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L. F. He et al.: Synthesis and oxidation of  $Zr_3Al_3C_5$  powders

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# Synthesis and oxidation of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> powders

Predominantly single phase Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> powders were synthesized in an Ar atmosphere using Zr-Al intermetallics and graphite as starting materials. The reaction path of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> synthesis was discussed based on differential scanning calorimetry and X-ray diffraction results. Lattice parameters of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> determined using the Rietveld method are a = 3.347 Å and c = 27.642 Å. In addition, the oxidation of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> powders was tested by using thermogravimetry-differential scanning calorimetry. The starting and complete oxidation temperatures are 400°C and 1200 °C, respectively. These temperatures are much higher than those for ZrC, suggesting that Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> has better oxidation resistance than ZrC. On the other hand, the oxidation degree of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub>, defined for the complete carbideoxide transformation, overshot 100% during oxidation. This overshooting is attributed to the formation of amorphous carbon. The phase evolution during the oxidation of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> was also investigated.

Keywords: Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub>; ZrC; Oxidation; XRD; DSC

#### 1. Introduction

Transition metal carbides (TMCs), such as TiC, ZrC, HfC, and NbC, display a unique combination of properties, including extremely high melting point and hardness, as well as excellent thermal and electrical conductivities and chemical stability. These merits make TMCs suitable as bulk and thin film materials or composite reinforcements in high temperature applications [1-4]. However, poor oxidation resistance inhibits their extensive applications at high temperatures [5-10]. An effective way to solve this problem is to add Al into these binary carbides to form ternary aluminum carbides. Successful examples can be found in Ti<sub>3</sub>AlC<sub>2</sub>, Ti<sub>2</sub>AlC and Cr<sub>2</sub>AlC, which are members of a family of ternary carbides with the common chemical formula  $M_{n+1}AC_n$  (where M is an early transition metal, and A is an A-group element), and have been extensively studied in the past few years [11–17]. The crystal structure of these MAC phases can be described as nanoscale blocks of nonstoichiometric edge-shared M<sub>6</sub>C octahedtra being interleaved by a two-dimensional close-packed layer of Al. Due to the weak cohesion of Al atomic planes with neighboring nonstoichiometric M<sub>6</sub>C blocks, a protective  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> scale can be readily formed during oxidation of these MAC phases [11, 13, 17].

Quite recently, Wang et al. [18] predicted by first-principles calculations that  $Zr_3Al_3C_5$  might possess mechanical properties comparable to ZrC with improved high temperature oxidation resistance. Figure 1 shows the crystal structure of  $Zr_3Al_3C_5$  [19]. This carbide can be described as non-stoichiometric  $ZrC_x$  blocks being interleaved by the planar close-packed Al and C atoms. The crystal structure of  $Zr_3Al_3C_5$  is similar to that of the MAC phase. In addition, the cohesion between Al-C units and  $ZrC_x$  blocks is quite weak [18]. Thus, it is expected that the Al in the Al-C unit could be easily oxidized to form protective  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> scale at high temperatures and consequently enhances the oxidation resistance of  $Zr_3Al_3C_5$ .

Only a few experimental studies on  $Zr_3Al_3C_5$  synthesis have been carried out and the oxidation of  $Zr_3Al_3C_5$  has not been reported to date. Michalenko et al. [20] discovered  $Zr_3Al_3C_5$  (previously reported with the chemical formula of  $ZrAlC_{2-x}$ ) and characterized its crystal structure. Hashimoto et al. [21] fabricated a composite consisting of Al,  $ZrAl_3$ , ZrC and  $Zr_3Al_3C_5$ , which showed a high oxidation

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resistance in air up to  $1000 \,^{\circ}$ C. Gesing et al. [19] isolated Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> from a sample prepared by the reaction of ZrC with an excess of Al in argon for 2 days at 1500  $^{\circ}$ C. Lately, bulk Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> was prepared by a two-step method, namely the synthesis of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> powders in a vacuum furnace at 1600  $^{\circ}$ C, followed by a pulse electric current sintering (PECS) at 2000  $^{\circ}$ C under a pressure of 40 MPa in vacuum [22, 23]. The initial materials in this work were Al, ZrC and amorphous carbon.

