

LOW-TEMPERATURE REACTION CASTING OF DENSE, NEAR NET-SHAPED CARBIDE/REFRACTORY METAL COMPOSITES WITH TAILORED PHASE CONTENTS

M. B. Dickerson and K. H. Sandhage

*Department of Materials Science and Engineering 481 Watts Hall, 2041 College Road
The Ohio State University
Columbus, OH 43210 USA*

Abstract:

High-melting metal/carbide composites can exhibit attractive combinations of properties for aerospace and other applications (e.g., erosion and creep resistance coupled with relatively high strength and toughness). In this paper, the feasibility of synthesizing dense, near net-shaped, refractory W/ZrC-bearing composites with tailored phase contents at modest temperatures is demonstrated through the use of a novel reaction casting process: the **PRIMA-DCP** method. Rigid preforms of porous WC, or porous mixtures of WC with W, were infiltrated with a Zr-Cu liquid at 1200-1300°C and at ambient pressure. A displacement reaction occurred between Zr in the liquid and WC in the preform to generate ZrC and W. Because the volume of the solid ZrC/W product mixture was nearly twice the volume of WC, these solid products filled the pores in the rigid preform. Such pore filling caused the excess, unreacted liquid to be expelled from the preform, so that a dense, refractory composite was produced. Because the preform remained rigid during such reactive infiltration, the final composite retained the shape and dimensions (to within 1%) of the starting preform (i.e., near net-shape processing). By varying the W:WC ratio of the preforms, composites with varied and controlled amounts of ZrC and W were fabricated.

Keywords: *PRIMA-DCP, Reaction Casting, Zirconium Carbide, Tungsten, Carbide/Metal Composites*

Resumen:

Los compuestos del metal/carburo de alto punto de fusión pueden exhibir combinaciones atractivas de propiedades para las aplicaciones aeroespaciales y otras (por ejemplo, erosión y resistencia al creep en conjunto con una resistencia y tenacidad relativamente altas). En este artículo, se demuestra la viabilidad de un sinterizado denso, cercano a la forma final, de compuestos de rodamientos de refractarios de W/ZrC- con volúmenes de fase ajustados y a temperatura relativamente bajas a través del uso de un nuevo proceso fundición reactiva: el método de PRIMA-DCP. Preformas rígidas de WC poroso, o mezclas porosas de WC con W, se infiltraron con Zr-Cu líquido a temperaturas de 1200-1300°C y presión ambiente. Una reacción del desplazamiento ocurrió entre el Zr líquido y WC en la preforma para generar ZrC y W. Debido a que el volumen del ZrC/W sólido era casi dos veces el volumen de WC, estos productos sólidos rellenaron los poros de la preforma rígida. Ese llenado de poros causó que el exceso, de líquido sin reaccionar fuera rechazado de la preforma, formando un compuesto refractario denso. Porque la preforma permanece rígida durante la infiltración reactiva, el compuesto final retuvo la forma y dimensiones (dentro de un 1%) de la preforma de arranque (por ejemplo, proceso cercano a la forma final). Variando la proporción de W:WC de la preforma, se fabricaron compuestos con variada y controladas cantidades de ZrC y W.

Palabras Clave: *PRIMA-DCP, Fundición Reactiva, Carburo de Zirconia, Carburo de Tungsteno, Compuestos Carburo/Metal*

1. Introduction

Refractory metals (W, Re, Ta, Mo, Nb) and their alloys can exhibit exceptional properties at elevated temperatures (e.g., high modulus and strength, low vapor pressure, good creep resistance) [1]. As a result, refractory metals have been used, or are being considered for use, in a variety of high-temperature applications (e.g., solid-fuel rocket nozzles, leading edges and nose caps for re-entry vehicles, crucibles, hot gas valves, heating elements, susceptors, heat shields) [1-5]. However, refractory metals tend to be relatively heavy and, in some cases, can be relatively difficult to form in complex shapes at low cost. Lower weight composites of refractory metals with high-melting ceramics, that can be fabricated into dense, near net shapes at low temperatures, would be particularly attractive for advanced aerospace applications.

