# Synthesis and Characterization of Bulk Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> Ceramic

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Polycrystalline Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> was fabricated by an *in situ* reactive hot-pressing process using zirconium (zirconium hydrides), aluminum, and graphite as starting materials. The investigation on reaction path revealed that the liquid Al played an important role in triggering the formation of ternary zirconium aluminum carbides. The mechanical properties of Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> at room temperature were measured (Vickers hardness of 10.1 GPa, Young's modulus of 362 GPa, flexural strength of 405 MPa, and fracture toughness of 4.2 MPa  $\cdot$  m<sup>1/2</sup>). The electrical resistivity and thermal expansion coefficient were determined as 1.10  $\mu\Omega \cdot m$  and 8.1  $\times 10^{-6}$  K<sup>-1</sup>, respectively.

#### I. Introduction

THE ZrC is an important high-temperature structural material with good mechanical properties, such as high hardness, high stiffness, and retained strength at high temperatures.<sup>1,2</sup> However, its poor high-temperature chemical stability in air and intrinsic low toughness have restricted its application.<sup>1,2</sup> Recent developments in synthesizing ternary aluminum carbides (TACs), such as Ti<sub>3</sub>AlC<sub>2</sub> and Ti<sub>2</sub>AlC, by incorporating Al into binary carbides, highlight a possible way of solving these problems. Compared with binary carbides, these TACs possess a unique combination of properties, including ready machinability, damage tolerance at room temperature, and resistance to thermal shock, and high-temperature oxidation.<sup>3,4</sup>

 $Zr_2Al_3C_4$ , a novel TAC, has been less investigated due to the difficulty in synthesizing a single-phase and dense bulk sample. Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> was first synthesized by Schuster and Nowotny via arc melting of a mixture of Zr or ZrC, Al, C powders at 1000°C.<sup>5</sup> It was found that  $Zr_2Al_3C_4$  readily form equilibria with  $Zr_3Al_3C_5$ , ZrC, and Zr-Al intermetallics. Recently, bulk Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> was fabricated by a two-step process: firstly Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> powders were synthesized by a solid-state reaction of ZrC, Al, C in a vacuum furnace at 1600°C for 1 h,6 and secondly Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> bulk materials were sintered by a pulse-electric current sintering technique at 2000°C under a pressure of 40 MPa in vacuum.7 The as-synthesized bulk samples have a density of 4.58 g/cm<sup>3</sup>, which is about 95% of the theoretical (4.80 g/cm<sup>3</sup>) one. Essentially, *in situ* reactive synthesis of a highly pure and dense  $Zr_2Al_3C_4$  has been a problem to date, which prevents further investigation on the properties of bulk  $Zr_2Al_3C_4$ .

In this paper, we present an *in situ* method to synthesize bulk  $Zr_2Al_3C_4$  using zirconium, aluminum, and graphite as starting

materials. Moreover, the mechanical and physical properties were also investigated.

## **II. Experimental Procedure**

Commercially available zirconium (zirconium hydrides, including ZrH and ZrH<sub>1.66</sub>, denoted as  $ZrH_x$ ) powders (99%, -400 mesh, the content of hydrogen is < 1 wt%, from the Institute of Non-Ferrous Metals, Beijing, China), aluminum powders (99%, -200 mesh, from the Institute of Non-Ferrous Metals), and graphite powders (99%, -200 mesh, from China's No. 4 Grinding Wheel Inc., Shandong, China) were used as starting materials. The molar ratio of Zr:Al:C was 2:3.1:3.9, which is the optimized composition in this work to synthesize single-phase Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub>. Excess Al powders were added to compensate for the loss of Al during the heating process. Deficient C in the starting materials is properly related to intrinsic carbon vacancy in Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub>. The powders of Zr, ZrH<sub>x</sub>, Al, and graphite were mixed and ball-milled for 24 h in absolute ethanol. Afterwards, the milled powders were dried and hot-pressed under 30 MPa for 1 h at 1900°C in a flowing Ar atmosphere and then annealed at 1600°C in low vacuum ( $\approx 10^{-2}$  Pa) for 0.5 h.