For practical purposes, synthesis of  $Zr_3Al_3C_5$  powders enables the development of bulk single phase  $Zr_3Al_3C_5$  as well as  $Zr_3Al_3C_5$ -based composite materials. In the present work, we attempted to synthesize  $Zr_3Al_3C_5$  powders in an Ar atmosphere using Zr-Al alloy and graphite as starting materials. The reaction path was investigated to understand the formation mechanism and to optimize the processing parameters of  $Zr_3Al_3C_5$ . In addition, the oxidation behavior of  $Zr_3Al_3C_5$  was studied and compared with that of ZrC.

#### 2. Experimental

2.1. Preparation of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub>

Zr–Al intermetallic compounds (including Zr<sub>3</sub>Al<sub>2</sub>, Zr<sub>5</sub>Al<sub>3</sub>, ZrAl<sub>3</sub>, and ZrAl<sub>2</sub>, 95% pure, –400 mesh), with minor amounts (4%) of ZrC, and graphite (99% pure, –200 mesh) were selected as starting materials. These powders were weighted with different compositions and ball-milled using stainless steel balls coated with a layer of polyurethane for 12 h to ensure good mixing. Afterwards the mixed powders were compacted uniaxially under a pressure of 10 MPa in a BN-coated graphite mold. The compacted mixture was heated to 1500 °C at a heating rate of 15 °C min<sup>-1</sup> and kept for 1 h in a flowing Ar atmosphere. To study the effect of composition on the purity of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub>, three groups of starting powders with the Zr:Al:C molar ratios of 3:3:5, 3:4.5:5, and 3:5:5, respectively, were chosen. The surface layer of the sample was machined off using a SiC grinding wheel to remove any contaminants from the graphite mold or from the BN, and then the sample was drilled by a high-speed steel drill bits, and ground in an agate mortar. Excess Al in the heat treated powders was removed by rinsing in 15% hydrochloric acid (HCl). The soluble impurities were removed by repeatedly washing the powders with deionized water until no trace of Cl<sup>-</sup> was detected using AgNO<sub>3</sub> solution. The suspension was vacuum-filtered under ambient conditions and then dried at 50 °C for 10 h.

Differential scanning calorimetry (DSC) experiment was conducted in a Setsys 16/18 thermal analyzer (SETARM, France) to follow the thermal history during the formation of  $Zr_3Al_3C_5$ . The powder blend with Zr:Al:C molar ratio of 3:5:5 was held in an alumina crucible and heated to 1500 °C at a heating rate of 10 °C min<sup>-1</sup> in a flowing Ar atmosphere.

Phase identification was conducted via a step-scanning X-ray diffractometer (XRD) with Cu-K<sub> $\alpha$ </sub> radiation (Rigaku D/max-2400, Japan). The lattice parameters of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> were refined using the Rietveld method (a DBWS code in Cerius<sup>2</sup> computational program for materials research, Molecular Simulation Inc., USA) [24, 25]. The microstructures of the powder samples were observed in a SUPRA 35 scanning electron microscope (SEM) (LEO, Germany) equipped with an energy-dispersive spectroscopy (EDS) system.

#### 2.2. Oxidation test

The BET specific surface area of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> powders and ZrC powders prior to oxidation testing was measured in an ASAP 2010 volumetric analyzer (Micromeritics Inc., USA). The BET specific surface area was determined by calculating the volume of absorbed nitrogen at 77 K. The oxidation of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> powders was studied through simultaneous thermogravimetry (TG)-differential scanning calorimetry (DSC) experiments. In a typical experiment, Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> powders with a total weight of approximately 30 mg were placed in an alumina crucible and heated to the desired temperature at a heating rate of  $10^{\circ}$ C min<sup>-1</sup> in flowing air, and then cooled rapidly at a cooling rate of approximately 50 °C min<sup>-1</sup>. For comparison, the oxidation of binary carbide, ZrC, powders (98% pure, -300 mesh) were also investigated under the same experimental conditions. Oxidation products were analyzed by XRD and EDS, and the morphologies of the powders were observed by SEM.

#### 3. Results and discussion

#### 3.1. Phase evolution in the formation of $Zr_3Al_3C_5$

Initially, we attempted to produce single-phase  $Zr_3Al_3C_5$ with the stoichiometry of Zr:Al:C = 3:3:5 at 1500 °C for 1 h. But ZrC was always observed as the dominant phase, as indicated by the powder XRD pattern shown in Fig. 2a. The ZrC content decreased with increasing Al content in the starting powder (Fig. 2a-c), and disappeared when the Zr:Al:C molar ratio was 3:5:5 (Fig. 2c). A predominantly single phase of  $Zr_3Al_3C_5$  with a trace of  $Zr_2Al_3C_4$  (Fig. 2d), could be readily obtained via washing the sample with HCl to get rid of the residual Al.