Tungsten is the highest melting ($3410\pm 20^\circ\text{C}$) refractory metal and also one of the heaviest ($\rho[\text{W}] = 19.3 \text{ g/cm}^3$) [1,3,4,6]. Transition metal carbides tend to be much lighter than tungsten and are among the highest melting ceramic compounds [6-8]. Composites of tungsten with refractory carbides can exhibit an attractive combination of chemical, thermal, and mechanical properties. Consider, for example, composites of zirconium carbide and tungsten. ZrC is a hard (up to 2900 kg/mm^2), high-melting (up to 3420°C) compound that possesses one-third of the density of tungsten ($\rho[\text{ZrC}] = 6.63 \text{ g/cm}^3$) [6-8]. Composites of tungsten and zirconium carbide are chemically stable at high temperatures; that is, these phases exhibit low mutual solid solubility and do not react to form other compounds [9]. ZrC/W composites should be resistant to internal stress buildup and cracking due to thermal cycling (unlike most ceramic/metal composites), since ZrC and W possess similar thermal expansion coefficients and are both good thermal conductors¹ [1,3,4,10-13]. ZrC/W composites should also exhibit excellent creep resistance at $\approx 2000^\circ\text{C}$, where tungsten and its alloys undergo recrystallization [3-5,7,14]. The ductility of tungsten above 400°C (i.e., above the brittle-to-ductile transformation temperature [1,4]) can endow such composites with resistance to fracture. Indeed, hot-pressed composites comprised of 80 vol% W/20 vol% ZrC have exhibited flexure strengths of 979 MPa at 1200°C [15].

Although dense W/ZrC composites can be produced by hot pressing at $\approx 2000^\circ\text{C}$, such batch processing is relatively slow and expensive [15]. A costly machining operation must also be conducted to convert the hot-pressed composites into components with more complicated (non-axisymmetric) shapes. An attractive,

alternate route to dense, near net-shaped ceramic/metal composites that avoids the use of high applied pressures or temperatures has recently been developed at The Ohio State University: the **PRIMA-DCP** method (**P**ressureless **R**eversible **I**nfiltration of **M**olten **A**lloys by the **D**isplacive **C**ompensation of **P**orosity) [16-19]. In this process, a low-melting metallic liquid is allowed to wet and infiltrate into a porous, shaped, rigid ceramic preform at ambient pressure. Upon infiltration, the liquid undergoes a displacement reaction with the preform to yield new ceramic and metal phases. A unique feature of this process, relative to other reactive infiltration routes (e.g., the infiltration-alumina-aluminide-alloy process; reactive metal penetration [20-22]), is the increase in ceramic volume that occurs upon reaction. With the **PRIMA-DCP** method, the ceramic product possesses a larger volume than the ceramic reactant. As the displacement reaction proceeds, the prior pore volume becomes filled with new solid ("displacive compensation of porosity"). The excess metallic liquid in the preform is gradually squeezed back out into the surrounding bath ("reversible infiltration") until a dense, refractory composite is produced. By lightly sintering the preform prior to reactive infiltration, necks can be built up between the reactant particles to endow the preform with sufficient rigidity as to avoid distortion or cracking during infiltration. The specimen then remains rigid as the internal reactant network is replaced by a more voluminous internal network of solid product(s). Dense, fully-reacted composites can thereby be produced with a retention of the shapes and external dimensions of the starting preforms.

To date, a variety of dense, near net-shaped composites have been synthesized at modest temperatures ($1000\text{-}1300^\circ\text{C}$) by the **PRIMA-DCP** process, including MgO/Mg-Al alloy composites (lightweight, hydration-resistant, electrically-insulating composites with MgO contents in excess of 83 vol%), $\text{MgAl}_2\text{O}_4/\text{Fe-Ni-Al}$ alloy composites (tough, creep-resistant composites reinforced with a co-continuous, heat-resistant alloy), and ZrC/WC/W composites (highly refractory, creep-resistant composites) [16-19]. The purpose of the present paper is to demonstrate that the **PRIMA-DCP** method can be tailored to produce carbide/refractory metal composites with a wide range of phase contents (<20 vol% to >70 vol% carbide).

