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The fundamental conversion mechanism for the following net liquid/solid displacement reaction has been examined: (Zr) + WC(s)=ZrC(s)+W(s) (1) where (Zr) refers to zirconium dissolved within a Zr-Cu melt. Such mechanistic knowledge is needed in order to be able to predict the time required, under various processing conditions, for full conversion of porous WC performs into dense ZrC/W composites (e.g., for rocket nozzle applications) by the DCP method. For this fundamental study, dense wafers of WC were prepared by hot isostatic pressing at 1850oC. The wafers were then immersed in a vertical orientation in a Zr-Cu melt at temperatures in the range of 1150-1400oC for times up to 24 hours. After such exposure, the polished WC surfaces were found to be coated with two reaction product layers. A layer of tungsten was observed to be in direct contact with the WC. A second, external layer of ZrC separated the W layer from the melt. The thicknesses of the W and ZrC layers were found to: i) increase at a parabolic rate with time, ii) be independent of the relative vertical position on the WC surface, and iii) increase

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AFOSR Final Performance Report

Project Title:	Fabrication of Dense, Near Net-Shaped W/ZrC Composites by the PRIMA-DCP Process
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Start Date:	Aug. 1, 2001
Program Manager:	Dr. Joan Fuller Program Manager Ceramic and Non-Metallic Materials Program Air Force Office of Scientific Research 801 N. Randolph St., Room 732 Arlington, VA 22203-1977 E-mail: joan.fuller@afosr.af.mil Phone: (703) 696-7236 Fax: (703) 696-8451
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Objective:

This project has been focused on developing a better understanding of the fundamental kinetic mechanism(s) (i.e., rate-limiting step(s), kinetic rate law(s)) of the DCP (Displacive Compensation of Porosity) process for fabricating ZrC/W composites.

Approach and Key Results:

The fundamental conversion mechanism for the following net liquid/solid displacement reaction has been examined:

$$(Zr) + WC(s) = ZrC(s) + W(s) \qquad (1)$$

where (Zr) refers to zirconium dissolved within a Zr-Cu melt. Such mechanistic knowledge is needed in order to be able to predict the time required, under various processing conditions, for full conversion of porous WC preforms into dense ZrC/W composites (e.g., for rocket nozzle applications) by the DCP method. For this fundamental study, dense wafers of WC were prepared by hot isostatic pressing at 1850°C. The wafers were then immersed in a vertical orientation in a Zr-Cu melt at temperatures in the range of 1150-1400°C for times up to 24 hours. After such exposure, the polished WC surfaces were found to be coated with two reaction product layers. A layer of tungsten was observed to be in direct contact with the WC. A second, external layer of ZrC separated the W layer from the melt. The thicknesses of the W and ZrC layers were found to: i) increase at a parabolic rate with time, ii) be independent of the relative vertical position on the WC surface, and iii) increase exponentially with temperature (i.e., Arrhenius behavior).

Conclusions:

The effects of time, temperature, and vertical position on the thickening rates of the W and ZrC product layers, and the influence of infrequent disruptions in these product layers on the local WC consumption rate, indicated that the passive incongruent reduction of WC by reaction with a Zr-Cu melt was controlled by solid-state diffusion of carbon (either through the lattice of the W layer and/or through grain boundaries in the ZrC layer).

Fuller

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Final Project Report

"Fabrication of Dense, Near Net-Shaped W/ZrC Composite by the PRIMA-DCP Process"

Project Award No. F49620-01-1-0477

Air Force Office of Scientific Research

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Dense, Near Net-Shaped, Carbide/Refractory Metal Composites at Modest Temperatures by the Displacive Compensation of Porosity (DCP) Method

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Dense, near-net-shaped, carbide-rich, carbide/tungsten composites have been produced at modest temperatures by the displacive compensation of porosity (DCP) method. Porous, freestanding WC preforms were infiltrated and reacted with a Zr_2Cu liquid at 1300°C and ambient pressure. The carbon in the WC was displaced by zirconium in the melt to yield ZrC_x and tungsten. The increase in solid volume associated with this displacement reaction was compensated by the prior pore volume of the preform. Dense ZrC_x/WC/W composites that possessed <5 vol% residual copper-bearing phase, and retained the shape and dimensions of the preform, were produced.