Fig. 2. Powder XRD patterns of samples with different Zr:Al:C molar ratios after firing at 1500 °C in Ar for 1 h. (a) 3:3:5, (b) 3:4.5:5, (c) 3:5:5, and (d) 3:5:5 washed with HCl.  $\alpha = Zr_3Al_3C_5$ ;  $\beta = Zr_2Al_3C_4$ ; C = graphite; ZC = ZrC; A = Al.

Figure 2 illustrates that it is difficult to synthesize single phase Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> with the stoichiometric Zr:Al:C molar ratio of 3:3:5. Leela-adisorn et al. [26] removed the ZrC impurity and obtained nearly single phase Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> by firing the sample with a ZrC:Al:C molar ratio of 14:21:15 in vacuum. The Al content in their starting materials also exceeded the stoichiometry of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> and excess Al evaporated in the vacuum furnace. In our previous work, we synthesized pure Ti<sub>3</sub>SiC<sub>2</sub> [27] and Ti<sub>3</sub>AlC<sub>2</sub> [12] through adding excess Si and Al, respectively, in starting materials. In this work, it was also found that the excess Al is necessary to remove ZrC impurity in the ternary system of Zr-Al-C, which confirms the results of Leela-adisorn et al. [22, 26]. It is possible that the excess Al, which is a liquid phase, covers all the particles, then prevents O<sub>2</sub> and N<sub>2</sub> from dissolving into ZrC [22, 26] and enhances the reaction between ZrC, Al and C.



Fig. 3. DSC curve of the starting powder mixture with a Zr:Al:C molar ratio of 3:5:5 at a heating rate of  $10^{\circ}$ C min<sup>-1</sup> in Ar up to  $1500^{\circ}$ C.

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Figure 3 shows a typical DSC curve obtained by heating a mixture of Zr-Al and graphite powders with a Zr:Al:C molar ratio of 3:5:5 up to 1500 °C at a heating rate of  $10^{\circ}$ C min<sup>-1</sup> in Ar atmosphere. It can be seen that there are only two exothermic peaks during the heating process. One is a broad exothermic peak in the range of 400-1100 °C, and the other is a sharp exothermic peak at around 1360 °C. To understand the phase evolution during the heating process, parallel runs were conducted in the temperature range of 500-1500°C, i.e., compacts of the mixed powder were heated from ambient temperature to a desired temperature at 10 °C min<sup>-1</sup> and held there for 10 minutes, and then rapidly cooled to room temperature. These samples were examined by XRD for phase identification, and the results are shown in Fig. 4. Only Zr-Al intermetallic compounds, unreacted graphite and ZrC were present at 500-1300 °C. In addition, the main phases of Zr-Al intermetallics changed from ZrAl\_3 and Zr\_3Al\_2 at 500  $^\circ C$  to ZrAl\_2 and  $Zr_2Al_3$  at 1300 °C. When the temperature reached 1400 °C, Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> and Al appeared and no reflections of Zr-Al intermetallics were detected.

Based on the temperature dependence of the DSC and XRD results in Fig. 3 and Fig. 4, respectively, the broad exothermic peak from DSC corresponds to the reactions among the Zr–Al intermetallic compounds, and the sharp exothermic peak at about 1360 °C originates from the reactions between ZrAl<sub>2</sub>, Zr<sub>2</sub>Al<sub>3</sub> and graphite. The sharp exothermic peak reveals that the reaction to form Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> and liquid Al was extremely rapid. In addition, part of the liquid Al should react further with ZrC and C to form Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> at temperatures above 1360 °C. Accordingly, the reaction path of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> synthesis can be described with the following equations:

$$4Zr_{3}Al_{2}(s) + 9ZrAl_{3}(s) = 7Zr_{2}Al_{3}(s) + 7ZrAl_{2}(s)$$
(500-1300°C)
(1)

$$ZrAl_2(s) + Zr_2Al_3(s) + 5C(s) = Zr_3Al_3C_5(s) + 2Al(l)$$
  
(1360 °C) (2)

$$3Al(l) + 3ZrC(s) + 2C(s) = Zr_3Al_3C_5(s)$$
(1360-1500°C) (3)



Fig. 4. Powder XRD patterns of starting powders with the Zr:Al:C molar ratio of 3:5:5 heated at different temperatures for 10 minutes. (a) 500 °C, (b) 1300 °C, and (c) 1400 °C.  $\mu$  = ZrAl<sub>3</sub>;  $\nu$  = Zr<sub>3</sub>Al<sub>2</sub>;  $\lambda$  = ZrAl<sub>2</sub>;  $\omega$  = Zr<sub>2</sub>Al<sub>3</sub>;  $\alpha$  = Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub>;  $\beta$  = Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub>; C = graphite; ZC = ZrC; A = Al.