The density of sintered samples was determined by the Archimedes method. Phase identification was conducted via a step-scanning X-ray diffractometer (XRD) with CuK $\alpha$  radiation (Rigaku D/Max–2400, Tokyo, Japan). Quantitative phase analysis was performed by the Rietveld method (a DBWS code in Cerius<sup>2</sup> 4.2 computational program for materials research, Molecular Simulation Inc., San Diego, CA).<sup>8</sup>

The microstructures of the samples were studied by a SUPRA 35 scanning electron microscope (SEM) (LEO, Oberkochen, Germany). The samples were etched for 1 h in a 1:1:5 (by volume) solution of HF, HNO<sub>3</sub>, and H<sub>2</sub>O before SEM observation.

The dynamic Young's modulus, shear modulus, and Poisson's ratio of  $Zr_2Al_3C_4$  were evaluated by the impulse excitation technique.<sup>9</sup> The flexural strength was determined by three-point bending tests using samples with dimensions of 3 mm × 4 mm × 40 mm.

The Vickers microhardness was measured at loads of 10 and 50 N, respectively. The fracture toughness was determined on the basis of the following equation<sup>10</sup>:

$$K_c = 0.4636(P/a^{3/2})(E/H)^{2/5}(10^F)$$
(1)

where  $F = -1.59-0.34B-2.02B^2+11.23B^3-24.97B^4+16.32B^5$ and  $B = \log (c/a)$ . *P* is the peak load (50 N in this work), *a* is the indentation half-diagonal, *c* is the crack length, *E* is the Young's modulus, and *H* is the hardness.

The electrical resistivity at room temperature was measured by the standard four-probe technique using samples with dimensions of 1 mm  $\times$  1 mm  $\times$  10 mm. The average thermal expansion coefficient (TEC) at 100°–1000°C was measured using a Setsys–24 thermal mechanical analyzer (TMA) (Setaram, Caluire, France) with a heating rate of 5°C/min under flowing Ar.

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## III. Results and Discussion

Figure 1(a) shows the XRD patterns of phase evolution from 1100° to 1700°C during the *in situ* synthesis of Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub>. At 1100°C, the main phases are ZrC, unreacted graphite, and Zr-Al intermetallics, including ZrAl<sub>2</sub>, Zr<sub>2</sub>Al<sub>3</sub>, and ZrAl<sub>3</sub>. At 1135°C, a few weak peaks for ternary carbides, Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub>, and Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> were detected, and those peaks for ZrC became stronger. On the other hand, Zr<sub>2</sub>Al<sub>3</sub> disappeared, ZrAl<sub>2</sub> decreased greatly, and the major intermetallic compound became ZrAl<sub>3</sub>, indicating that Zr/Al equilibrium shifted to a higher Al content. As the temperature increased to 1200°C, Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> became the major phase while Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> did not increase in content. Furthermore, ZrC decreased gradually with increasing temperature. The peaks for ZrAl<sub>2</sub> and ZrAl<sub>3</sub> weakened and disappeared with increasing temperature, but a characteristic peak of Al with  $2\theta = 44.7^{\circ}$  was detected at 1160°C, and became a little bit stronger at 1200°C. It is not surprising to note that Al was not detected at the starting temperature for the formation of Zr-Al-C carbides because the liquid Al formed reacted rapidly with ZrAl<sub>2</sub> and graphite to



**Fig.1.** (a) Powder X-ray diffraction (XRD) patterns of the samples heated at  $1100^{\circ}$ -1700°C for 5 min using starting powders with the composition of Zr : Al : C = 3 : 3.1 : 3.9; (b) Powder XRD pattern of the as-synthesized Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub>.

form  $ZrAl_3$  and  $Al_4C_3$ , respectively, leading to the augmentation of  $ZrAl_3$  and  $Al_4C_3$ .

$$2ZrAl_2(s) + C(s) = ZrC(s) + ZrAl_3(s) + Al(l)$$
(2)

$$Al(l) + ZrAl_2(s) = ZrAl_3(s)$$
(3)

$$4\mathrm{Al}(\mathrm{l}) + 3\mathrm{C}(\mathrm{s}) = \mathrm{Al}_4\mathrm{C}_3(\mathrm{s}) \tag{4}$$

When ZrAl<sub>2</sub> was depleted, ZrAl<sub>3</sub> began to react with graphite to produce ZrC and liquid Al.

