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# Interfacial behaviors of magnesia partially stabilized zirconia with nickel-based superalloy

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ABSTRACT

Interfacial behaviors of magnesia partially stabilized zirconia (MgO-PSZ) ceramic by nickel-based superalloy were investigated. And the effect of zirconia reduction on interfacial behaviors was considered. The contact angle became stable at 1390 °C and was larger than 90° during the continuous temperature rise, and the equilibrium contact angle was 92°. The interfacial reaction between MgO-PSZ ceramic and nickel-based superalloy occurred at high temperature. The $ZrO_2$ was reduced to suboxide ($ZrO_{2-x}$), and the loss of oxygen led to the formation of $Al_2O_3$. The interfacial reaction was influenced by the reduction of $ZrO_2$. The destabilization of MgO-PSZ ceramic was caused by the presence of $Al_2O_3$.



## 1. Introduction

Nickel-based superalloy has been widely used in aircraft and power-generation turbines for their excellent mechanical properties [1]. Vacuum induction melting (VIM) is the principal melting process for the production of nickel-based superalloy. However, this process is the only vacuum melting method that uses refractory crucible [2]. The harmful trace elements (e.g., O, C, N) from the ceramic have a tendency to enter into nickel-based superalloy during melting and cause the deterioration of mechanical properties [3]. Compared with traditional refractories such as magnesia and alumina, zirconia based ceramics show better chemical stability [4]. Previously, Virieux et al. [5] reported that there was non-wetting between nickel-based superalloy and zirconia materials. Kanetkar et al. [6] and Valenza et al. [7] observed the phenomenon that oxides were formed on the surface of zirconia substrate after sessile drop experiment. However, the reason for the formation of oxides was not clear. Besides, zirconia may lose oxygen with the formation of sub-oxide ($ZrO_{2-x}$) in a vacuum or reducing atmosphere [8]. Hence, the interfacial reaction of zirconia materials by nickel-based superalloy may be influenced by the reduction of $ZrO_2$. Recently MgO-PSZ ceramic becomes one of the most promising refractory in melting nickel-based superalloy for their excellent chemical and mechanical properties [9]. However, it can only be realized unless understanding high-temperature interfacial behavior of molten nickel-based superalloy on MgO-PSZ ceramic. In this work, interfacial behaviors of magnesia partially stabilized zirconia (MgO-PSZ) ceramic by nickel-based superalloy were investigated. And the effect of zirconia reduction on interfacial behaviors was considered.

## 2. Experimental procedure

The compositions of nickel-based superalloy used in this work were (wt%) 0.11 C, 0.04Zr, 2.60Ti, 4.28Mo, 4.50Co, 4.81W, 5.90Al, 11.84Cr and 65.92Ni. Commercial magnesia partially stabilized zirconia (MgO-PSZ) was used as the substrate (20 mm diameter × 2 mm thickness).

The sessile drop experiments were conducted in a furnace by placing a nickel-based superalloy (4 mm thickness × 4 mm width × 4 mm length) cubic on the surface of MgO-PSZ substrate. The specimens were heated to1450 °C at a rate of 5 °C/min under a vacuum of 10 Pa. A digital camera was used to record images of contact angle of the drop with an accuracy of ±3°.

The interfacial region between nickel-based superalloy and MgO-PSZ substrate was examined by X-ray diffraction (XRD), scanning electron microscopy (SEM). The valence state of Zr and O was investigated by X-ray photoelectron spectra (XPS). Peak fitting of the XPS spectra was performed with XPS Peak software.

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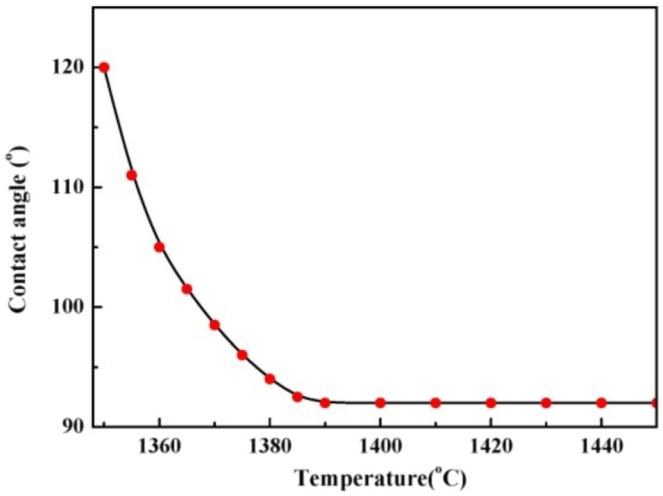


**Fig. 1.** Variation of contact angle between nickel-based superalloy and MgO-PSZ substrate with temperature.

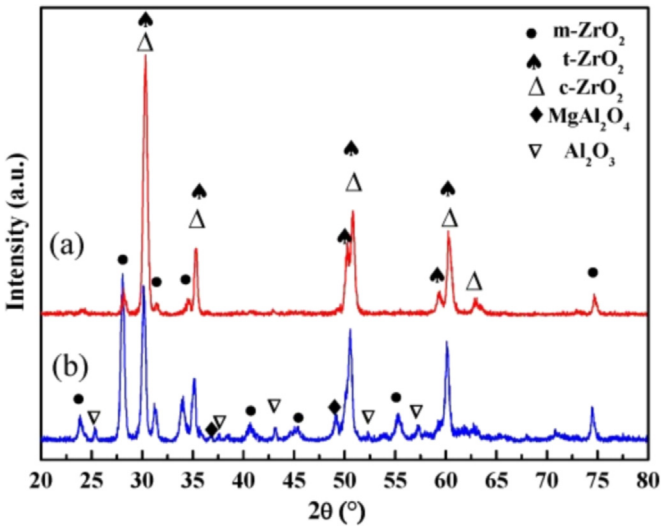


**Fig. 2.** X-ray diffraction patterns of (a) original MgO-PSZ substrate and (b) interface of MgO-PSZ ceramic corroded by nickel-based superalloy.

