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Letter

# Pore evolution regulation in synthesis of open pore structured Ti–Al intermetallic compounds by solid diffusion

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ABSTRACT

A method based on diffusion model simulation and calculation was used to discuss the pore evolution regulation of porous Ti–Al intermetallic compounds. According to the basic structure characteristics of Ti–Al compacts, a sandwich core–shell structured powder diffusion couple model and two pore evolution conditions were used to reveal the pore evolution regulations in Ti–Al porous alloy, which is mainly caused by the Kirkendall effect. The growth of the pore evolution layer is consistent with the consumption of the initial Al shell, and the dimension of the pore evolution layer is independent on the dimension of the core of Ti particle. An equation reflecting the evolution porosity and the physical parameters of diffusion components was established. The evolution porosity was confirmed to be a function of the concentration and density of diffusion elements.



## 1. Introduction

In solid phase diffusion procedure, the Kirkendall effect reveals a fact that the realization of atom diffusion depends on the exchanges between atoms and vacancies, instead of the direct exchanges between atoms [1–3]. In the diffusion couple of two components with different self-diffusion coefficients, excessive vacancies will generate in the faster diffusion component and finally condense into pores. As a result, this diffusion effect was used to fabricate functional materials with closed pore structure, such as hollow structure [4,5] and nano hollow sphere [6]. Currently, two-component diffusion couple models used to discuss the evolution behavior of Kirkendall pores include plane diffusion couple model [7–9] and sphere diffusion couple model [10,11]. Plane diffusion couple model is characterized by an infinite contact plane between two components, while the latter is characterized by a structure with the faster diffusion component as the core and the other one as the shell.

The Kirkendall effect has been utilized to fabricate porous material with high open porosity. A notable example is the preparation of TiAl intermetallic compound porous material [12,13], which has the advantages of currently applied both porous metals and porous ceramics [14–16], such as excellent environmental corrosion resistivity, sound mechanical properties at room and elevated temperature, good weldability for sealing, enough machinability, etc. This novel porous material can be applied in some rugged environments such as high temperature oxidation and strong corrosion conditions [12], which shows great application potentials. The fabrication of TiAl porous material is based on a developed powder metallurgy (PM) method. The mixed Ti and Al elemental powders were cold pressed into compacts with porosity of 5–10%, followed by a reactive synthesis procedure in which pores formed through the Kirkendall effect with the overall porosity of 30–60% and the open porosity proportion of more than 90% [17].

The current sphere diffusion couple model used to discuss the formation of closed pores cannot be applied to explain the evolution behavior of this novel porous material with high open porosity. In fact, the open pore structures due to the Kirkendall effect depend on the composition of mixed powders [17,18]. The evolution behavior of the Kirkendall open pores in these porous materials has not been discussed. In this letter, an improved sandwich sphere diffusion couple model is presented to discuss the evolution of the Kirkendall pores in porous TiAl intermetallic compound, based on the characters of Ti/Al powders and compacts.

## 2. Synthesis method and characteristics

2 kinds of synthesis methods can be used to fabricate Ti–Al porous alloy through Ti/Al elemental powders: self-propagation high-temperature synthesis (SHS) [19,20] and reactive synthesis based on solid diffusion [17,18,21]. There is a great difference of heat release between these 2 methods. Fig. 1 shows the DTA profiles

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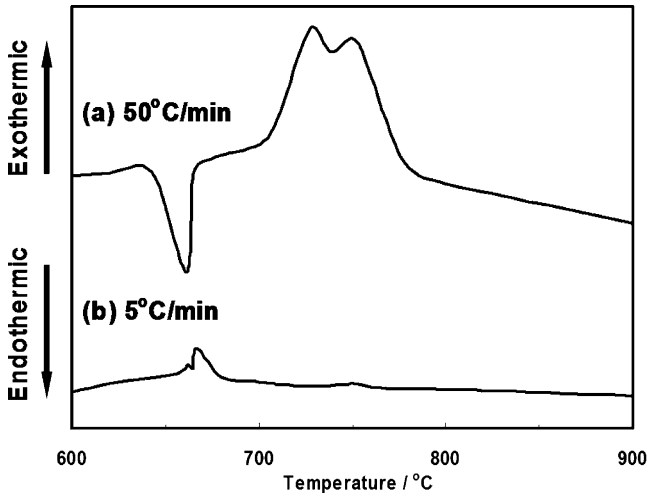


**Fig. 1.** DTA profiles of specimen with the nominal composition of Ti–50 at.% Al produced by reactive sintering with various heating rates: (a) 50 °C/min and (b) 5 °C/min.

of specimen with the nominal composition of Ti–50 at.% Al elemental powders during the sintering procedure with various heating rates: (a) 50 °C/min and (b) 5 °C/min. SHS occurs at a relatively large heating rate (Fig. 1a) and shows a strenuous exothermal reaction.