$$ZrAl_3(s) + C(s) = ZrC(s) + 3Al(l)$$
(5)

Then liquid Al reacted quickly with ZrC and graphite to form ternary carbides,  $Zr_3Al_3C_5$  and  $Zr_2Al_3C_4$ .

$$3Al(l) + 3ZrC(s) + 2C(s) = Zr_3Al_3C_5(s)$$
 (6)

$$3Al(l) + 2ZrC(s) + 2C(s) = Zr_2Al_3C_4(s)$$
 (7)

It is followed that liquid Al triggered the formation of the ternary Zr–Al–C carbides, which is consistent with the results of Lin *et al.*<sup>11</sup> They confirmed by TEM that Al could efficiently reduce the twin boundary energy of ZrC and consequently lead to the formation of ternary Zr–Al–C carbides. Thus, excess Al was of assistance to synthesize Zr–Al–C carbides, which was supported by previous works.<sup>5,6,12,13</sup>

 $Zr_2Al_3C_4$  combined with ZrC to produce  $Zr_3Al_3C_5$ , which was responsible for the augmentation of  $Zr_3Al_3C_5$  with increasing temperature while there was no obvious change of  $Zr_2Al_3C_4$  in content when ZrC was present.

$$Zr_2Al_3C_4(s) + ZrC(s) = Zr_3Al_3C_5(s)$$
(8)

As the temperature increased to  $1700^{\circ}$ C, minor amounts of Al<sub>4</sub>O<sub>4</sub>C were detected. Al<sub>4</sub>O<sub>4</sub>C can readily form from the reduction of Al<sub>2</sub>O<sub>3</sub> by carbon and/or from the reaction of Al<sub>4</sub>C<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> at high temperatures, <sup>14</sup> where Al<sub>2</sub>O<sub>3</sub> originated from the oxidation of fractional Al and/or Al-containing compounds by the trace amount of O<sub>2</sub> in argon.

$$2Al_2O_3(s) + 3C(s) = Al_4O_4C(s) + 2CO(g)$$
(9)

$$4Al_2O_3(s) + Al_4C_3(s) = 3Al_4O_4C(s)$$
(10)

The possible reaction leading to the conversion of  $Al_4O_4C$ , graphite, and  $Zr_3Al_3C_5$  into  $Zr_2Al_3C_4$  is shown below:

$$\begin{split} &8Zr_{3}Al_{3}C_{5}(s) + 3Al_{4}O_{4}C(s) + 17C(s) \\ &= 12Zr_{2}Al_{3}C_{4}(s) + 12CO(g) \end{split} \tag{11}$$

The above reaction should be affected by the partial pressure of the generated CO gas. It is followed that the formation of  $Zr_2Al_3C_4$  should become easier when the sample was heated in vacuum. When the sample was sintered at 1900°C for 1 h and annealed in vacuum at 1600°C for 30 min,  $Al_4O_4C$  and graphite disappeared and most of  $Zr_3Al_3C_5$  changed into  $Zr_2Al_3C_4$ (Fig. 1(b)).

To confirm the content of the  $Zr_2Al_3C_4$  phase, Rietveld XRD analysis was conducted. The crystal structure models of  $Zr_2Al_3C_4$  and  $Zr_3Al_3C_5$  used for refinement can be found in Lin et al.<sup>11</sup> The symmetry of both carbides was recently determined by selected-area electron diffraction and convergent beam electron diffraction. Both carbides crystallize in *P*6<sub>3</sub>/*mmc* symmetry with two formulae per unit cell. The lattice parameters are a = 3.3 Å and c = 27.6 Å for  $Zr_3Al_3C_5$ , and a = 3.3 Å and c = 22.4 Å for  $Zr_2Al_3C_4$ . The phase composition determined by Rietveld method was 97.1 wt%  $Zr_2Al_3C_4$  and 2.9 wt%  $Zr_3Al_3C_5$  and the reliability indices for a final result were  $\tilde{R}P = 8.37\%$ , and  $\tilde{R}WP = 11.62\%$ .



Fig. 2. Scanning electron microscopy of polished and etched surface of  $Zr_2Al_3C_4$ .

The as-synthesized Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> has an anisotropic microstructure consisting of elongated and rod-like and/or plate-like grains (Fig. 2). The estimated aspect ratio of the grains is about 6 and the average grain size is approximately 8.5 µm in length and 1.4 µm in width.