## 3. Results and discussions

### 3.1. Contact angle

Fig. 1 shows the changes in contact angle of the drop during the continuous temperature rise. With increasing of the experiment temperature, the contact angle of molten nickel-based superalloy on MgO-PSZ substrate decreased rapidly, and finally became stable at 1390 °C and was larger than 90°. The equilibrium contact angle was 92°.

### 3.2. Interfacial reaction of MgO-PSZ substrate by nickel-based superalloy

The strength of binding between the phases can be assessed by the work of adhesion $W_\alpha$ [10]. Because of small value of $W_\alpha$, the drop of nickel-based superalloy can be easily removed from MgO-PSZ substrate after cooling. Fig. 2 shows the XRD patterns of MgO-PSZ substrate before and after sessile drop experiment. For the original MgO-PSZ substrate, t-$ZrO_2$ and c-$ZrO_2$ phases are the main constituent with small amounts of m-$ZrO_2$ (Fig. 2(a)). The $(101)_t$ and $(111)_c$ peaks overlap each other because they have nearly the same lattice parameters for the tetragonal and cubic phases [11]. After sessile drop experiment, new phases of $Al_2O_3$ and $MgAl_2O_4$ in the substrate were observed (Fig. 2(b)). It was indicated that interfacial reaction between MgO-PSZ substrate and nickel-based superalloy occurred. Meanwhile, it also can be seen that the diffraction peaks intensity of m-$ZrO_2$ phase increased but that of t-$ZrO_2$ and c-$ZrO_2$ phases decreased. It means that phase transformation from t-$ZrO_2$ to m-$ZrO_2$ occurred. In view of the tremendous technological applications, the final material failure was caused by the phase transformation.

Aluminum content is as high as 5.9% in the nickel-based superalloy. The vapor pressure of the aluminum element was a function of temperature [12]. The saturated vapor pressure of aluminum was 100 Pa at 1450 °C. The aluminum evaporation was promoted by high vacuum environment in our experiment condition. The SEM micrographs of MgO-PSZ substrate before and after sessile drop experiment are shown in Fig. 3. For the original substrate, it shows a microstructure with clear grain boundaries (Fig. 3(b)). After sessile drop experiment, the whole surface of MgO-PSZ substrate was covered by the network structure (Fig. 3 (c) and (d)). Hence, the existence of aluminum was caused by the aluminum evaporation from nickel-based superalloy.

To investigate the effect of zirconia reduction on interfacial behaviors, the substrate before and after sessile drop experiment was studied by XPS, as illustrated in Fig. 4. Fig. 4(A) shows the XPS spectra in the O 1s region. Peak-fitting was adopted for the spectra. For the original substrate, two distinctive peaks situated at bind energies of 529.7 and 531.4 eV were observed. The results are in good with the O 1 s binding energies of pure MgO [13] and $ZrO_2$ [14], respectively. After sessile drop experiment, the O 1 s binding energies of Mg-O and Zr-O in the substrate remained almost unchanged, but a new peak with higher binding energy appeared. Because the O 1s binding energy of Al-O is about at 532.7 eV [15], the peak is attributed to the appearance of $Al_2O_3$. This phenomenon was consistent with XRD result.

Fig. 4(B) shows the XPS spectra in the Zr 3d region. For the original substrate, the binding energies of Zr $3d_{5/2}$ and Zr $3d_{3/2}$ are 182 eV and 184.38 eV, respectively, which correspond to zirconium in the $Zr^{4+}$ state [16]. After sessile drop experiment, the binding energies of Zr $3d_{5/2}$ and Zr $3d_{3/2}$ of the substrate slightly reduced and the peak of suboxide ($ZrO_{2-x}$) with a lower binding energy was observed. The reducing of binding energies of Zr $3d_{5/2}$ and Zr $3d_{3/2}$ was caused by phase transformation from t-$ZrO_2$ to m-$ZrO_2$ [17], which was in good agreement with XRD analysis. The binding energy of Zr $3d_{5/2}$ of suboxide was about 3 eV lower than that of $Zr^{4+}$ $3d_{5/2}$. Morant [18] proved that the four oxidation states of zirconium are equally spaced in energy by a value of 1.06 eV. The binding energy of $Zr^{2+}$ $3d_{5/2}$ is about 2.0 eV lower than that of $Zr^{4+}$ $3d_{5/2}$ [19]. Therefore, in our case the valence state of Zr about suboxide ($ZrO_{2-x}$) is near +1. The reaction occurred in the substrate:

$$ZrO_2 \rightarrow ZrO_{2-X} + [O] \quad (1)$$

Consequently, the $ZrO_2$ was reduced to suboxide ($ZrO_{2-x}$). The $Al_2O_3$ was formed because of the reaction between the aluminum from nickel-based superalloy and the oxygen from substrate. Interfacial reaction of MgO-PSZ substrates by nickel-based superalloy was influenced by the reduction of $ZrO_2$. Subsequently, the $Al_2O_3$ reacted with MgO from MgO-PSZ substrate, leading to the formation of $MgAl_2O_4$. Hence, the destabilization of MgO-PSZ ceramic was caused by the presence of $Al_2O_3$. Further, the t→m phase transformation occurred, consistent with the XRD result. Simultaneously, because of the change of contact angle (Fig. 1), the wetting was affected by interfacial reaction of MgO-PSZ ceramic by nickel-based superalloy.