2. Experimental Procedures

ZrC/W-bearing composites were produced by the reactive casting of a Zr_2Cu liquid into porous, WC-bearing preforms at $1200\text{-}1300^\circ\text{C}$ and at ambient pressure. The phase content of the fully-reacted composites was tailored by adjusting the phase content of the preforms. That is, ZrC-rich composites were produced by starting with preforms containing only WC, whereas W-rich composites were generated from preforms containing a mixture of inert W and WC. For the latter preforms, the molar W/WC ratio was varied

¹Average linear coefficients of thermal expansion from 25°C to 2700°C range from $4.5 \times 10^{-6}/^\circ\text{C}$ to $9.2 \times 10^{-6}/^\circ\text{C}$ for W and $4.0 \times 10^{-6}/^\circ\text{C}$ to $10.2 \times 10^{-6}/^\circ\text{C}$ for ZrC [12,13]. W and ZrC possess thermal conductivities of $105\pm 10 \text{ W/m-K}$ and $40\pm 10 \text{ W/m-K}$, respectively, from $1000\text{-}2200^\circ\text{C}$ [3,4,10,11].

from 0.59 to 5.8. Bar and disk-shaped preforms were produced by uniaxial powder pressing. The starting W and WC powders^{1,2} possessed purities of >99.9% and particle sizes of <12 μm and <10 μm , respectively. For some of the W-rich preforms, 5-10 wt% of Ni powder² (=3.0 μm , 99.9% purity) was added as a sintering aid [23]. After blending with 5-10 wt% of an aqueous polyvinyl alcohol solution³, the mixtures were pressed into bars (0.25 cm X 1.1 cm X 1.1 cm) and disks (1.3 cm dia., X 3.5 mm thick) at peak stresses of 34-48 MPa. The polyvinyl alcohol binder was removed by heating the preforms to 400°C for 4 h in flowing argon. Annealing was then conducted for either 2 h at 1750°C (for preforms without nickel) or 0.5 h at 1100°C (for nickel-bearing, tungsten-rich preforms) in flowing Ar to produce rigid preforms with relative densities of 50-60%.

The low-melting intermetallic compound, Zr_2Cu , was used as the reactive infiltrant [24]. A Zr_2Cu ingot was prepared by vacuum induction melting of a copper rod (99.9% purity) and zirconium sponge (99.6% purity) within a magnesia crucible. The ingot composition and phase purity were confirmed by inductively-coupled plasma spectroscopy and x-ray diffraction analysis. Prior to reaction casting, solid pieces of the Zr_2Cu ingot were placed in contact with the porous, WC-bearing preform inside a magnesia crucible. The Zr_2Cu /preform assembly was then heated in a flowing argon atmosphere to 1200-1300°C for 1-8 h. After cooling to room temperature, the phase content, microstructure, and macro-structure (shape, dimensions) of the resulting composites were evaluated with x-ray diffraction analyses (using Cu-K α radiation and a scan rate of 0.5°C/min), scanning electron microscopy⁴, and optical microscopy. For microscopic analyses, specimens were cross-sectioned with a diamond wafering saw and then polished with a series of SiC-embedded papers.

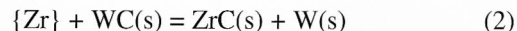
3. Results and Discussion

Owing to its relatively high affinity for carbon, pure molten zirconium will undergo the following displacement reaction with solid tungsten:



Indeed, the Gibbs free energy change per mole of this reaction at 1900°C is -144.8 kJ/mole [25]. This reaction is also strongly favored for zirconium-bearing liquids at temperatures well below the melting point of pure zirconium (1852 \pm 2°C [26]).

For example, the standard Gibbs free energy change for the reaction



at 1200°C is -149.5 kJ/mole (where {Zr} refers to Zr dissolved in a liquid metal solution and where a pure liquid Zr reference state and pure solid WC, ZrC, and W reference states are assumed) [25]. The activity of zirconium dissolved within a liquid metal solution would need to drop below 5.0×10^{-6} in order for reaction (2) to be avoided at 1200°C. Hence, it is likely that Zr-rich liquids will undergo displacement reactions with WC at temperatures well below the melting point of pure Zr. In order to allow for pressureless reaction casting into porous WC preforms, a Zr-bearing liquid must wet WC. Upon reaction, the Zr-depleted liquid should also exhibit minimal reaction with the solid W product (e.g., to avoid the formation of low-melting W compounds or alloys). The Zr_2Cu liquid used in the present work satisfied these conditions. Zr_2Cu melts congruently at only 1025°C (i.e., far below the melting point of pure zirconium [24]). At =1100°C, $\text{Zr}_2\text{Cu(l)}$ was observed to wet and quickly infiltrate into porous WC-bearing preforms. The zirconium in this liquid can undergo the following net reaction with solid tungsten carbide at =1200°C:



where {Cu} refers to Cu-rich liquid (note: the peak liquidus temperature for Cu-Zr compositions with >33.3 at% Cu is 1115°C [24]). Molten copper does not form stable compounds with ZrC or W and has negligible solubility in either phase (indeed, the melting point of W is lowered by only 8°C in the presence of Cu [27]).

