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# $Ti/Al_2O_3$ interfacial diffusion: Kinetic equation for growth of reaction layer and formation mechanism

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ABSTRACT

$Ti/Al_2O_3$ composites are prepared by vacuum hot-pressing sintering in order to study the elements diffusion and formation of the reaction layer at the interfaces. The results indicate that the forming process of the reaction layer can be separated into three stages, and the thickness of the interfacial layer is greatly related to the sintering temperature and holding time. By calculating, the kinetic equation for the growth of the thickness is expressed as $d = 1.2864 \times 10^3 \exp(-(153.1 \times 10^3)/RT)t^{0.96}$. When temperature is above 1250 °C, Al element has more powerful diffusion ability than Ti, so reaction layer mainly composed of TiAl and $Ti_3Al$ is formed at the side of Ti zone. In the case of $Al_2O_3$ phase, Al ions dissolve in the Ti phase substitutionally and migrate by exchanging with vacancies, which is in contrast with the direct interstitial mechanism of Ti and O ions.



## 1. Introduction

$Al_2O_3$ ceramics are attractive because of its remarkable mechanical properties, such as superior high hardness, excellent compressive strength, good wear resistance and high elastic modulus [1–3]. However, their application as structural materials has been limited by the low fracture toughness and weak thermal shock resistance [4,5]. According to the previous researches, one of the most effective methods is to add some reinforced phases [6,7]. Metallic Ti and alloy, as lightweight components, are widely used in engineering practice with the increasing demand [8,9]. Pure Ti has a high melting point of 1668 °C which is higher than the sintering temperature of $Al_2O_3$, at the same time, it performs good physicochemical consistency with $Al_2O_3$ [10–12]. Hence, Ti can be chosen as ideal reinforced phase for brittle $Al_2O_3$ ceramics.

Nowadays, combination of useful properties in $Ti/Al_2O_3$ composites makes them very attractive materials, but the studies have not achieved the desired results. It has been reported that strong interfacial reactions between Ti and $Al_2O_3$ at high temperature lead to the formation of Ti–Al intermetallic compounds [13–15], such as TiAl and $Ti_3Al$. Appropriate amount of interfacial reaction products are conducive to the interface bonding, but excessive amount can decreases the mechanical properties due to their brittleness at room temperature, which restricts the application of the composites [16,17]. Thus, the knowledge of the diffusion characteristics and understanding of diffusion mechanisms at the $Ti/Al_2O_3$ interface are of great importance to the entire area of research and the design of $Ti/Al_2O_3$ composites.

Reaction dynamics is used to find out the process and degree of reaction at a certain temperature [18,19]. The solid-state reaction between Ti and $Al_2O_3$ mainly depends on elements diffusion at the interface, so the growth of the reaction layer can be described by kinetic equation which is based on diffusion reaction. Julcour [20] done some researches on dynamics of internal diffusion during the hydrogenation of 1,5,9-cyclododecatriene on $Pd/Al_2O_3$ and found that kinetics was mainly limited by the diffusion of hydrogen. Moreover, Yao [21] reported that the process of the Ti/Al joint formation could be separated into four stages. At the initial stage, new phase $TiAl_3$ was nucleated, then the diffusion reaction began when the concentration rate of Ti and Al reached that of $TiAl_3$, afterwards, grain phases grew and jointed together to form a layer, finally, a $TiAl_3$ layer expanded to the regions of both Ti and Al. There are also some researches on the $Ti/Al_2O_3$ diffusion bounding and phase compositions under conditions of electric field or heating [22,23], however, hardly any investigations concerning the $Ti/Al_2O_3$ diffusion and dynamics by vacuum hot-pressed sintering have been reported. According to the above, we study the mechanism of the

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interfacial evolution and establish the kinetic equation for the growth of the reaction layer in order to provide basis for designing the Ti/$Al_2O_3$ composites conveniently.

## 2. Experimental procedures

$Al_2O_3$ powder (99.8% pure, an average grain size of 1.5 μm, Henan Changxing Co., Ltd, China), Ti plate (99.6% pure, an average grain size of 27.5 μm, Shanghai ST-Nano Science and Technology, China) were used as raw materials in this experiment. Laminated composites were fabricated in order to investigate the interfacial evolution with the increasing of sintering temperature. The detailed preparation process is as follows. Firstly, 15 g $Al_2O_3$ powder was poured into a graphite mold (inner diameter is 45 mm, outer diameter is 105 mm) and spread out, then the Ti plate was placed above the $Al_2O_3$ powder followed by another 15 g $Al_2O_3$ powder spread out. After that, the sintering process was performed in vacuum hot pressing device (VVPgr-80-2300, China) with heating rates of 10 °C/min. The samples were held at temperature of 1150 °C, 1250 °C, 1350 °C, 1400 °C, 1420 °C and 1450 °C for different holding time (from 1.5 to 2.5 h) under pressure of 30 MPa. The schematic diagrams of the experimental device and Ti/$Al_2O_3$ composites are shown in Fig. 1. Lastly, the sintered composites were taken out when cooled naturally in the stove to about 100 °C.

The phase compositions of the reaction layers were characterized by X-ray diffraction (D8-ADVANCE, Germany), the microstructure and elements distribution were analyzed by scanning electron microscopy (SEM, FEI QUANTA FEG 250, United States) equipped with an energy dispersive spectroscopy (EDS) and electron probe microanalyser (EPMA, EPMA-1600, Japan).

