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14. ABSTRACT

Dense, near net-shaped ZrC/W-based composites have been fabricated at modest temperatures and at ambient pressure by a reactive infiltration process known as the Displacive Compensation of Porosity (DCP) method. Porous WC preforms with hourglass shapes (for rocket nozzle liners) were produced by gel casting, whereas simple bar-shaped preforms were produced by uniaxial pressing. The porous preforms were exposed to molten Zr_2Cu at 1200-1300°C and ambient pressure. The Zr_2Cu liquid rapidly infiltrated into the preforms and underwent a displacement reaction with the WC to yield a more voluminous mixture of solid products, ZrC and W. This displacement reaction-induced increase in internal solid volume filled the prior pore spaces of the preforms ("displacive compensation of porosity") to yield dense, ZrC/W-based composites. Because the preforms remained rigid during reactive infiltration, the final composites retained the external shapes and dimensions of the starting preforms. A DCP-derived, ZrC/W-based nozzle insert was found to be resistant to the severe thermal shock and erosive conditions of a Pi-K rocket motor test. The DCP process enables dense, ceramic/refractory metal composites to be fabricated in complex and near net shapes without the need for high-temperature or high-pressure densification or for extensive machining (i.e., relatively expensive processing steps are avoided). *© 2004 Kluwer Academic Publishers.*

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Near net-shape, ultra-high melting, recession-resistant ZrC/W-based rocket nozzle liners via the displacive compensation of porosity (DCP) method

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1. Introduction

The ever more demanding requirements for enhanced performance in aerospace vehicles continue to provide new opportunities for advanced materials. Novel, high-melting, lightweight materials that are chemically, mechanically, and thermally robust are needed to allow for significant improvements in the operating conditions and lifetimes of key rocket and jet engine components [1, 2]. One of the most severe environments encountered in aerospace applications exists in the throat region of a solid-fueled rocket nozzle. Solid, aluminum-bearing fuels generate combustion products (molten aluminum oxide droplets and gas) that impact the nozzles at supersonic speeds and at temperatures in excess of 2500°C [3–5]. Under these extreme conditions, rocket nozzle materials need to exhibit minimal vaporization, erosion, ablation, and creep [1–7]. Nozzle materials must also be highly resistant to thermal shock, given the rapid rise in temperature upon ignition [1, 2, 4, 5, 8]. Among the refractory metallic materials, tungsten possesses the highest melting point (3422°C) and is relatively noble (minimal volatilization and oxidation) under the extreme temperatures and reaction conditions within solid, aluminum-fueled rocket nozzles [9–12]. However, the high density (19.3 g/cm^3), reduction in strength at elevated temperatures, and fabrication costs for monolithic tungsten make this material less than ideal for rocket components [10–16].

Composites of refractory metals with covalently-bonded ceramics can possess attractive properties for high-temperature rocket applications. Consider, for example, composites of tungsten and zirconium carbide. Zirconium carbide is a hard (up to 2900 kg/mm^2), high melting (up to 3540°C) compound that is considerably lighter than tungsten (the density of ZrC, 6.63 g/cm^3, is about one-third of the density of W) [13, 17, 18]. Tungsten and zirconium carbide are chemically, thermally, and mechanically compatible. These phases exhibit little mutual solid solubility at elevated temperatures (e.g., $\leq$7 mol% at 2800°C) and do not react to form other compounds [19]. Unlike many ceramic/metal composite systems, zirconium carbide and tungsten possess similar thermal expansion coefficients (e.g., 4.5×10^{-6}/°C for W vs. 4.0×10^{-6}/ °C for ZrC at room temperature; 9.2×10^{-6}/ °C for W vs. 10.2×10^{-6}/ °C for ZrC at 2700°C) [20, 21]. Both phases also possess relatively high thermal conductivities (105 ± 10 W/m-K for W, and 40 ± 10 W/m-K for ZrC over the temperature range of 1000–2200°C) [22, 23]. As expected from these thermal properties, ZrC/W composites have been found to be resistant to thermal shock [24]. The carbide phase should endow co-continuous ZrC/W composites with enhanced high-temperature stiffness and creep resistance relative to monolithic tungsten, whereas the ductility of tungsten above 400°C (i.e., above the brittle-to-ductile transformation temperature) should provide enhanced resistance to fracture relative to monolithic zirconium carbide [10, 11, 14–16, 18]. Indeed, Song *et al.* have reported that a W/ZrC composite with 30 vol% ZrC possessed enhanced stiffness relative to monolithic tungsten at 1200°C (about 345 GPa for W/ZrC vs. about 270 GPa for W) [25]. Such composites also exhibited flexural strengths (three-point bending) of 810 MPa at 1200°C [25].

Although dense ZrC/W composites have been produced by high-temperature hot pressing (e.g., at 2000°C and 20 MPa [24–26]), this process is relatively slow and expensive, and is not well-suited for the fabrication of complex-shaped composites such as rocket nozzles. An attractive alternative method for fabricating dense carbide/refractory metal composites in complex shapes is the recently-patented Displacive Compensation of Porosity (DCP) method [27–35]. To date, the DCP process has been used to fabricate a variety of dense, near net-shaped ceramic/metal composites (e.g., MgO/Mg-Al, $MgAl_2O_4$/Fe-Ni-Al, MgO/FeAl, ZrC/W) at modest temperatures [27–35]. However, such prior work involved the fabrication of dense composites with relatively simple shapes (disks, bars, plates). The goal of this paper is to demonstrate that the DCP method can be used to fabricate complex-shaped, ZrC/W-based rocket nozzle inserts. The performance of such nozzles in a solid-fueled rocket test is also discussed in this paper.

2. DCP approach

With the DCP process, a shaped, porous ceramic preform is infiltrated at ambient pressure with a low-melting, reactive metallic liquid. Upon infiltration, the liquid undergoes a displacement reaction with the ceramic preform to generate new ceramic and metal phases within the preform. Unlike other reactive infiltration methods, reactions are chosen that yield a ceramic product with a larger molar volume than the ceramic reactant [27, 28]. Hence, as the displacement reaction proceeds within the infiltrated preform, the prior pore volume becomes filled with new solid ("displacive compensation of porosity"). The excess metallic liquid is then gradually squeezed back out into the surrounding liquid bath, so that a dense, ceramic-rich composite is produced. If the porous preform is lightly sintered prior to infiltration, so that the ceramic particles in the preform are necked, then the preform remains rigid as the internal network of reactant ceramic is replaced by the more voluminous solid product(s). The process is completed when either the ceramic reactant is fully consumed or the pores become filled with solid material, which ever happens first. In the latter case, the kinetics of reaction slow appreciably prior to complete consumption of the reactant ceramic phase. The final dense composite retains the shape and dimensions of the starting rigid preform (i.e., near net-shape processing). By using thermodynamically-favored internal reactions at modest temperatures to generate desired high-temperature phases and to fill porosity, the DCP process avoids the need for densification by high-pressure or high-temperature sintering. Furthermore, low-cost conventional ceramic processes (e.g., slip casting, gel casting, powder injection molding, etc.) may be used to produce porous ceramic preforms with complex shapes that are then preserved upon DCP conversion. That is, extensive, time-consuming, and costly diamond machining of green or sintered ceramic bodies is not required to obtain complex shapes.