Reflections (h k l)	$2 heta_{ ext{Cal.}}$ (°)	$2 heta_{ m Obs.}$ (°)	$2 heta_{JCPDS.}$ (°)	1/I <sub>0Cal.</sub> (%)	1/I <sub>0Obs.</sub> (%)	1/I <sub>0JCPDS.</sub> (%)
002	6.45	6.40	6.41	100.00	100.00	100
004	12.93	12.80	12.81	2.43	2.42	2
006	19.45	19.25	19.27	2.35	2.99	2
008	26.03	25.76	25.78	4.24	5.65	3
101	31.32	31.00	31.04	2.15	2.80	6
102	31.84	31.51	31.57	2.76	2.70	4
103	32.69	32.35	_	45.03	56.74	-
0010	32.70	32.36	32.40	11.91	7.20	42
104	33.85	33.50	33.53	46.84	58.10	38
105	35.29	34.92	34.95	0.66	1.84	3
106	36.98	36.60	36.63	28.29	37.62	21
107	38.90	38.50	38.54	41.26	56.01	37
0012	39.48	39.07	39.10	12.29	18.97	9
108	41.02	40.59	40.64	17.86	25.69	20
109	43.32	42.87	42.90	8.87	14.39	9
1010	45.78	45.30	45.34	0.77	1.01	1

Table 1.	Reflections, 2	$\theta$ , and intensities	data of Zr <sub>2</sub> Al <sub>2</sub> C <sub>5</sub> from	calculation (Cal.).	experiment (Obs.	) and JCPDS car	d No. 32-0030.
rable r.	reflections, 2	o, and mensicles	und of Lightiges from	culculation (Call),	experiment (0005.		u 110. 52 0050.

To confirm the Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> phase, Rietveld XRD analysis for the Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> powders obtained was conducted. The crystal structure models of 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> used for refinement can be found in Ref. [16]. Both carbides crystallize in P6<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<sub>3</sub>Al<sub>3</sub>C<sub>5</sub>, and a = 3.3 Å and c = 22.4 Å for Zr<sub>2</sub>Al<sub>3</sub>C<sub>4</sub>. Reliability indices for a final result were R-P = 10.70%, and R-WP = 15.43%, and S = 4.5, respectively (Fig. 5). The



Fig. 5. Comparison between observed (+ marks) and calculated (upper solid line) pattern of  $Zr_3Al_3C_5$  and  $Zr_2Al_3C_4$ . The difference plot is shown in the lower part of the figure. Vertical marks indicated the position of possible Bragg reflections.

Table 2. Comparison of lattice parameters of  $Zr_3Al_3C_5$  obtained by Rietveld refinement and those from previous work.

Lattice pa	Reference	
<i>a</i> (Å)	<i>c</i> (Å)	
3.346 3.347 3.347	27.649 27.65 27.642	[19] [20] Present work

phase composition determined was 99.2 wt.%  $Zr_3Al_3C_5$ and 0.8 wt.%  $Zr_2Al_3C_4$ . Table 1 lists the calculated and experimental data of reflections,  $2\theta$ , and intensities for  $Zr_3Al_3C_5$ . For comparison, the data from JCPDS [28] were also given. Lattice parameters of  $Zr_3Al_3C_5$  determined by comparing the calculated data with the experimental ones are a = 3.347 Å and c = 27.642 Å (Table 2). The calculated lattice parameters for the powders synthesized by our method agree well with those from Gesing et al. (a = 3.346 Å and c = 27.649 Å) [19] and from Mikhalenko et al. (a =3.347 Å and c = 27.65 Å) [20], indicating that the obtained powders are  $Zr_3Al_3C_5$ .

### 3.2. Oxidation of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> and ZrC powders

The as-synthesized  $Zr_3Al_3C_5$  powders have a broad particle size distribution (PSD) from smaller than 0.1 µm to several micrometers, as shown in Fig. 6a. The PSD of ZrC powders is relatively narrow with a main size of about 6 µm, as observed by SEM (not shown here for brevity). The BET specific surface area of  $Zr_3Al_3C_5$  and ZrC powders are 2.54 m<sup>2</sup> g<sup>-1</sup> and 1.85 m<sup>2</sup> g<sup>-1</sup>, respectively.