The measured properties of Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> are listed in the first column of Table I. For comparison, those for Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> synthesized by liquid-phase sintering using Y2O3 and Si as additives at  $1750^{\circ}$ C<sup>15</sup> are also included. The Young's (E) and shear (G) moduli for the Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> sample with 98.6% TD at room temperature are 362 and 152 GPa, respectively. The Poisson's ratio (v) is 0.19, which is the same as that of  $Zr_3Al_3C_5$ . The calculated bulk modulus (B) according to the relationship of B = E/[3(1-2v)] is 195 GPa. The Young's modulus, shear modulus, and bulk modulus of Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> at room temperature are close to those of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub>, indicating that Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> possesses stiffness comparable with Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub>. The Vickers hardnesses of Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> at loads of 10 and 50 N are about 10.5 and 10.1 GPa, respectively, which are a little bit lower than those of  $Zr_3Al_3C_5$ .

Given the crystal structures of  $Zr_3Al_3C_5$  and  $Zr_2Al_3C_4$ , <sup>11,12</sup> the relatively lower stiffness and hardness of Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> are not too surprising. The structural difference between Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> and  $Zr_3Al_3C_5$  is the thickness of  $(ZrC)_m$  units between the  $Al_3C_2$ units, where m = 2 and 3, respectively. Compared with ZrC, Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> has a relatively lower stiffness and hardness.<sup>15</sup> Accordingly, Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> can be regarded as Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> losing a (ZrC) unit, and it should be weaker than Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> in stiffness and hardness.

The fracture toughness determined by the indentation method is  $4.20 \pm 0.56$  MPa  $\cdot$  m<sup>1/2</sup>, which is close to that of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub>. The relatively high toughness is related to its elongated morphology of grains. The measured flexural strength of Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> is  $405\pm41$  MPa at ambient temperature, which is about 83% of that for Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub>.

The average TEC of  $Zr_2Al_3C_4$  (8.1 × 10<sup>-6</sup> K<sup>-1</sup>) is quite close to that of  $Zr_3Al_3C_5$  (7.7 × 10<sup>-6</sup> K<sup>-1</sup>), which is reasonable according to their stiffness. Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> exhibits metal-like behavior with an electrical resistivity of 1.10  $\mu\Omega \cdot m$  and can be machined by electro-discharge machining.

## IV. Conclusions

In this work, polycrystalline Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> ceramic was fabricated via hot-pressing zirconium (zirconium hydrides), aluminum, and graphite powders. Liquid Al formed during the synthesis process and triggered the formation of ternary zirconium aluminum carbides. In addition, the process for the formation of  $Zr_2Al_3C_4$ could be achieved readily when the sample was annealed in vacuum.

Table I. Comparison of Some Properties of Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub> and Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub>

$Zr_2Al_3C_4$	ZraAlaC <sup>15</sup>
	213/11305
4.80	5.28
99	95
362	374
152	157
0.19	0.19
195	202
10.5	13.1
10.1	12.5
$4.20 \pm 0.52$	$4.68 \pm 0.74$
$405 \pm 41$	$488 \pm 43$
1.10	1.45
8.1	7.7
	$\begin{array}{r} 4.80\\ 99\\ 362\\ 152\\ 0.19\\ 195\\ 10.5\\ 10.1\\ 4.20\pm0.52\\ 405\pm41\\ 1.10\\ 8.1\end{array}$

The as-synthesized sample has an anisotropic microstructure, which is composed of fine, elongated, and rod-like/plate-like grains. The properties of Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub>, including hardness (10.1 GPa), stiffness (Young's modulus of 362 GPa, shear modulus of 152 GPa), fracture toughness  $(4.20 \pm 0.52 \text{ MPa} \cdot \text{m}^{1/2})$ , strength (flexural strength of  $405 \pm 41$  MPa), electrical resistivity (1.10  $\mu\Omega \cdot m$ ), and TEC (8.1 × 10<sup>-6</sup> K<sup>-1</sup>), are close to those of  $Zr_3Al_3C_5$  due to their similar crystal structures.  $Zr_2Al_3C_4$  is a novel ternary carbide and its processing-microstructureproperty relationships should be systematically investigated in the near future.

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