In the present work, the following type of liquid/solid displacement reaction was used to convert porous WC preforms into dense ZrC/W-based composites:

$$\frac{1}{2}\mathrm{Zr_2Cu(l)} + \mathrm{WC(s)} \rightarrow \mathrm{ZrC(s)} + \mathrm{W(s)} + \frac{1}{2}\mathrm{Cu(l)} \quad (1)$$

This reaction is of the DCP type; that is, the sum of the molar volumes of the solid products, ZrC and W, is twice the molar volume of solid WC (i.e., V_m[ZrC] + V_m[W] = $2.01V_\mathrm{m}$[WC]) [13]. Reaction (1) is also strongly favored from a thermodynamic perspective. Using available thermodynamic data for ZrC, WC, and Zr-Cu liquids, the Gibbs free energy change per mole of reaction (1) at 1300°C is calculated to be −135.2 kJ [36–38]. A Zr_2Cu melt was used in this reaction, instead of pure liquid zirconium, in order to reduce the temperature required for melting and infiltration processing (i.e., to avoid the energy costs and complications associated with handling pure zirconium liquid, which melts at 1855°C [39]). Although comprised of two-thirds zirconium, Zr_2Cu melts congruently at only 1025°C (note: a congruently-melting Zr-Cu compound was preferred, in order to avoid phase separation and uncontrolled segregation during melt infiltration) [39]. Another important consideration in selecting Cu as an alloying element for the Zr-bearing melt was the minimal chemical reaction of Cu with ZrC and with W. Copper does not react with zirconium carbide to form a more stable carbide [36, 40]. Stable compounds also do not form between Cu and W at ambient pressures, and the solidus temperature of tungsten is only slightly reduced in the presence of copper (from 3422 to 3414°C) [9]. Indeed, copper has been intentionally introduced as a secondary phase in tungsten-based, solid-fueled rocket nozzles for enhanced transpirational cooling (i.e., the latent heats of fusion and of vaporization of copper can be used to absorb some of the heat experienced by a solid-fueled rocket nozzle) [12, 41].

3. Experimental procedure

Composites of zirconium carbide and tungsten were generated by the reactive infiltration of $Zr_2Cu(l)$ into porous tungsten carbide preforms. WC preforms in the shape of an hourglass (for rocket nozzle inserts) were prepared by gel casting. An aqueous solution containing 6.4 wt% of a proprietary gelling agent (MetaMateria Partners, LLC, Columbus, OH) was first prepared. WC powder (99.9% purity, 5.6 μm ave. size, Novel Technologies, Inc., Morristown, TN) was then added to this solution to obtain a mixture comprised of 43 vol% WC. The mixture was then was cast into an aluminum mold. After allowing the casting to set for 45 min, the mold was removed and the casting was allowed to dry at room temperature and then overnight at 55°C. The casting was then heated in flowing Ar to 400°C for 4 h (to remove the organic material) and then to 1450°C for 4 h (to produce rigid porous preforms). WC preforms in the shapes of bars were also prepared by uniaxial pressing of a mixture of the WC powder with 5 wt% of an aqueous solution of 4 wt% polyvinyl alcohol (Airvol 2005 PVA, Air Products and Chemicals, Allentown, PA). The mixture was uniaxially pressed into bars (11 mm long × 9.9 mm wide × 2.5 mm thick) at a peak stress of 300–340 MPa. The green bars were heated to 400°C for 4 h in flowing Ar (to remove the PVA binder) and then to 1600–1700°C for up to 2 h in a vacuum furnace (to produce rigid porous preforms).

Zr_2Cu ingots were prepared by induction melting or by arc melting. For induction melting, a 1 kg charge comprised of zirconium sponge (99.6% purity, 0.8–19 mm dia. pieces, Johnson-Matthey, Ward Hill, MA) and a copper rod (99.99% purity, 2.5 cm dia. × 5.9 cm thick, Atomergic Chemetals, Farmingdale, NY) were placed within a magnesia crucible (96% dense, 10.2 cm dia. × 15.2 cm high, Ozark Technical Ceramics, Webb City, MO). The charge was then sealed within a silica enclosure located inside a water-cooled copper coil connected to a 60 kV induction power supply (Mark IV, Inductotherm, Rancocas, NJ). After repeated evacuation and backfilling with argon, the charge was induction melted and stirred for 4 min. Inductively-coupled plasma spectroscopy (Optima 3000 ICP-OES, Perkin Elmer Corp., Norwalk, CT) indicated that the solidified ingot possessed a composition of 67.5 at% Zr/32.5 at% Cu, which was close to the desired Zr_2Cu composition (note: for ICP analyses, 100 mg of the solidified ingot was completely dissolved in an aqueous solution containing 8 vol% HF and 22 vol% HCl). X-ray diffraction (XRD) analyses of the ground ingot also revealed peaks consistent with Zr_2Cu. Arc melted Zr_2Cu ingots were prepared by ACI Alloys, Inc. (San Jose, CA). Charges of 0.6 kg comprised of a mixture of zirconium chips (99.8 wt% purity, 1 cm × 1 cm × 0.1 mm thick) and copper cylinders (99.99 wt% purity, 6 mm dia. × 4 cm long) were melted with a single arc on a water-cooled copper hearth into disk-shaped ingots (8–10 cm dia. × 1.3 cm thick). To allow for homogenization, each ingot was flipped and remelted, with a total exposure time to the arc of at least 15 min. XRD analyses of the solidified arc-melted ingots yielded peaks consistent with Zr_2Cu.

