig 3, it could be concluded that the Kirkendall pores were 30.36%. The sum of the pores of the mesopores and volume expansion pores were 12.04%.
Fig. 3 The effect of Al content on the porosity of Ti-Al porous alloy

The pore-forming porosity and the ratio of kirrendall porosity to the residual porosity were plotted for the pore-forming agent content, as was shown in Fig 4. As was depicted in Fig 4, The pore-forming porosity and the ratio of kirrendall porosity to the residual porosity were plotted for the pore-forming agent content. With the increasing of pore-forming agent content, the ratio of Kirkendall porosity to total porosity gradually decreased. This may be because of the gap between powder particles increased after the addition of pore-forming agent, which affected the Kirkendall diffusion process and its diffusion pores. The proportion of degrees has decreased. The porosity of the pore-forming agent, the ratio of the pore volume and the volume expansion hole to the total porosity increased. Indicating that the increasing of porosity was mainly caused by the above three factors.

Fig 4. The effect of different pore proportion in porous TiAl intermetallics

4. Conclusion
1) When the mass fraction of the pore-forming agent (NH₄)₂CO₃ was 7%, the porosity reached a maximum of 49.9%, and the maximum gas permeability was 307.3 m³•m⁻²•kpa⁻¹•h⁻¹. Although the pore-forming agent had a limited effect on the increase of porosity but it had a great effect on increasing the through-hole so that it could meet the original intention of the experimental design.
2) The pore-forming coefficient of the pore former was 0.60, and the pore ratio of the Kirkendall reaction was 0.92. The pore porosity of Kirkendall was 30.36%, and the sum of the pores of the clearance hole and the volume expansion hole was 12.04%. The increasing of porosity was mainly affected by pore former, Kirkendall diffusion process and volume expansion of porous TiAl intermetallics.
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