I. Introduction

DISPLACEMENT reactions involving liquid metals have been used by several authors[1–8] over the past decade to convert ceramic preforms into dense, near net-shaped oxide/metal or oxide/intermetallic composites at modest temperatures. For example, Al_2O_3/Al-Si, $Al_2O_3/TiAl_3$, MgO/Mg-Al, and $MgAl_2O_4$/Fe-Ni-Al composites have been produced by reactive penetration or reactive infiltration of aluminum-bearing or magnesium-bearing liquids into shaped oxide preforms at 900°–1200°C.[1–7] Dense, non-oxide/metal composites have also been produced by displacement reactions, although at much higher processing temperatures. For example, dense ZrB_2/ZrC/Zr composites have been produced by the reaction of molten zirconium with porous B_4C powder beds (within graphite molds) at 1850°–2000°C.[8]

The purpose of this paper is to demonstrate that porous, rigid carbide preforms can be converted at modest temperatures into dense, near-net-shaped, carbide/refractory metal composites by the displacive compensation of porosity (DCP) method.[4,5] In this work, a Zr_2Cu liquid is allowed to infiltrate and undergo the following displacement reaction with a porous WC preform at 1300°C:

$$\{Zr\} + xWC(s) \rightarrow ZrC_x(s) + xW(s) \quad (1)$$

where {Zr} refers to zirconium present in molten Zr_2Cu. Zr_2Cu melts congruently only at 1025°C (i.e., ~800°C lower than pure zirconium).[9] A thermodynamic calculation using available data for ZrC_x, WC, and Zr-Cu alloy liquids indicates that reaction (1) should proceed spontaneously at 1300°C for Zr-Cu melts with >0.092 at.% zirconium.[10–12] The products of this reaction, $ZrC_x(s)$ and W(s), possess a combined volume that is larger than the molar volume of WC(s).[13] This displacement-reaction-induced increase in solid volume can be used to fill the prior pore volume of the preform ("displacive compensation of porosity"). As the internal solid content of the preform increases at 1300°C, the residual copper-enriched liquid can be extruded back out of the body. Hence, copper can act as an attractive fugitive element, by greatly reducing the temperature required for reactive infiltration and then leaving the specimen via extrusion during reaction. Furthermore, since copper exhibits negligible chemical interaction with zirconium carbide, tungsten carbide, and tungsten, small amounts of entrained copper should not degrade the refractoriness of the final composite (e.g., the melting point of tungsten, 3410° ± 20°C, is reduced only by 8°C in the presence of copper).[14] Indeed, modest additions of copper to tungsten have been proposed to enhance the ductility, toughness, and thermal conductivity of tungsten-bearing composites used in rocket combustion chambers and nozzles.[15]

II. Experimental Procedure

Porous WC preforms were prepared from a mixture of WC powder (99.9% purity, 10 μm average size, Aldrich Chemical Co., St. Louis, MO) with 5 wt% of an aqueous solution of 4 wt% poly(vinyl alcohol) (Airvol 2005 PVA, Air Products and Chemicals, Allentown, PA). The mixture was uniaxially pressed into bars (50 mm × 11.5 mm × 3 mm) at a peak stress of 240 MPa. The green bars were heated to 400°C for 4 h in flowing argon (to remove the PVA binder) and then to 1700°C for 2 h in a vacuum furnace (to produce rigid preforms). The bars were cut and ground into plates (12 mm × 11.3 mm × 3 mm) for subsequent reactive infiltration with Zr_2Cu liquid.

A Zr_2Cu ingot was prepared by induction melting. A 1 kg charge comprised of zirconium sponge (99.6% purity, 0.8–19 mm diameter pieces, Johnson-Matthey, Ward Hill, MA) and a copper rod (99.99% purity, 2.5 cm diameter × 5.9 cm thick, Atomergic Chemetals, Farmingdale, NY) was placed within a magnesia crucible (99.4% purity, 96% dense, 10.2 cm diameter × 15.2 cm high, Ozark Technical Ceramics, Webb City, MO). The charge was 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.% zirconium/32.5 at.% copper, which was close to the desired Zr_2Cu composition. X-ray diffraction (XRD) analyses of the ground ingot also revealed peaks consistent with Zr_2Cu.