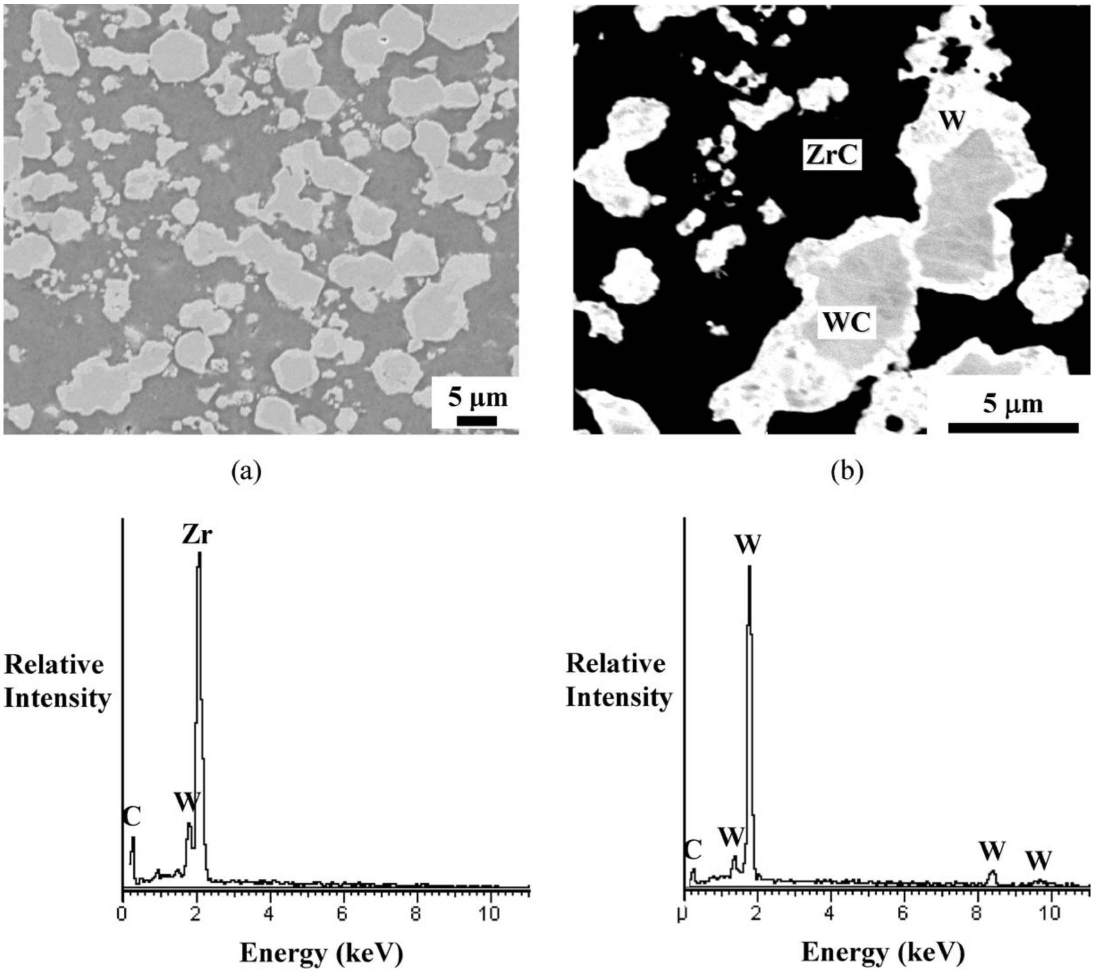
Reactive infiltration of the nozzle-shaped WC preforms was conducted by immersion in a $Zr_2Cu(l)$ bath. Prior to immersion, the nozzle-shaped preform was suspended above the bath on a graphite support. The $Zr_2Cu(l)$ bath was contained within a cylindrical magnesia crucible (96% dense, 15.2 cm dia. × 15.2 cm tall, Ozark Technical Ceramics). The molar ratio of Zr_2Cu in the bath to WC in the preform was 8.8:1, which was well in excess of the amount required for complete consumption of the WC. After thermal equilibration of the preform and the bath at 1200°C in a 3% H_2/Ar flowing gas atmosphere, the preform was lowered into the $Zr_2Cu(l)$ bath. After immersion for 10 min, the preform was raised above the bath and heated at 2°C/min to 1300°C. This increase in temperature was conducted to enhance the rate of chemical reaction after the molten metal had infiltrated into the preform. The preform was then cooled to room temperature. For the smaller bar-shaped WC preforms, pieces of the solid Zr_2Cu ingot were placed on top of the WC plates within a flat-bottomed magnesia combustion boat (96% dense, 1.27 cm deep × 10.2 cm long × 5.1 cm wide, Ozark Technical Ceramics). The molar ratio of Zr_2Cu:WC used in the bar infiltration experiments was maintained at 1.5–1.6:1, (i.e., in excess of the amount required for complete consumption of the WC). The Zr_2Cu-covered preforms were heated at 7°C/min to 1200–1300°C for 1–8 h and then cooled at 7°C/min to room temperature. The phase content and microstructure of the resulting composites were evaluated with a scanning electron microscope (XL-30 SEM, Philips Electron Instruments, Eindhoven, The Netherlands) equipped with an energy-dispersive X-ray (EDX) detector (Edax International, Mahwah, NJ) and with XRD analyses. Image analyses (Clemex Vision 3.0.027 image analyses software, Langueuil, Quebec, Canada) of backscattered electron images ($\geq$10 images per sample) were conducted to determine the phase contents of the reacted composites.

A composite rocket nozzle liner was tested in a Pi-K demonstration motor (Propulsion Directorate, Air Force Research Laboratory, Edwards, CA). Prior to testing, the liner was wrapped with continuous T-300 carbon fibers (7 μm diameter, Cytec Carbon Fibers LLC, Alpharetta, GA; produced by carbonization of polyacrylonitrile fibers). The fibers were then densified via the *In Situ* Densification process using naphthalene as the matrix precursor [42]. The fiber-wrapped nozzle liner was immersed in naphthalene, which completely infiltrated the voids between the carbon fibers. The naphthalene was then polymerized *in situ* with the use of an $AlCl_3$ catalyst. The polymerized perform was heated to 1100°C in order to convert the polymer matrix material to carbon. The carbon-carbon composite surrounding the insert was then machined to the final shape required by the test motor. A steel shoulder was adhesively bonded to the carbon-carbon overwrap to enable the nozzle assembly to be held in the Pi-K motor. The completed nozzle was then placed in a Pi-K test motor that had been previously loaded with a solid propellant comprised of 19 wt% aluminum. The propellant grain was ignited and burned for 4.6 s with a maximum pressure of 3.5 MPa.

4. Results and discussion

4.1. Phase and microstructural characterization of DCP-derived composites

Secondary and backscattered electron images of polished cross-sections of a composite generated by the reactive infiltration of $Zr_2Cu(l)$ into a bar-shaped WC preform at 1300°C are shown in Fig. 1a and b, respectively. The WC preform associated with this composite possessed a porosity of 43.5% prior to reactive infiltration. The secondary electron image in Fig. 1a revealed that, after reactive infiltration, the specimen was comprised of a particulate phase encased within a dense matrix. Isolated, fine (<2 μm) pores were detected within the matrix or particulate phases. The higher-magnification backscattered electron image in Fig. 1b revealed that the particles consisted of a grey core and a relatively bright (higher atomic number) coating. The coated particles were enveloped by a darker matrix phase. The matrix phase was found to be enriched in zirconium and carbon by EDX analyses (Fig. 1c), which was consistent with zirconium carbide. EDX analyses (Fig. 1d) revealed that the grey core of the particles was comprised of tungsten and carbon, which was consistent with unreacted tungsten carbide. The composite associated with the images in Fig. 1a and b was generated by exposure



(a) (b) (c) (d)

Figure 1 (a) Secondary electron and (b) backscattered electron images of a composite specimen generated by the reactive infiltration of $Zr_2Cu(l)$ into a porous WC preform (43.5 vol% porosity) at 1300°C for 8 h. EDX patterns obtained from the dark matrix phase and the grey core of the particles in (b) are shown in (c) and (d), respectively. (e) Backscattered electron image of a composite specimen generated by the reactive infiltration of $Zr_2Cu(l)$ into porous WC preform (42.4 vol% porosity) at 1300°C for 0.5 h. (f) XRD patterns obtained from WC preforms (46 ± 1% porosity) after infiltration and reaction with $Zr_2Cu(l)$ for 0.5, 2, 4 and 8 h. (g) EDX pattern obtained from an isolated region containing a Cu-rich phase.