 $g^{-1}$  and 1.85 m<sup>2</sup> g<sup>-1</sup>, respectively. The oxidation of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> powders was investigated using simultaneous TG–DSC measurements, as shown in Fig. 7a. The degree of oxidation,  $\alpha$  (%), is defined as the ratio of the measured mass gain to a theoretical one [7], where the theoretical mass gain of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> is calculated by assuming the complete conversion of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> to ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> based on the following equation:

$$4Zr_{3}Al_{3}C_{5}(s) + 41O_{2}(g) = 12ZrO_{2}(s) + 6Al_{2}O_{3}(s) + 20CO_{2}(g)$$
(4)

From the TG results, it is known that oxidation initiated at 400 °C and was greatly accelerated at 600 °C. The degree of oxidation exceeded 100% at about 750 °C, and rose to a maximum value of 148% at about 870 °C (position A in Fig. 7a), and then gradually returned to 100% through two steps, i.e., the first one was from the maximum to about 135% in the temperature range of 870–1000 °C (AB), and the next step was from 135% to about 100% at 1000–1200 °C (BC). At the same time, an exothermic oxidation determined by DSC began at around 400 °C and terminated

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Fig. 6. SEM microstructures of  $Zr_3Al_3C_5$  powders (a) before oxidation, (b) after oxidation at 1500 °C.

at 1200 °C (position C in Fig. 7a), which corresponds to the observed rapid weight gain. These two temperatures correspond to the starting and complete oxidation temperatures of  $Zr_3Al_3C_5$  powders.

For comparison, we conducted a similar run on ZrC powders under the same experimental condition as that for  $Zr_3Al_3C_5$  powders. Figure 7b shows the simultaneous TG-DSC curves for the ZrC powders. The degree of oxidation for ZrC is determined using a theoretical mass gain calculated from the following equation:

$$ZrC(s) + 2O_2(g) = ZrO_2(s) + CO_2(g)$$
 (5)

From the TG–DSC results, it is seen that the temperatures for the starting and completion of ZrC oxidation are approximately 300 °C and 780 °C, respectively. These two temperatures are about 100 °C and 400 °C lower than those of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> correspondingly. Moreover, Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> powders have a smaller particle size and larger specific surface area than ZrC powders. At this point, it is reasonable to conclude that Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> has better oxidation resistance than ZrC. In addition, an over 100% oxidation degree was also found, which is in consonance with the previous result [7].

The degrees of ZrC and  $Zr_3Al_3C_5$  oxidation both overshot 100% based on the TG results. Shimada [7] ascribed this overshooting of ZrC oxidation to the formation of free

$$ZrC(s) + O_2(g) = ZrO_2(s) + C(s)$$
 (6)

Furthermore, he demonstrated by thermodynamic calculations that the oxidation of ZrC under low oxygen pressure could occur with the formation of equivalent amounts of ZrO<sub>2</sub> and carbon. Similarly, it is possible to form carbon, Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> simultaneously under low oxygen partial pressure during the oxidation of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub>. Low oxygen partial pressure is caused by the formation of ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> scales, which act as an oxygen diffusion barrier and contribute to a large decrease in the oxygen activity at the scale/substrate interface.

If the carbon in  $Zr_3Al_3C_5$  is unoxidized, the observed weight increase would reach 156% (see arrow on the *y*-axis in Fig. 7a) of the theoretical one based on the following equation:

$$4Zr_{3}Al_{3}C_{5}(s) + 21O_{2}(g) = 12ZrO_{2}(s) + 6Al_{2}O_{3}(s) + 20C(s)$$
(7)

This hypothetical value is in good agreement with the experimental maximum value (148%), suggesting that most carbon in Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> was unoxidized and retained in products at around 870°C. The decrease of  $\alpha$  value at 870–1200°C in Fig. 7a could be divided into two steps (AB and BC), which possibly correspond to the loss of retained carbon on and beneath the oxide scales, respectively.



Fig. 7. Simultaneous TG–DSC curves from the oxidation of  $Zr_3Al_3C_5$ (a) and ZrC (b) at a heating rate of 10 °C min<sup>-1</sup> in air up to 1500 °C.