Secondary and backscattered electron images, and associated x-ray maps, of a polished cross-section of a composite produced by the reactive infiltration of molten Zr_2Cu with a porous WC preform at 1300°C are shown in Figs. 1a-f. Similar microstructures were obtained for reaction times of 1-8 h at this temperature. The resulting composite was quite dense, with only a few isolated, fine pores detected in the secondary electron images. The composite consisted of two major phases: a bright particulate phase and a grey matrix phase. The x-ray maps indicate that the bright phase in Fig. 1b was enriched in tungsten, whereas the dark phase was enriched in zirconium and carbon. Comparison of these x-ray maps with x-ray diffraction (XRD, Fig. 2a) and energy dispersive x-ray (EDX) analyses of this specimen confirmed that the dark and bright phases were ZrC and W, respectively. The presence of polishing scratches running through the bright W phase, and the absence of such scratches in the dark ZrC phase, were also consistent with the known difference in hardness between ZrC and W [1,4,6,7].

¹Johnson Matthey, Ward Hill, MA

²Aldrich Chemical Co., St. Louis, MO

³Air Products and Chemicals, Inc., Allentown, PA

⁴Model XL-30 FEG-SEM, Philips Electron Instruments, Eindhoven, The Netherlands

High-contrast backscattered electron images also revealed a fine minor phase (not seen in Fig. 1). Although this phase was too fine to allow for unambiguous identification by EDX analysis (due to beam overlap with neighboring phases), such analysis did indicate that this phase was Cu-rich. Under an optical microscope, this phase possessed a tan color which was consistent with copper. Image analyses of several cross-sections indicated that this composite was comprised of 45.1 vol% zirconium carbide, 45.9 vol% tungsten, and 9.0 vol% copper. (Note: the absence of distinct diffraction peaks for a Cu-rich phase in Fig. 2a is likely to be due to the small amount and relatively poor x-ray scattering of this phase compared to W or ZrC.)

The absence of diffraction peaks for WC, Zr₂Cu, and Zr-Cu-bearing phases in Fig. 2a indicated that the displacement reaction (3) had gone essentially completion in this sample. The presence of polishing scratches running completely through the W particles also confirmed that the WC had been completely consumed. The absence of diffraction peaks for Cu or Cu-bearing phases revealed that the molten Cu-rich liquid product of reaction (3) had been largely extruded from the specimen at 1300°C. This was not surprising, given the change in solid volume associated with the displacement reaction. The solid products of reaction (3), ZrC + W, possess a combined volume that is close to twice (100.8%) the volume of the solid reactant, WC.