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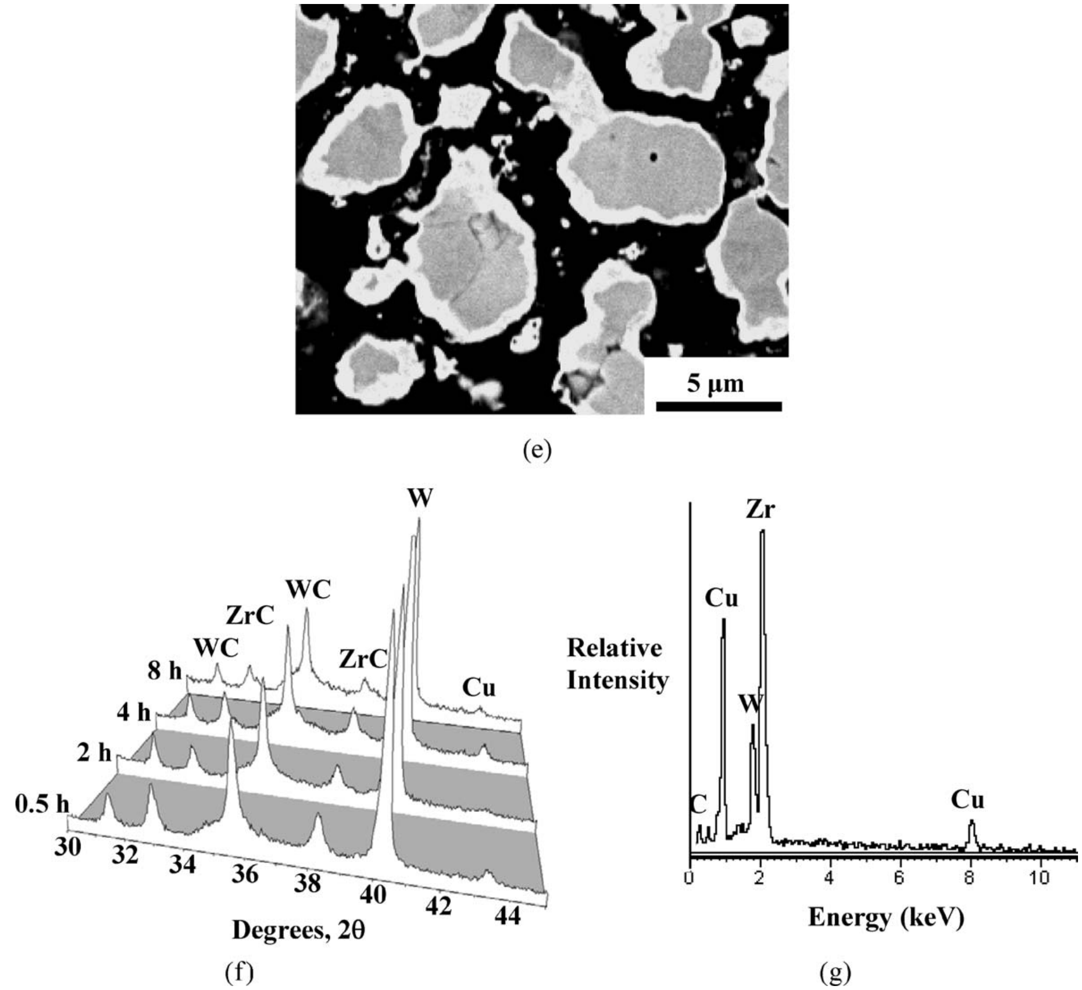


(e)

(f)

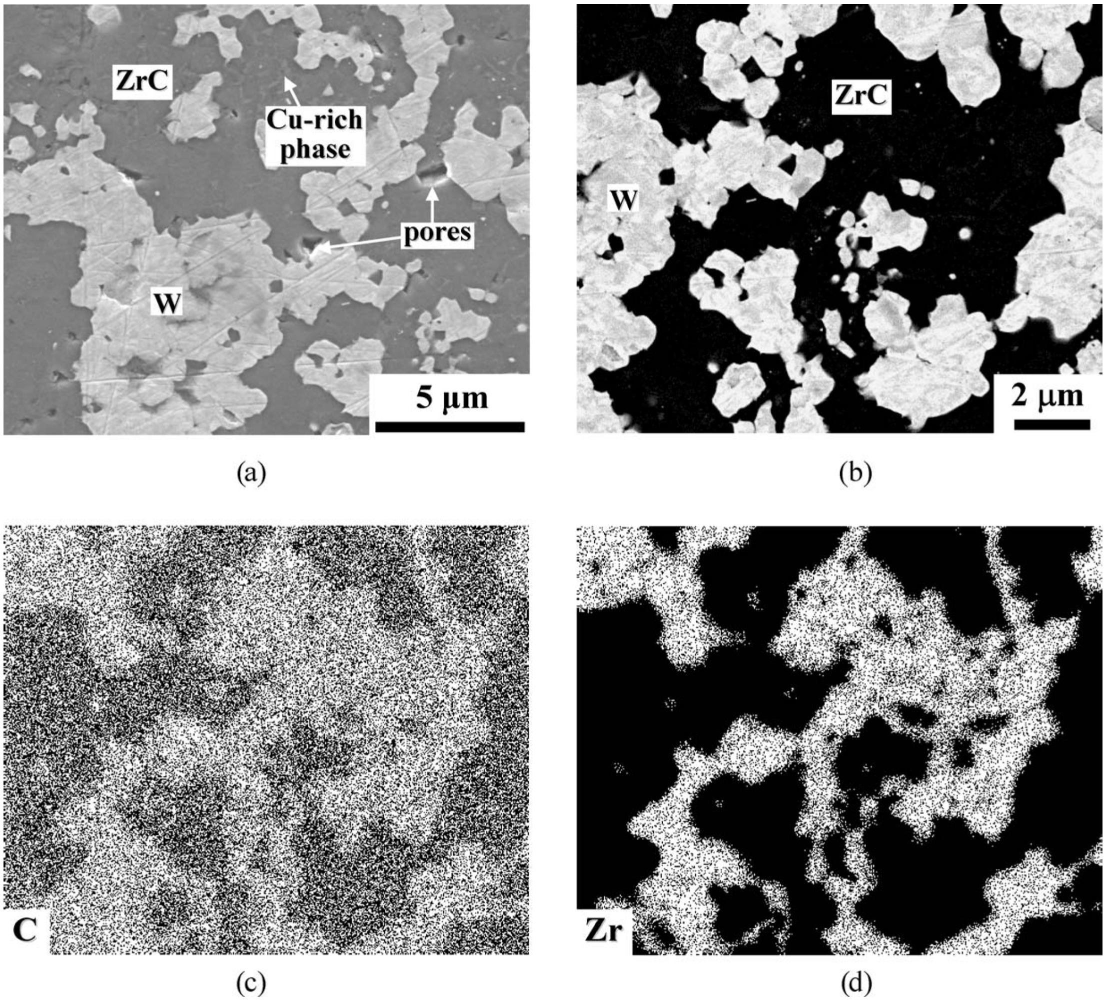
(g)