SHS method has the marked characteristic of self-sustaining and the advantages of time and energy savings, however, this strenuous synthesis procedure that releases massive heat and gas, in which a large number of pores formed, made it extremely difficult to control the shape and pore structure of the porous materials [22], which thus limited their applications. Reactive synthesis method based on solid diffusion has a relatively gentle heat release procedure, in which the pores formed mainly due to the Kirkendall effect through the partial diffusion of Al [12,17,18,21]. In this letter, in order to investigate the pore evolution regulation in open pore structured Ti–Al alloy by solid diffusion, the reactive synthesis method based on solid diffusion was adopted, in which SHS procedure was avoided through controlling the heating rate and prereaction process according to the reference [21].

## 3. Structure characters in Ti–Al compact

As for the Ti–Al elemental powder compact and the final Ti–Al porous alloy, there are some basic characters as follows.

(1) It is more reasonable to regard the powder particle as a sphere than an infinite plane, so the sphere diffusion couple model is more suitable than the plane considering the size and shape of powders.
(2) As shown in Fig. 2, in a powder compact, the size of Ti and Al elemental powder is usually smaller than 100 μm, and the Ti and Al powder particles are neighbored and surrounded by each other.
(3) As shown in Fig. 3, the pore structure of the Ti–Al porous alloy fabricated by the reactive synthesis of Ti–Al elemental powder compact exhibits high proportion of open pores, while the current sphere diffusion couple is usually used to describe the formation of closed pores.

## 4. Sandwich core–shell structured diffusion couple model

Based on the structure characters above mentioned, a Ti–Al powder diffusion couple model was presented, as shown in Fig. 4.

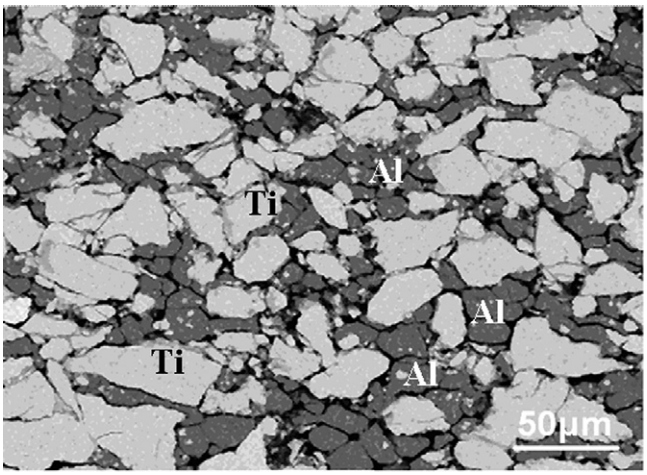


**Fig. 2.** Conformation feature in Ti–Al green compacts.

In the Ti–Al powder diffusion couple model, the Ti particle is the core, surrounded by the shell of evenly distributed Al particle. Outside the Al layer exists a discontinuous Ti particle layer, which constitutes a sandwich sphere model. The structure parameters for this diffusion couple model are shown in Fig. 4. The model hypotheses are as follows:

(1) In the sphere model for Ti–Al green compact, as shown in Fig. 4a, the outer discontinuous Ti particle layer, which surrounds the middle Al layer, acts as a support for the evolution pores formed during the reactive synthesis of Ti and Al. Compared with the diffusion flux of Al into the Ti core, the diffusion flux of Al into the outermost Ti particle layer is ignored in the model.
(2) As shown in Fig. 4b, in the sphere model for Ti–Al porous alloy, the Ti–Al alloy core keeps the similar shape with the initial Ti core. The outermost Ti–Al alloy layer, which remains discontinuous and surrounds the middle evolution pore layer, supplies channels for the pores to connect with each other. The porosity for connection is ignored when compared with the porosity for the middle pore lay in the model.

## 5. Model calculation and confirmation

Based on the sandwich diffusion model, two simple pore evolution conditions [10,11,23] can be considered to describe the pore evolution regulations in Ti–Al porous alloy. The 2 evolution conditions are based on the same presuppositions as follows. (1) The material mass keeps constant after the reaction of Ti and Al elements. (2) Considering the near same molar volume of Ti and Al atoms, the volume effect during the phase transformation procedure is ignored. The material volume is supposed to be constant, that is, the model parameters as shown in Fig. 4 should obey the expression: $r_a = r_e$.