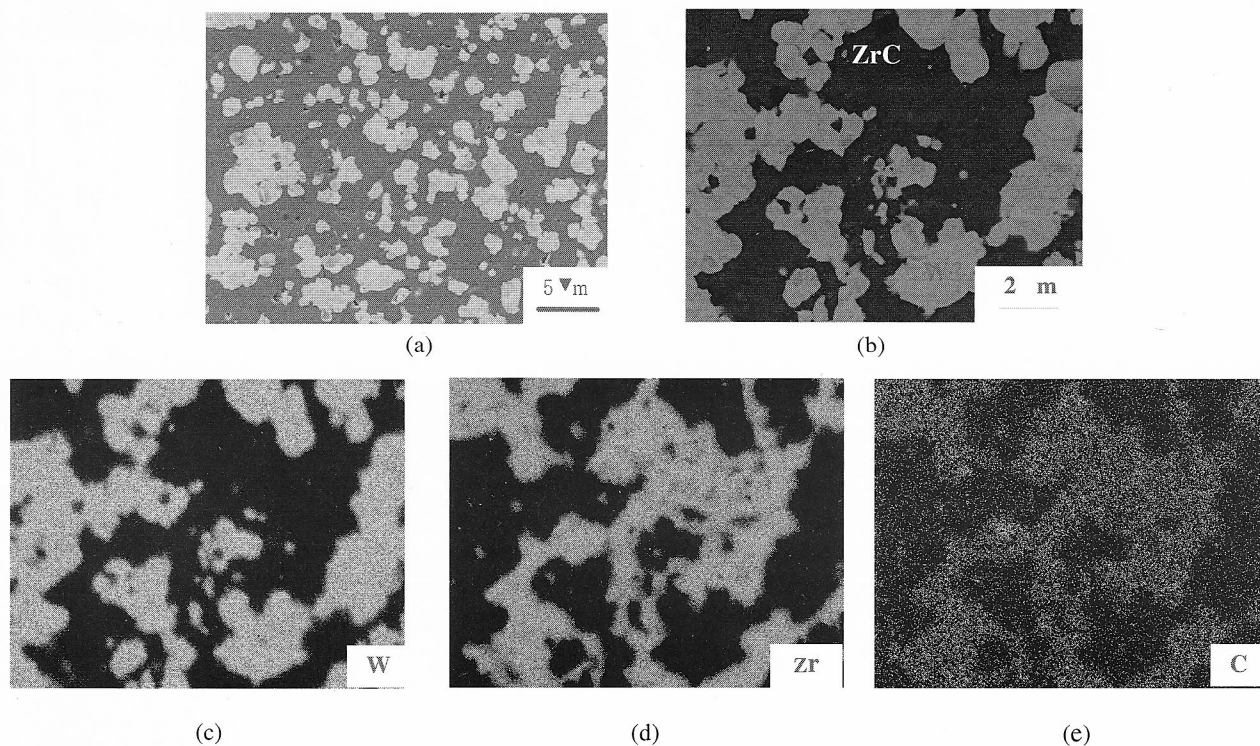


Fig. 1. a) Secondary electron image, and b) backscattered electron image with associated x-ray maps for c) W, d) Zr, and e) C obtained from a polished cross-section of a ZrC/W composite produced by the reaction casting of Zr₂Cu(l) into a porous WC preform at 1300°C.

Hence, a rigid, pure WC preform must possess at least 50.2% porosity in order to accommodate this increase in internal solid volume without a change in external dimensions. Because the preform used to generate the composite shown in Fig. 1 possessed a relative porosity of 51.6%, the near doubling of internal solid volume associated with reaction (3) caused the prior pore volume to become largely filled with ZrC and W (reaction-induced densification) so that only a small amount of residual Cu-rich liquid was retained in the specimen. Furthermore, because the specimen remained rigid as the WC network in the starting preform was replaced by a more voluminous ZrC+W network,

the final composite retained the shape and dimensions of the starting preform. Dimensional measurements of bar and disk-shaped specimens before and after reaction casting yielded average dimensional changes of less than 1%. The carbide-to-metal ratio in the final composite can be modified by altering the preform porosity and/or the preform phase content. Prior work has demonstrated that rigid, pure WC reforms with less than 50% porosity can be converted into dense, near net-shaped ZrC/WC/W composites with a total carbide (ZrC + WC) content in excess of 70 vol% (i.e., a carbide-to-metal ratio in excess of 2.3:1) [17].

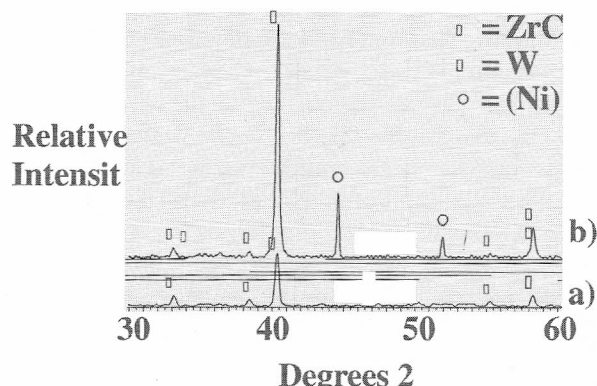
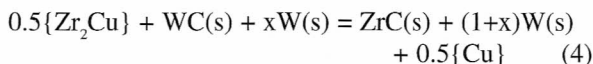


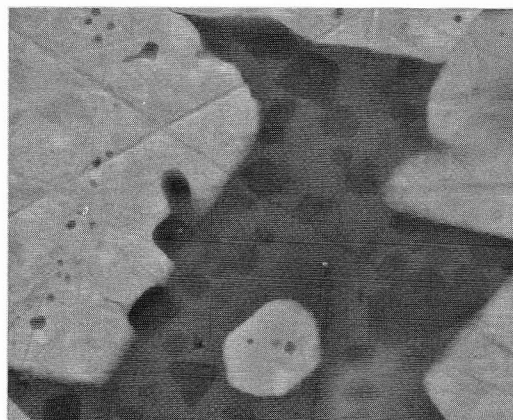
Fig. 2. XRD patterns of ZrC/W-bearing composites produced by the reaction casting of $Zr_2Cu(l)$ into: a) a porous WC preform at 1300°C and b) a porous, Ni-doped W/WC preform at 1250°C.