Figure 1 (*Continued*).

to $Zr_2Cu(l)$ for 8 h. Composites with similar microstructures were also produced after only 0.5 h of exposure of WC preforms of comparable porosity (42.4 vol%) to the Zr_2Cu melt (Fig. 1e). XRD patterns obtained after exposure of WC preforms (with porosities of 46 ± 1%) to the Zr_2Cu melt at 1300°C for various times are shown in Fig. 1f. Distinct diffraction peaks for W, WC, and ZrC were observed. Similar amounts of these phases were detected for reaction times of 0.5 to 8 h [13]. These XRD analyses, along with the EDX analyses in Fig. 1c and d, and the differences in phase contrast observed in the backscattered electron images of Fig. 1b and e, were consistent with composites comprised of tungsten-coated particles of residual (unreacted) tungsten carbide encased within a zirconium carbide-based matrix. A weak diffraction peak for copper was also observed after each reaction time. Small, isolated amounts of a Cu-rich phase (not seen in Fig. 1a, b, and e) were also occasionally detected by EDX analyses (Fig. 1g) in polished composite cross-sections. The weight gain exhibited by a specimen of comparable starting porosity (44.6%) was 32.9%. For the stoichiometry of reaction (1), this weight gain corresponds to a phase content of 23.8 vol% tungsten, 28.4 vol% unreacted tungsten carbide, 38.9 vol% zirconium carbide, and 8.9 vol% copper (or a ZrC + Cu total of 47.8 vol% for the matrix). These values were not far from those obtained by image analyses of backscattered electron images from the specimen shown in Fig. 1a and b: 18.5 ± 2.3 vol% tungsten, 30.9 ± 6.1 vol% unreacted tungsten carbide, and 50.6 ± 5.4 vol% of the matrix phases (the zirconium carbide and copper-rich phases). (Note: independent evaluation of the amount of the copper-rich phase within the matrix was difficult to obtain by image analyses, owing to the isolated occurrence of this phase, the small contrast difference relative to zirconium carbide, and the fine phase width of $<0.2\ \mu$m). The phase mixture obtained from the measurement of weight gain possessed a theoretical density of 12.4 g/cm^3. The bulk density measured for a composite specimen generated from a 44.6% porous WC preform was 11.7 g/cm^3, which corresponds to a density of 94.4% (5.6% porosity).

The ZrC matrices and the W coatings on particles observed in the microstructures in Fig. 1a, b, and e were generated within the pore spaces present in the starting WC preforms. The presence of residual WC in these reacted specimens was a result of pore filling prior to complete consumption of the WC. The WC preforms used to generate the composites associated with Fig. 1a–g possessed porosities of 42.4–47.0 vol%. These values of porosity were smaller than what was required to accommodate the internal increase in solid volume from complete conversion of tungsten carbide into zirconium carbide and tungsten (note: in order to accommodate the 101% increase in internal solid volume due to completion of reaction (1), a target porosity of 50.2 vol% was required [13]). Once the pores become filled, further migration of Zr_2Cu(l) into the preform, and further consumption of WC, were inhibited. The similarities in XRD patterns and microstructures of the specimens generated within 0.5 and 8 h of exposure to Zr_2Cu(l) indicated that the pores were filled, and the reaction was effectively terminated, within 0.5 h at 1300°C.

Secondary electron and backscattered electron images of a polished cross-section of a composite specimen generated by reactive infiltration of Zr_2Cu(l) into a 52.0% porous WC preform are shown in Fig. 2a and b, respectively. The secondary and backscattered electron images reveal a relatively dense specimen, containing a few fine ($<2\ \mu$m) isolated pores, comprised of a particulate phase contained within a darker matrix. X-ray maps for carbon, zirconium, and tungsten associated with the backscattered electron image in Fig. 2b are shown in Fig. 2c–e, respectively. The matrix phase was enriched in carbon and zirconium, which was consistent with zirconium carbide. The particulate phase was enriched in tungsten and depleted in carbon, which was consistent with metallic tungsten; that is, the particles did not contain residual tungsten carbide. The uniformity in brightness of the particles in the backscattered electron image (i.e., the absence of a relatively bright cladding layer surrounding each particle), and the presence of distinct scratches through the particulate phase (Fig. 2a), were also consistent with particles of relatively soft metallic tungsten in a much harder zirconium carbide matrix. A minor amount of a copper-rich phase (Fig. 2a and f) was also detected by EDX analyses (Fig. 2g). XRD analysis of this specimen (Fig. 2h) revealed peaks for zirconium carbide and tungsten, and a weak peak for copper. Distinct peaks for tungsten carbide were not detected. The weight gain exhibited by a specimen with the same starting porosity (52.0%) was 49.0%. For the stoichiometry of reaction (1), this weight gain corresponds to a phase content of 37.2 vol% tungsten, 60.7 vol% zirconium carbide, and 2.1 vol%



(a) (b)

(c) (d)

Figure 2 (a) Secondary electron and (b) backscattered electron images of composite specimens fabricate by the reactive infiltration of Zr_2Cu(l) into porous WC preforms (52.0 vol% porosity) at 1300°C. (c) C and (d) Zr X-ray maps associated with the backscattered electron image in (b). (e) W X-ray map associated with the backscattered electron image in (b). (f) Higher magnification secondary electron image of the Cu-rich phase in (a). (g) EDX pattern obtained from the volume containing this Cu-rich phase. (h) XRD pattern obtained from the specimen shown in (a–g).