## 3. Results and discussions

### 3.1. Interfacial evolution and phases characterization at Ti/$Al_2O_3$ interfaces

The interfacial microstructures and elemental analysis of laminated composites at the Ti/$Al_2O_3$ interfaces which were sintered at different temperatures (1150 °C, 1250 °C, 1350 °C, 1400 °C, 1420 °C and 1450 °C) for 1.5 h are shown in Fig. 2. According to EDS analysis, the bright and dark zones can be identified as Ti and $Al_2O_3$ phases, which are the base materials. It is clear that the $Al_2O_3$ phase diffuses into the pure Ti as temperature increases, at the same time, the interfacial microstructures are greatly changed. The thickness of

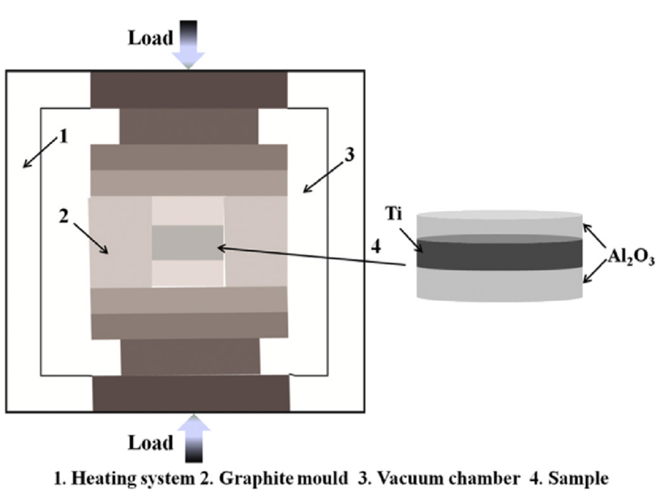


**Fig. 1.** Schematic diagrams of the experimental device and the Ti/$Al_2O_3$ composites.

reaction layers, which can be distinguished by the darker color (in the Web version) compared with the Ti phase, are significantly growing with the temperature increasing from 1150 °C to 1450 °C, suggesting that temperature plays a major role in accelerating the growth of reaction layer.

At 1150 °C, no obvious reaction layer can be found in Fig. 2(a). Combined with the results of linear scan along the yellow lines (in the Web version), it can be known that concentrations of the elements (Al, O and Ti) sharply reduce at the interfaces, implying the diffusion of the elements is very limited. But Al and O elements have obviously diffused into Ti phase, so the reaction layer has started to form at this temperature. Moreover, loose microstructure with apparent defects of Ti and $Al_2O_3$ is obtained due to the low sintering temperature.

When temperature increases, reaction layers can be clearly seen at the interfaces, suggesting that obvious interactive solid diffusion across the interface occurs due to larger atomic average kinetic energies caused by higher temperature [24,25]. As shown in Fig. 2, the thicknesses of the reaction layers have increased to about 28.6 μm, 65.3 μm, 78.2 μm, 91.7 μm and 112.2 μm at 1250 °C, 1350 °C, 1400 °C, 1420 °C and 1450 °C, respectively. Additionally, microstructures of the reaction layers become rather dense, pores have disappeared at 1420 °C and 1450 °C. However, obvious defects can be observed at Ti zones at 1450 °C, which may be bad for the mechanical properties of the composites [26,27].

According to the linear scan along the yellow lines (in the Web version) in Fig. 2, it can be known that the diffusion behavior of Ti, O and Al elements differ from each other. According to the previous report [22,28], diffusion coefficient ($D$) can be obtained from the general solution of semi-infinite solid contact diffusion equation, which is represented as

$$D = \frac{d^2}{t} \tag{1}$$

where $d$ is the thickness of the reaction layer, $t$ is the diffusion time. By calculating, diffusion coefficients of Al, O and Ti elements within the sintering temperature range are shown in Table 1. According to the results, Al element has the most powerful diffusion ability, however, there is hardly any Ti element being detected in $Al_2O_3$ layers when temperature is lower than 1420 °C. It has been suggested that Al can continually diffuse into Ti phase and its equilibrium concentration can reach 12 at.% [29,30]. This may be the dominant reason why the reaction layers form on the side of the Ti zone. O element has rather weaker diffusion ability, so little content can be detected in both reaction and Ti layers. At above 1420 °C, white Ti particles are observed in the $Al_2O_3$ zone nearby the reaction layer, but the content is very limited.

In order to assess the interfacial evolution of the reaction layers as temperature increases from 1150 °C to 1450 °C, XRD is used to investigate the phase compositions. As is pointed out in Fig. 2, reaction layers are formed nearby Ti zones, so fracture surfaces of Ti sides are detected and the results are shown in Fig. 3. When the sintering temperature is lower than 1250 °C, the combination between Ti and $Al_2O_3$ is weaker, so they can be split by outside force easily. When the temperature is higher than 1250 °C, the composites will be cut in direction perpendicular to the interface along the Ti phase. As depicted in Fig. 3(a), very limited product of diffusion reaction, such as TiAl and $Ti_3Al$, are formed when the sample was sintered at 1150 °C, which is in accord with the result in Fig. 2(a) that no obvious reaction layer can be observed. At the same time, there is no distinct difference between the intensity of the TiAl and $Ti_3Al$ peaks. As the temperature is increased to 1250 °C, sharp diffraction peaks of TiAl and $Ti_3Al$ appear, implying obvious reaction has been done by further elements diffusion, so obvious