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Sintering mechanisms of Yttria with different additives

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Abstract

The sintering behaviour of conventional yttria powder was investigated, with emphasis on the effect of sintering additives such as B_2O_3, YF_3, Al_2O_3, ZrO_2, and TiO_2, etc. at sintering temperatures from 1000 °C to 1600 °C. Powder shrinkage behaviour was analysed using a dilatometer. The powder sintering mechanisms were identified at different temperatures using powder isothermal shrinkage curves. This analysis showed that the sintering additives B_2O_3 and YF_3 could improve yttria sintering by changing the diffusion/sintering mechanisms at certain temperatures, while sintering additives TiO_2, Al_2O_3 and ZrO_2 appeared to retard the powder densification at temperatures around 1000 °C and are more suitable when used at temperatures in excess of 1300 °C. The powder with La_2O_3 added had the slowest densification rate throughout the test temperatures in this experiment and was also found to be more suitable when used at temperatures higher than 1550 °C.

Keywords: A. Sintering; C. Thermal expansion; D. Y_2O_3; E. Structural application

1. Introduction

Yttrium oxide (Y_2O_3) has excellent inertness, refractory character, high melting temperature (2410 °C) and optical properties, and has now become a very attractive material for industrial applications [1,2]. Because of its superior inertness to chemical attack from molten Ti alloys during investment casting, yttria has been widely used as a face-coat material in the investment casting of titanium aluminide alloys for a number of years [3–5]. As a rare earth material, yttria requires a very high sintering temperature, in excess of 1700 °C, in order to achieve a high density [6]. However, high sintering temperatures ($\geq$1400 °C) for an yttria face-coat will add to the production cost of the moulds. But reducing the sintering temperature will lead to poorly-bonded yttria particles on the finished mould surface. These loose particles will be easily pulled out during casting and will remain in the metal after solidification, becoming inclusions [7]. Meanwhile, the uneven mould surface will also affect the surface finish of the final components.

In order to enhance the sintering properties of yttria face-coats at relatively low temperatures, additives such as ZrO_2 [8], ThO_2 [9], Al_2O_3 [10,11], La_2O_3 [12], CaO [13], MgO [13], and B_2O_3 [14] were studied. These sintering additives can enhance yttria sintering by changing sintering mechanisms. Some of them can react with yttria to form new transient liquid phases at comparatively low temperatures and enhance yttria powder sintering. In this work, new sintering additive compounds such as YF_3, and TiO_2 are also investigated.

Powder sintering behaviour has been investigated by many researchers [15–20,22], and several methods have been published to identify the sintering mechanisms after introducing different sintering additives. Johnson and Cutler [19], and Matsui [18] reported that the sintering mechanical numerical constant '*n*' can be predicted by studying the isothermal shrinkage behaviour of the compacts. Wang [21] applied these methods to predict the sintering mechanisms and activation energy of sintering pure yttria, and the results show that by sintering at around 1400 °C, yttria suffers grain-boundary diffusion with activation energy of around 410 kJ/mol. Sintering additions of Mg and Nb can influence the yttria sintering rate by changing the activation energy.

The current research was carried out to study the shrinkage behaviour of yttria after adding sintering additives

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including B_2O_3, YF_3, TiO_2, Al_2O_3, and La_2O_3 to enhance powder sintering at temperatures of around 1000 to 1600 °C. In this study, the sintering mechanisms (n) of each sintering additive were analysed based on isothermal heating dilatometer methods. Powder particle morphologies at different sintering temperatures were observed using scanning electron microscopy (SEM), and the powder compositions at different temperatures were identified by X-ray diffraction (XRD).

2. Materials and methods

Yttria powder with a mean particle size of 14 μm (−200 mesh, Treibacher Industrie AG) was used as the starting powder and blended with the sintering additives listed in Table 1. Powders with additives were first mixed in deionised water overnight and dried. About 3 g of dried powder was weighed and pressed to a cylindrical compact (13 mm in diameter) under a constant pressure of 26 MPa using an Instron™ mechanical testing machine.

The particle size distributions of the various fillers were analysed using laser powder particle size measuring equipment (Coulter LS230), and the microstructure evolution of the powder compact was analysed using a scanning electron microscope after sintering at four different temperatures, 1000, 1200, 1400 and 1600 °C for 1 h in air. The anisotropic shrinkage of the compacts during heating was measured as a function of time using a dilatometer (NETZSCH DIL 402E). The compacts were heated at a rate of 20 °C/min to the different isothermal temperatures, namely 1000 °C, 1200 °C, 1300 °C and 1550 °C, held at temperature for 1 h and then cooled down at the same rate to room temperature in air. The phase transformations during the heating and dwelling process at each temperature range were identified using X-Ray diffraction with a beam incident angle between 20° and 100°.

3. Theory and calculation

3.1. Isothermal shrinkage

The sintering-rate equation for isothermal shrinkage at the initial sintering stage is given by Eq. (1) [19]:

$$\left(\frac{\Delta L}{L_0}\right) = \left(\frac{K\gamma\Omega D}{kTa^p}\right)^n t^n \quad (1)$$

where:

$\Delta L/L_0$ = fraction shrinkage, L_0 is the sample original length, and ΔL is the length change.
T = absolute temperature,
K = numerical constant,
D = self-diffusion coefficient,
γ = surface energy,
t = time,
k = Boltzmann's constant,
a = the spherical particle radius
n, p = sintering indices, themselves dependent on the diffusion mechanisms [22] and
Ω = atomic volume.

On taking logarithms, Eq. (2) is obtained:

$$\log\left(\frac{\Delta L}{L_0}\right) = n\log\left(\frac{K\gamma\Omega D}{kTa^p}\right) + n\log t \quad (2)$$

As, for certain sintering mechanisms and temperatures, $n\log(K\Omega\gamma D/kTa^p)$ equals to a constant A, the Eq. (2) can be written as: $\log(\Delta L/L_0) = A + n\log(t)$. Plotting $\log(\Delta L/L_0)$ against log(t), the mechanism specific constant n can be obtained. Johnson and Cutler [19,23] reported that the difficulty of measurement of the powder compact dimension change of isothermal sintering due to experimental errors caused by powder pre-sintering before reaching the set isothermal holding temperature. In order to minimise the pre-sintered problems of powder during heating, Matsui [18] applied a corrective factor δL in Eq. (2) with the correction time t_0 to analyse the sintering properties of ZrO_2 powder with small amounts of Y_2O_3 additives. Based on Matsui's research, a new method was developed and used in this research to predict powder sintering mechanisms at the early stage of sintering. This new method used a corrected length $\Delta L_{(cor)}$ to replace ΔL and a corrected isothermal sintering time $(t - t_o)$ to replace t in Eq. (2). The definition of each factor is illustrated in Fig. 1.

4. Results and discussion

4.1. Raw powder particle-size distribution and microstructure

The powder particle-size distribution before test is given in Fig. 2(a). It can be seen that the sintering additives had a

Table 1
sintering powder compositions.

Sample ID	Additives	wt% of pure element	mol% of sintering additives
Sample Y	As received pure yttria −200 mesh powder		
Sample YB	B_2O_3	2.0	17.4
Sample YAZ	Al_2O_3, ZrO_2	0.5 wt%Al_2O_3–0.5 wt%ZrO_2 commercially available powder	
Sample YT	TiO_2	2.0	8.56
Sample YF	YF_3	2.0	7.43
Sample YLa	La_2O_3	2.0	1.57