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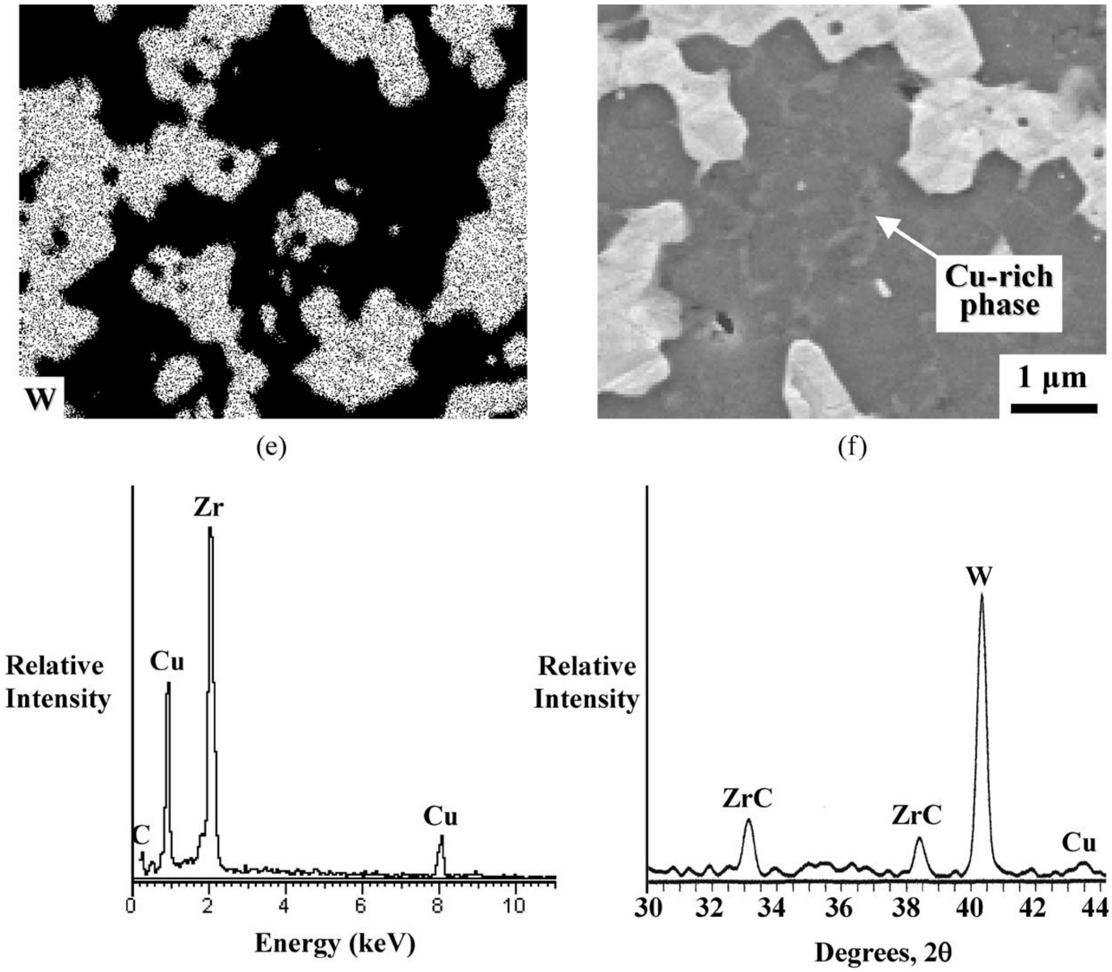


(e) (f)

(g) (h)

Figure 2 (*Continued*).

copper (or a ZrC + Cu total of 62.8 vol% for the matrix). These values were not far from those obtained by image analyses of backscattered electron images from the specimen shown in Fig. 2a and b: 43.7 ± 6.6 vol% tungsten and 56.3 ± 6.6 vol% of the matrix phases, zirconium carbide and the copper-rich phase. The phase mixture obtained from the measurement of weight gain possessed a theoretical density of 11.4 g/cm^3. The bulk density measured for a composite specimen generated from a 52.0% porous WC preform was 11.0 g/cm^3, which corresponds to a density of 96.5% (3.5% porosity). The enhanced porosity (52.0 vol%) of the starting rigid WC preform for this specimen provided sufficient open volume to enable the WC to be fully consumed just prior to complete filling of the pores.

4.2. Near net-shape fabrication of ZrC/W-based rocket nozzle liners

An optical photograph of a porous, nozzle-shaped WC preform prepared by gel casting followed by a modest sintering treatment (1450°C, 4 h) is shown in Fig. 3a. The geometry of this preform was chosen to be compatible with the Pi-K rocket test discussed below. The bulk density of this preform after light sintering was 7.52 g/cm^3, which corresponded to a porosity of 52.0 vol% (i.e., sufficient for completion of reaction (1)). An optical image of the nozzle insert after reactive infiltration with $Zr_2Cu(l)$ is shown in Fig. 3b. The same specimen is shown in Fig. 3c and d after excess solidified metal adhering to the nozzle surfaces was selectively removed by light polishing (note: the solidified Zr-Cu metal was much softer than the underlying carbide-bearing composite). The weight gain of this nozzle after reactive infiltration was 49.0%, which was not far from that expected (46.6%) for complete conversion of WC into ZrC and W. The nozzle insert retained the shape of the starting porous WC preform. Indeed, the diameters of the entry and exit cones of the nozzle insert changed by ≤ 0.3 mm after reactive infiltration. The ID of the entry cone changed from 9.63 to 9.65 cm, and the ID of the exit cone changed from 3.02 to 3.05 cm.

4.3. Pi-K rocket test

Prior to rocket testing, the ZrC/W-based insert (Fig. 3) was backed with a carbon-carbon composite. This lightweight C-C composite backing served two functions: (1) to bring the insert to the final external dimensions required for the rocket motor, and (2) to provide