For the first pore evolution condition, the ratio of the thickness of the evolution pore layer to the radius of the Ti–Al alloy core is supposed to be equal to the ratio of the thickness of the initial Al layer to the radius of the Ti core. That is, the dimension of the pore evolution layer is directly proportional to the dimension of the core. The model parameters should obey the following expression:

$$\frac{r_t - r_e}{r_e} = \frac{r_a - r_0}{r_0} = \text{const} \quad (1)$$

Considering the initial porosity $\theta_0$ in the Ti–Al green compact before sintering, the overall porosity $\theta$ should includes the initial porosity $\theta_0$ and the evolution porosity $\theta_E$ which includes the Kirkendall porosity $\theta_K$ and a porosity variable $\Delta\theta$. The Kirkendall porosity $\theta_K$

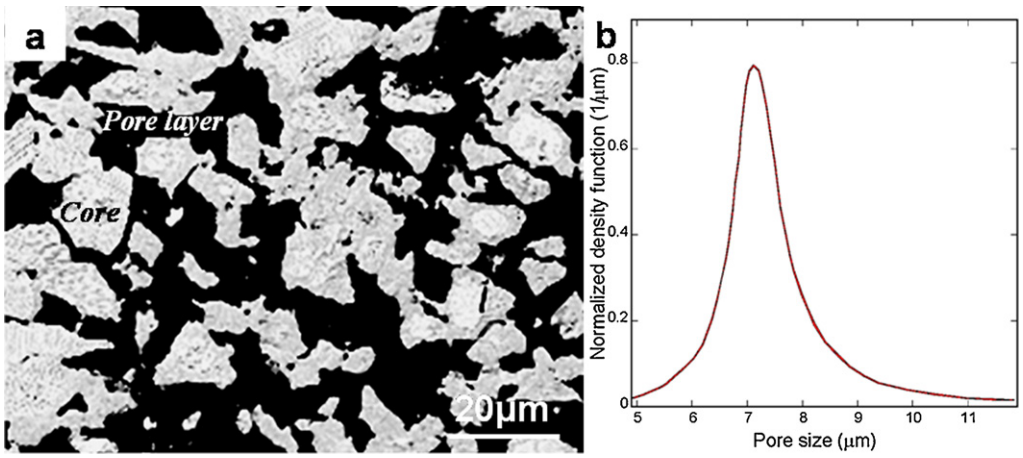


**Fig. 3.** Pore structure (a) and aperture distribution (b) in Ti–Al porous alloy sintered at 1300 °C.

is formed due to the partial diffusion of Al element during the reaction of Ti and Al elements, and the porosity variable $\Delta\theta$ includes a pore increment caused by heat and gas emission during the reaction procedure and a pore decrement due to the densification process during sintering of the porous structure. Thus the overall porosity can be expressed as follows:

$$\theta = \theta_0 + \theta_K + \Delta\theta = \theta_0 + \frac{r_t^3 - r_e^3}{r_t^3} \tag{2}$$

The Al content $c_A$ of the Ti–Al alloy can be expressed as a function of model parameters, Al metal density $\rho_A$ and Ti metal density $\rho_T$:

$$c_A = \frac{\rho_A \cdot (r_a^3 - r_0^3)}{\rho_A \cdot (r_a^3 - r_0^3) + \rho_T \cdot r_0^3} \tag{3}$$

Substitute the model parameters in Eq. (2) with Eqs. (1) and (3), we can the following expression:

$$\theta_E = \theta_K + \Delta\theta = \theta - \theta_0 = \frac{\rho_T}{\rho_A((1/c_A) - 1) + \rho_T} \tag{4}$$

For the second pore evolution condition, the thickness of the Kirkendall pore layer is supposed to be equal to the thickness of the initial Al layer. That is, the dimension of the pore evolution layer is independent of the dimension of the core. The model parameters should meet the following expression:

$$r_t - r_e = r_a - r_0 = \text{const} \tag{5}$$

Substitute the model parameters in Eq. (2) with Eqs. (5) and (3), we can the following expression:

$$\theta_E = \theta_K + \Delta\theta = \theta - \theta_0 = 1 - \frac{1}{(2 - (\rho_A(1-c)/(\rho_A(1-c) + \rho_T c))^{1/3})^3} \tag{6}$$

The relationships of Al content $c_A$ and the evolution porosity ($\theta_K + \Delta\theta$) described by Eqs. (4) and (6) are shown in Fig. 5. The corresponding experimental data is also shown for comparison.

For $c_A = 0$, we can get $\theta = \theta_0 + \Delta\theta$ according to Eqs. (4) and (6), that is, both the two pore evolution conditions obey the composition boundary condition. For $c_A > 63$ wt%, excessive Al metal will exist and block the generated pores after the reaction of Ti and Al elements according to Ti–Al binary phase diagram [24], which should not be considered in the diffusion couple model. Therefore, the Al content $c_A$ in equations and Fig. 5 should be in the range of $0 < c_A < 63$ wt%.