In this case, the preform pore volume was filled prior to complete consumption of the WC. In order to produce fully-reacted, tungsten-rich composites, some of the WC in the preform can be replaced with inert W, as indicated by the following reaction:

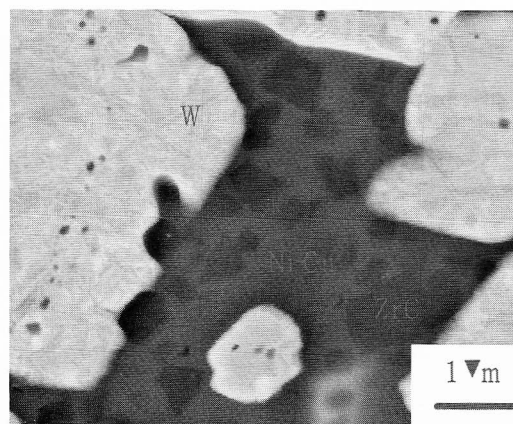


In the present work, preforms were prepared with a W:WC molar ratio as high as 5.8. A small amount of nickel (5-10 wt%) was also added to such tungsten-rich preforms to reduce the sintering temperature required for producing a rigid preform [23].

Secondary and backscattered electron images of a composite generated by the reaction casting of molten Zr_2Cu into a W-rich preform (W:WC = 5.8) at 1250°C are shown in Figs. 3 and 4. Three distinct phases can be observed in this dense composite: relatively large bright particles, finer dark particles, and a grey matrix phase. EDX analyses revealed that the bright particles were comprised of only tungsten. Although the fine dark particles and the grey matrix phase were too fine to allow for precise chemical evaluation by EDX analyses, the x-ray maps in Fig. 4 indicated that regions with a high density of dark particles were enriched in zirconium whereas the grey matrix was enriched in copper and nickel. XRD analysis of this composite (Fig. 2b) revealed diffraction peaks for W, ZrC, and a Ni-rich phase, which suggested that the dark particles seen in Fig. 3b were comprised of ZrC and the lighter grey matrix was comprised of a Ni-Cu alloy. This phase assignment was also consistent with the relative brightnesses of these phases seen in the backscattered electron (BSE) images of Figs. 3b and 4a, and with the relative hardnesses of these phases as indicated by scratch patterns in the secondary electron (SE) image of Fig. 3a. ZrC possesses a lower average atomic number than Ni-Cu alloys and, hence, appears darker in BSE images.



(a)



(b)

Fig. 3. a) Secondary electron image and b) backscattered electron image of a polished cross-section of a W/WC/Ni-Cu alloy composite produced by the reaction casting of $Zr_2Cu(l)$ into a porous Ni-doped-W/WC preform at 1250°C.

The observation of polishing scratches running across the bright W particles and the grey Ni-Cu matrix, but not across the darker ZrC particles, was also consistent with the considerably higher hardness of ZrC relative to W or Ni-Cu alloys [1, 4, 6, 7].

The absence of diffraction peaks for WC and Zr_2Cu in Fig. 2b indicated that these reactants were completely consumed within 4 h at 1250°C to produce the composite shown in Figs. 3 and 4. As expected, the relative intensities of the diffraction peaks for W, compared to those for ZrC, were higher for the composite derived from the W/WC preform (Fig. 2b) than for the composite derived from a pure WC preform (Fig. 2a). Image analyses of several polished cross-sections indicated that the dense specimen of Figs. 3 and 4 was comprised of 60.5 vol% W, 17.2 vol% ZrC, and 22.3 vol% Ni-Cu alloy. The change in solid volume upon converting a mixture of 1 mole of WC + 5.8 moles of W into a mixture of 1 mole of ZrC + 6.8 moles of W (i.e. for reaction (4) where $x = 5.8$) was only 18.6%.