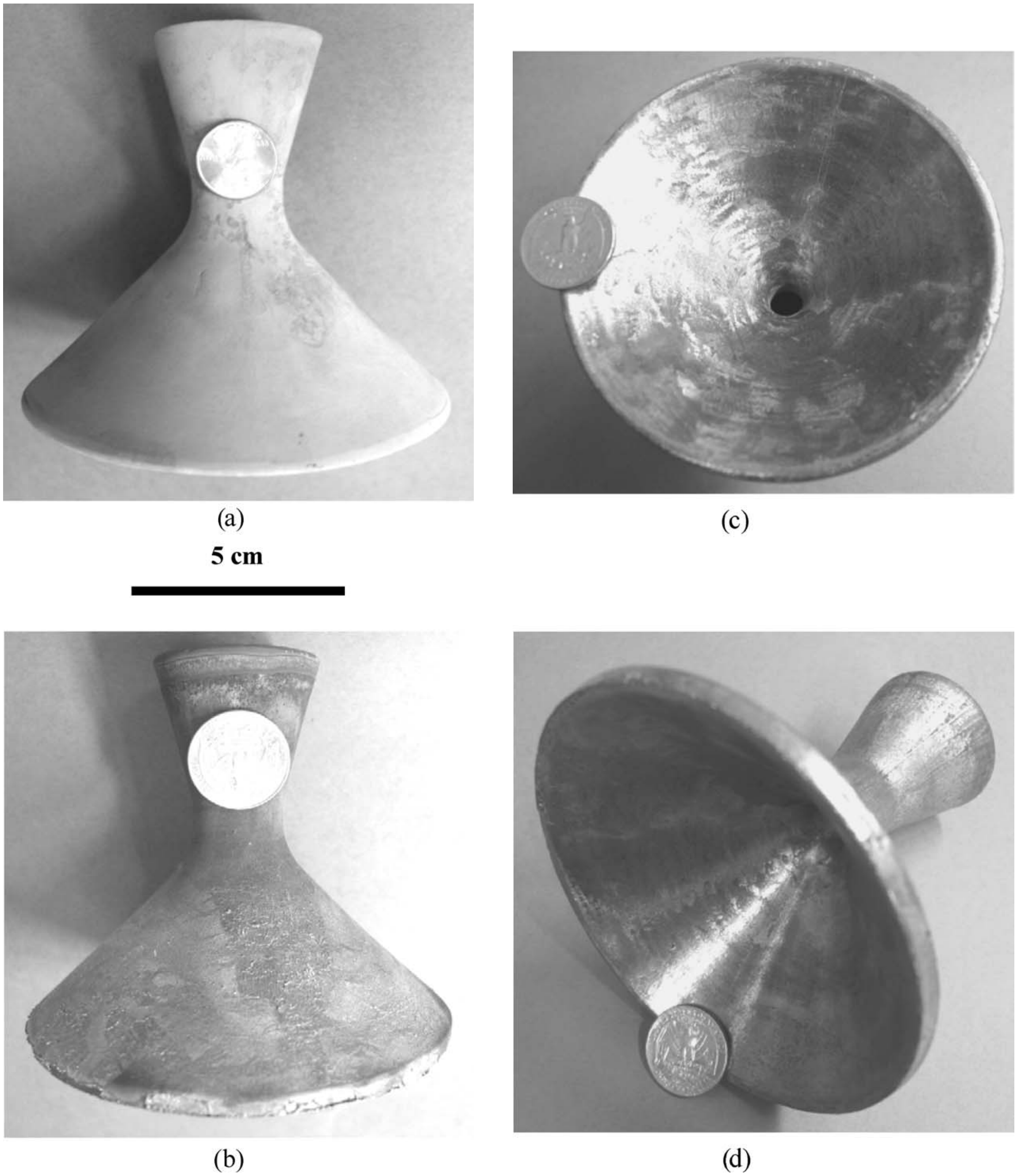
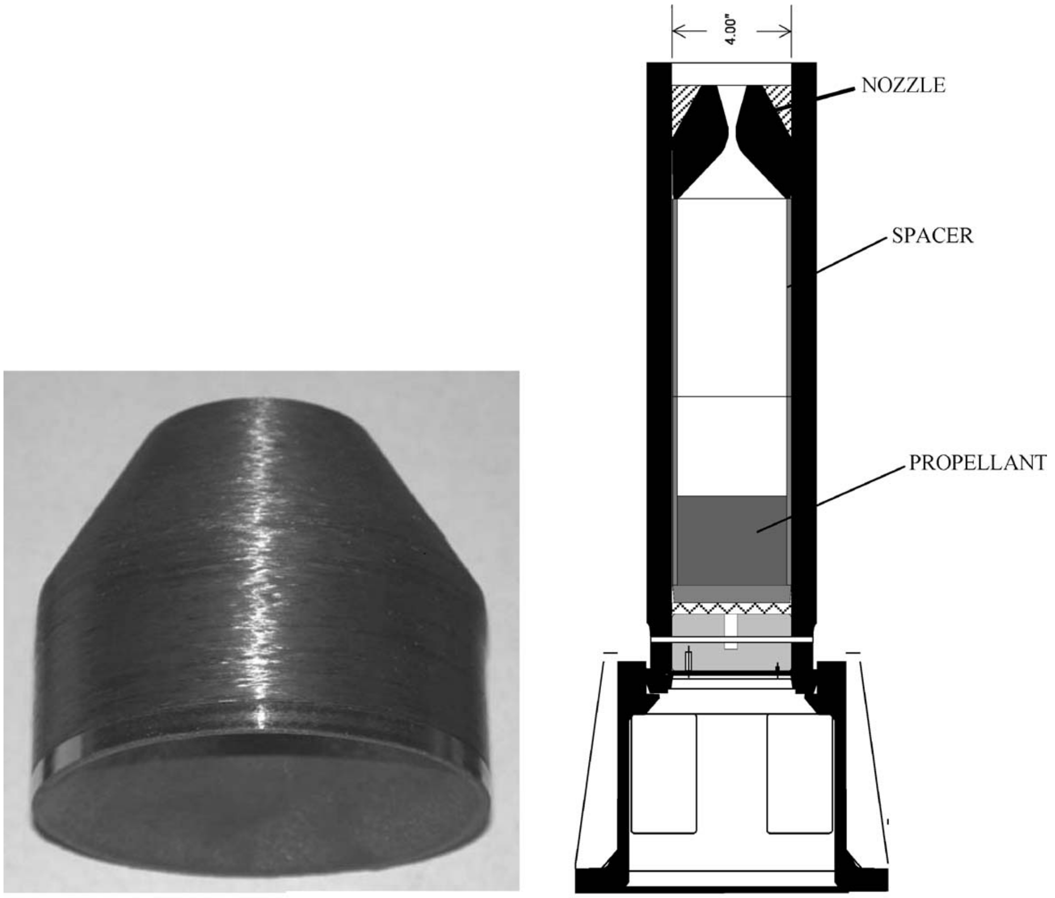


Figure 3 Optical photographs of (a) a nozzle-shaped WC preform (52.0 vol% porosity), and (b) the same specimen after reactive infiltration with $Zr_2Cu(l)$ (immersion for 10 min at 1200°C, followed by heating at 2°C/min to 1300°C), and (c), (d) after removal of the excess solidified metal on the nozzle surfaces by polishing.

mechanical backing to the insert while the interior of the insert was exposed to the high gas pressure during the firing. After machining the C-C backing and bonding a retaining ring to the backing, the completed nozzle (Fig. 4a) was placed in a Pi-K test motor (Fig. 4b), which had been previously loaded with a solid propellant comprised of 19 wt% aluminum. The propellant grain was ignited and burned (Fig. 5a) for 4.6 s with a maximum pressure of 3.5 MPa. The temperature that the throat experienced upon combustion of this propellant was predicted by thermal-chemical calculations to be 3245 K [43]. During the rapid heat up at the start of the test, the pressure within the nozzle increased to a relatively uniform value of about 510 psi (3.5 MPa) (Fig. 5b), which indicated that the nozzle insert survived the critical initial thermal shock associated with rapid heat up. Examination of the nozzle insert after the test indicated that the throat of the nozzle had remained intact. The exit side of the nozzle throat is shown in Fig. 6, where some solidified alumina deposit can be seen. Although the internal surfaces of the insert appeared to be unaffected by the firing (i.e., roughening or recession of the surface was not observed), hairline compression cracks formed on the entrance end of the insert. Such cracking is likely to have resulted from the difference in thermal expansion between the ZrC/W-based insert and



(a) (b)

Figure 4 (a) ZrC/W nozzle insert after it had been wrapped with carbon fibers, infiltrated with naphthalene, polymerized, fired (1100°C) to form a C-C composite backing, and machined to size for the test motor. (b) Schematic of Pi-K test motor.

the carbon-carbon backing. Indeed, a distinct cracking sound was heard about 3.3 s from the start of the firing that coincided with the small perturbation seen in the pressure trace in Fig. 5b. Such cracking may be avoided with the use of a compliant layer between the insert and the carbon-carbon backing. In any event, the absence of solidified alumina at the interface of the carbon-carbon backing with the ZrC/W-based insert, or within the hairline cracks in the insert, at the nozzle entrance indicated that appreciable penetration of the combustion products to the carbon-carbon backing did not occur. Although more extensive testing needs to be conducted, the present work indicates that the nozzle insert survived the extreme thermal shock and erosion of the Pi-K test.