As shown in Fig. 5, the pore evolution amplitude with increasing the Al content by Eq. (4) is larger than the experimental data obviously; however, the curve by Eq. (6) is in accordance with the experimental data. That is, the evolution pores is dependent on the consumption of faster diffusion Al element. From the presupposition of Eqs. (4) and (6), we can get the point that the dimension of the pore evolution layer is independent on the dimension of the core, and that the thickness of the pore evolution layer is consistent with the thickness of the initial Al layer.

The pore evolution in Ti–Al porous alloy, which is mainly caused by the Kirkendall effect, was restricted by the reaction

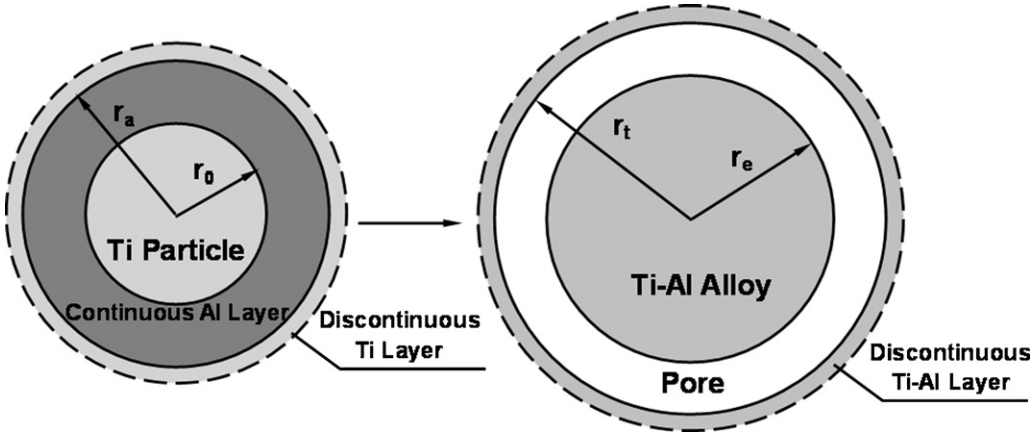


**Fig. 4.** Diffusion couple model for Ti–Al elemental powder compacts.

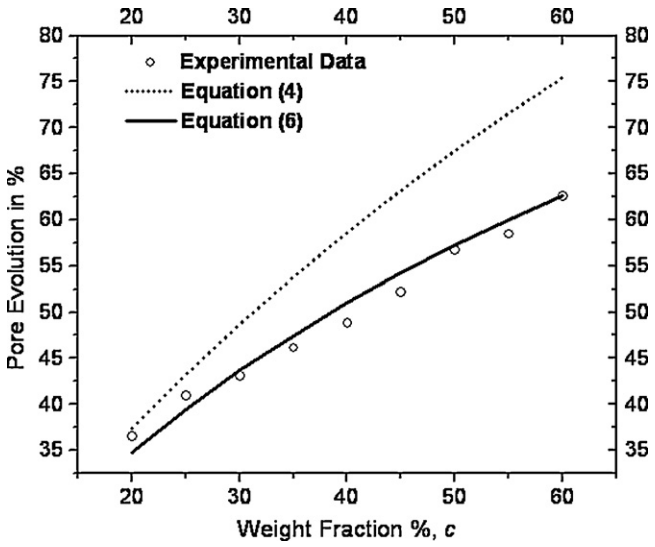


**Fig. 5.** Pore evolution in Ti–Al porous alloy as theoretically calculated and experimentally observed.

consumption and the dimension alteration of Al particle layer, as disclosed by Eq. (6) and Fig. 5. During the reaction synthesis of Ti and Al elements, since the diffusion rate of Al is significantly larger than that of Ti [25], the net movement and consumption of Al element must be balanced by the opposite net vacancy flux, which will result in excessive vacancies. To reduce the Gibbs free energy for the system the supersaturate vacancies condense into Kirkendall pores [12]. That is, with the faster diffusion and consumption of Al element, Kirkendall pores formed at the site of Al metal as a result of aggregation and collapse of vacancies. Finally, the Kirkendall pores substitute the site of the original Al metal layer with their dimension consistency until the completion of the diffusion reaction and the depletion of Al metal.

## 6. Summary

A sandwich core–shell structured powder diffusion couple model was presented to investigate the pore evolution regulations in open pore structured Ti–Al intermetallics. The equation reflecting the evolution pores and the diffusion component concentration was established. The dimension of the pore evolution layer is independent on the dimension of the core, and that the thickness of the pore evolution layer is consistent with the thickness of the initial Al shell. The coherence between the equation and experimental data indicates that the core–shell structured diffusion model could be suitable for investigations on the pore evolution based on the Kirkendall effect in powder compacts.

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