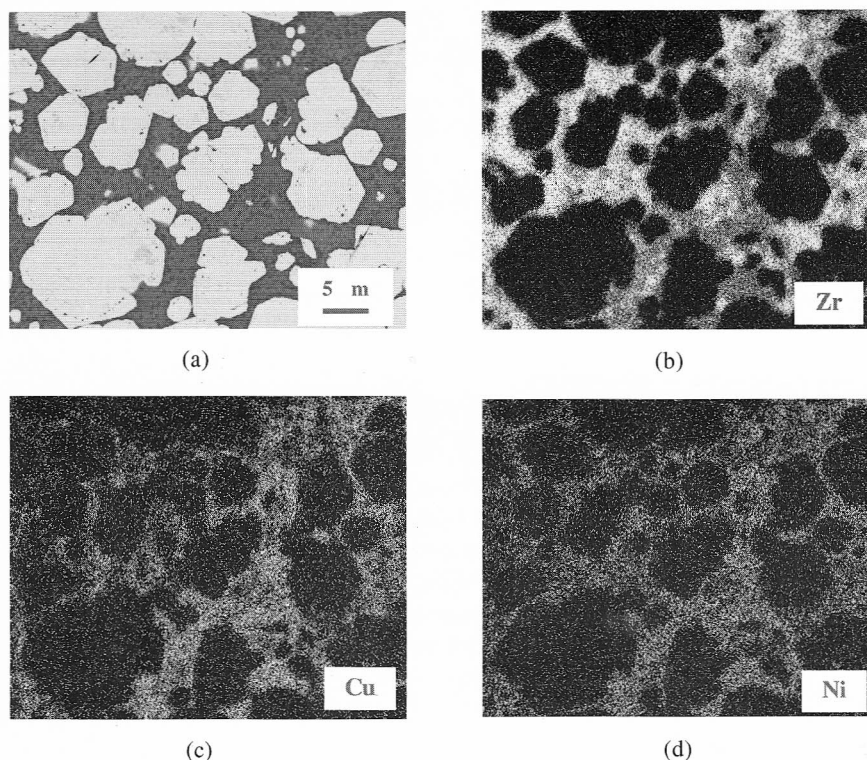


Fig. 4. a) Backscattered electron image and associated x-ray maps for b) Zr, c) Cu, and d) Ni obtained from a polished cross-section of a W/ZrC/Ni-Cu alloy composite produced by the reaction casting of $Zr_2Cu(l)$ into a porous Ni-doped W/WC preform at 1250°C.

Because the relative porosity of the W/WC-bearing preform used to produce this composite was 44.0%, the available pore volume was well beyond that needed to accommodate the reaction-induced increase in internal solid volume. Consequently, an appreciable amount of residual Cu(l) was retained within the specimen. This molten copper reacted with the nickel to produce the grey Ni-Cu alloy phase seen in Fig. 3. It is interesting to note that many of the bright W particles and dark ZrC particles seen in Figs. 3 and 4 possessed flat surfaces. Such faceted grains are likely to have formed so as to minimize solid/liquid interfacial energies at 1250°C.

4. Conclusions

Shaped, carbide-bearing preforms with controlled pore and phase contents can be converted at modest temperatures (1200-1300°C) and ambient pressure into dense, near net-shaped, refractory metal/carbide-bearing composites with a wide range of phase contents by the **PRIMA-DCP** process. A Zr-Cu liquid, formed by the congruent melting of Zr_2Cu at 1025°C, was reaction cast into WC and W/WC-bearing preforms at 1200-1300°C. Upon infiltration, the Zr in the metallic liquid underwent a displacement (oxidation-reduction) reaction with the solid WC in the preforms to yield the solid products, ZrC and W. Because these solid products possessed a combined volume that was nearly twice

the volume of the consumed WC, this reaction could be used to fill the pores within rigid, WC-bearing preforms. The reaction casting of $Zr_2Cu(l)$ into a WC preform with a relative porosity of 51.8% yielded a dense composite comprised of 45.1 vol% ZrC, 45.9 vol% W, and 9.0 vol% Cu. Because the specimen remained rigid during the course of such reactive infiltration, the final dense composite retained the shape and dimensions (to within 1%) of the starting porous preform. Composites with reduced carbide contents were fabricated by replacing some of the WC in the preform with inert metallic W. A dense composite comprised of 60.5 vol% W, 17.2 vol% ZrC, and 22.3 vol% Ni-Cu alloy was produced within 4 h at 1250°C by the reaction casting of $Zr_2Cu(l)$ into a porous, Ni-doped preform with a W:WC ratio of 5.8:1.

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