Although the present work has focused on the ZrC/W-based composites for rocket nozzles, the DCP process is not limited to these compositions or to this application. Complex-shaped composites containing a variety of other ceramic phases (carbides, borides, nitrides, oxides, etc.) and refractory metals may also be produced for use in a wide range of other high-temperature aerospace (combustion liners, valves, leading edges, exhaust flaps, etc.) and other applications (e.g., erosion-resistant dies for extrusion, drawing, pressing or forming; wear-resistant plates for brakes, skids, or runners; stiff, creep-resistant structural components; hard, lightweight armor) [27, 28].

5. Conclusions

Near net-shaped composites containing the ultra-high-melting phases, zirconium carbide and tungsten, were fabricated at modest temperatures and at ambient pressure by the Displacive Compensation of Porosity (DCP) method. Porous, gel-cast WC preforms in the shape of an hourglass (for rocket nozzle liners) were infiltrated at only 1200–1300°C with molten Zr_2Cu. The zirconium in the liquid displaced the carbon from tungsten carbide to form zirconium carbide and metallic tungsten. Because these latter solid products (ZrC, W) possessed twice the volume of tungsten carbide, the prior pores within the preform became filled by these solid products ("displacive compensation of porosity") and excess liquid was squeezed back out of the preform. Since the WC preform remained rigid during the course of reaction, the external shape and dimensions of the starting preform were preserved in the final nozzle-shaped composite. A DCP-derived, ZrC/W-based nozzle insert backed with a carbon-carbon composite was found to be resistant to the thermal shock and erosive conditions of a solid-fueled Pi-K rocket test. This work

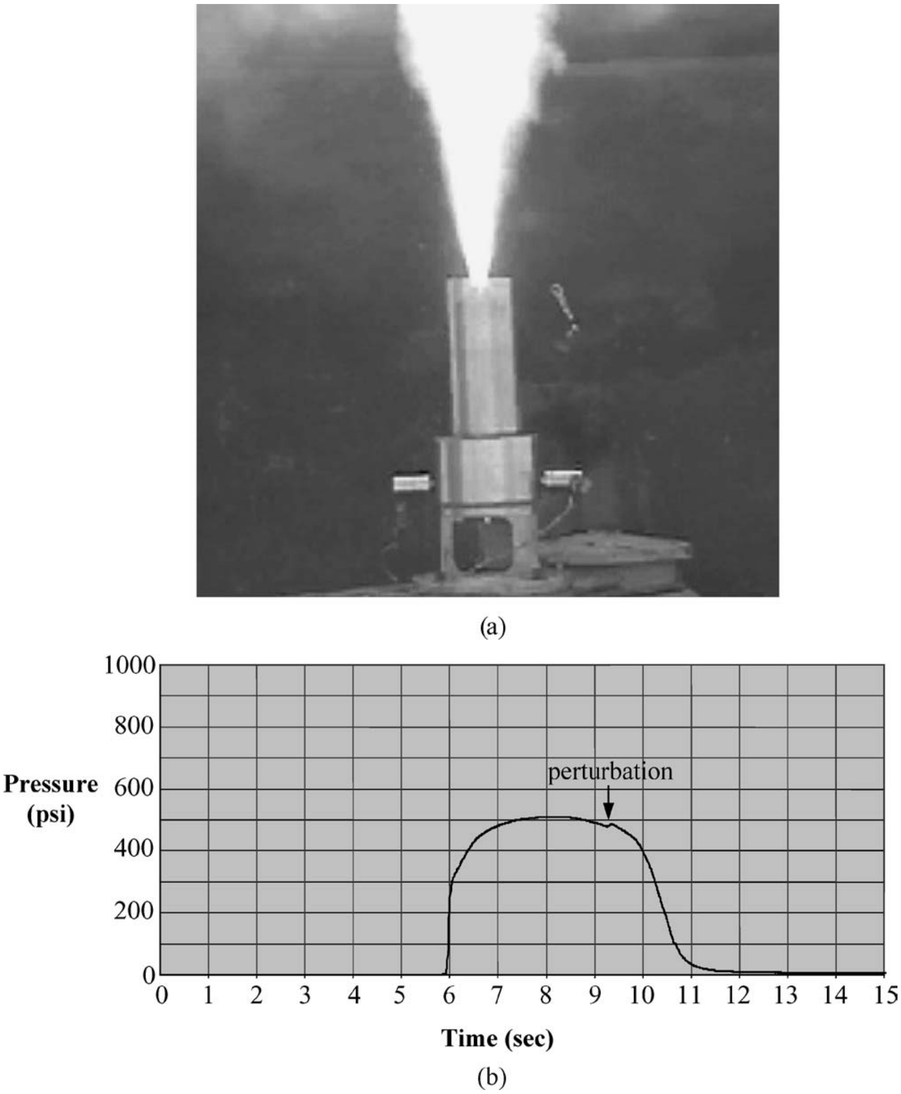


Figure 5 (a) Test firing of Pi-K motor with carbon-carbon backed ZrC/W insert. (b) Pressure trace during test firing (the perturbation indicated in the pressure trace coincided with a distinct cracking sound).

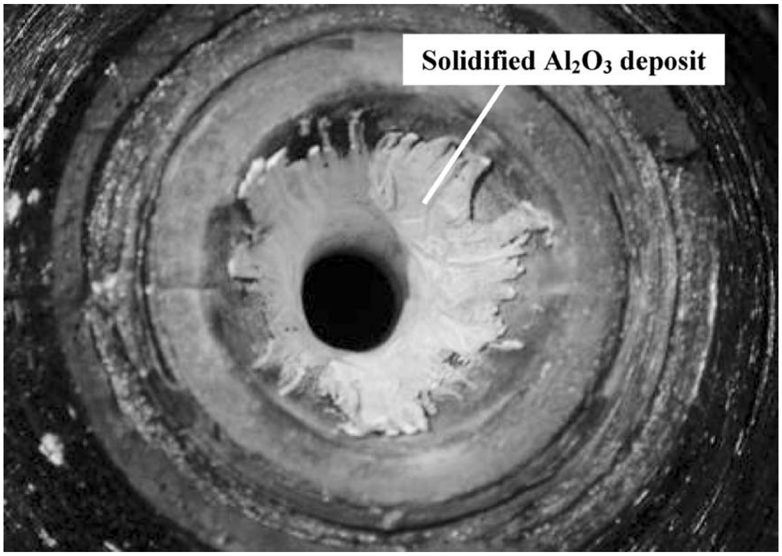


Figure 6 Exit of tested nozzle showing the aluminum oxide deposit on the surface of the ZrC/W insert that is surrounded by the carbon-carbon composite.

demonstrates that the DCP process may be used to fabricate dense, ultra-high-melting, erosion-resistant ceramic/refractory metal composites in complex and near net shapes without the need for high pressure or high temperature densification or extensive machining.

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