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#### 3.3. Phase evolution during the oxidation of $Zr_3Al_3C_5$

Figure 8a shows the XRD patterns of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> samples after oxidation at different temperatures. At 700 °C no other crystalline phases but  $Zr_3Al_3C_5$  were identified within the resolution of the diffractometer. When the temperature went up to 850 °C only a few weak peaks of  $Zr_3Al_3C_5$  were detected, indicating that most Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> suffered oxidation and oxidation products are most likely amorphous. In addition, a broadened peak appeared at about  $2\theta = 30^\circ$ , which corresponds to the tetragonal  $ZrO_2$  (t- $ZrO_2$ ) (101) peak. At 900 °C Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> was not detected anymore, suggesting that it was completely oxidized before this temperature. Al<sub>2</sub>O<sub>3</sub> was not detected within the resolution of the diffractometer, but EDS results (not shown here) revealed that the Al/Zr ratio in the products was almost constant from room temperature to 1500 °C. It is possible that Al<sub>2</sub>O<sub>3</sub> took an amorphous form. At the temperature range of 900-1200 °C, the t-ZrO<sub>2</sub> (101) peak became sharper and shifted to lower angles (Fig. 8b). It can be concluded that the crystallite size and lattice parameters of t-ZrO2 increased gradually with increasing oxidation temperature. The co-existance of tetra-



Fig. 8. Powder XRD patterns of the products during the conversion of  $Zr_3Al_3C_5$  to  $ZrO_2$  and  $Al_2O_3$ . (a) 700–1500 °C, and (b) 900–1200 °C within the 28–32° range of 2 $\theta$  value.  $\alpha = Zr_3Al_3C_5$ ; t = t-ZrO<sub>2</sub>; m = m-ZrO<sub>2</sub>; AO =  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

gonal and monoclinic ZrO<sub>2</sub> (m-ZrO<sub>2</sub>) was clearly detected at 1100 °C, and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> also emerged at this temperature. With further increasing temperature, most of the tetragonal phase gradually converted to the monoclinic phase and only the weak t-ZrO<sub>2</sub> (101) peak was detected after oxidation at 1500 °C, whereas the intensities of the diffraction peaks for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> increased profoundly. Figure 6b shows the SEM microstructures of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> powders after oxidation at 1500 °C. It can be seen that small particles, less than 1 µm in size, uniformly distributed on the sample surface after oxidation. These particles were confirmed by EDS (not shown for brevity) to contain Al, Zr and O, which should correspond to Al<sub>2</sub>O<sub>3</sub> and/or ZrO<sub>2</sub>.

Recently the mechanisms of room temperature tetragonal phase stabilization in zirconia were reviewed in detail by Shukla et al. [29]. In this work, the occurrence of stabilized t-ZrO<sub>2</sub> in oxidation products mainly results from the doping of trivalent  $Al^{3+}$  cations, which can increase the concentration of oxygen vacancies in ZrO<sub>2</sub>. Furthermore, the incorporation of  $Al^{3+}$ , which is a smaller cation than Zr<sup>4+</sup>, causes the decrease in the lattice parameters of t-ZrO<sub>2</sub> [30, 31]. Thus, the gradual increase in the lattice parameters of t-ZrO<sub>2</sub> with increasing temperature (Fig. 8b) is due to the decrease in the  $AlO_{1.5}$  content of the ZrO<sub>2</sub>, which agrees well with the results of Štefanić et al. [30]. In addition, the reduction of oxygen vacancies with increasing temperature favors the martensitic tetragonal-to-monoclinic transformation of ZrO<sub>2</sub> on cooling [29, 30].

#### 4. Conclusions

Predominantly single phase Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> powders were synthesized using Zr-Al intermetallics and graphite as starting materials in an Ar atmosphere. Excess Al is in favor of forming single phase Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> and can be readily rinsed out from the sample with HCl. The starting and complete oxidation temperatures of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> are much higher than those for ZrC, suggesting that Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub> has better oxidation resistance than ZrC. It sets a good example to enhance oxidation resistance of transition metal carbides by incorporation of Al. An over 100% oxidation degree was observed during the oxidation of Zr<sub>3</sub>Al<sub>3</sub>C<sub>5</sub>. A large amount of retained carbon in the products is responsible for this overshooting of oxidation. The interaction between Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> contributes to the occurrence of a metastable t-ZrO<sub>2</sub>. In addition, the decrease of AlO<sub>1.5</sub> content in ZrO<sub>2</sub> triggers the tetragonal-to-monoclinic transformation of ZrO<sub>2</sub>.

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