Before reactive infiltration, pieces of the solid Zr_2Cu ingot were placed on top of the WC preform within a flat-bottomed magnesia

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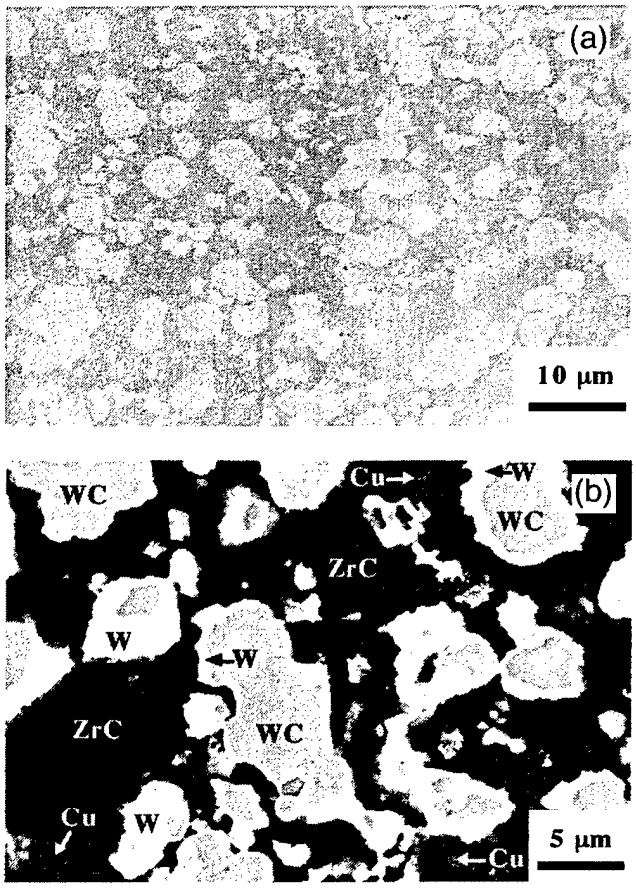

Fig. 2. SEM micrographs ((a) secondary electron image and (b) back-scattered electron image) of a polished cross section of a composite specimen produced by the reactive infiltration of $Zr_2Cu(l)$ into porous WC(*s*) at 1300°C.

the mixture of solid products shown in reaction (2). On reactive infiltration, the specimen increased in weight by a factor of 1.34, which was similar to the weight gain expected for the reaction shown in reaction (2) (i.e., a factor of 1.39).

The reaction-induced increase in volume associated with reaction (2) was sufficient to fill the pores within the WC preform with little change in external dimensions (see Table I). The 55.1% dense WC preform of Fig. 1(a) was converted to the 99.6% dense ZrC/WC/W-bearing composite shown in Figs. 1(b) and (c) (ρ_{theo}[WC] = 15.67 g/cm^3, ρ_{theo}[composite] = 11.54 g/cm^3).[13] Micrometer measurements indicated that the volume of the final composite was only 0.87% larger than that of the starting preform. Hence, the volume of solid within the final composite must have been a factor of 1.82 times larger than that of the preform (i.e., 1.0087(99.6)/55.1 = 1.82). This value was not far from the factor of 1.89 increase in volume calculated for reaction (2).[13] As the internal solid volume increased at 1300°C, residual copper-enriched liquid was extruded back out of the specimen, so that only a small amount (4.5 vol%) of a copper-rich phase was retained in the final composite. Because the preform remained rigid during the course of such reactive infiltration, the shape and dimensions of the preform were retained in the final composite to within 1.3%.

IV. Conclusions

The feasibility of fabricating dense, near net-shaped, carbide-rich ZrC_y/WC/W-bearing composites at 1300°C by the displacive compensation of porosity (DCP) method has been demonstrated. On infiltration of porous WC with molten Zr_2Cu, the zirconium in the liquid underwent a displacement reaction with the WC to yield ZrC_y and tungsten. The net increase in internal solid content due to this reaction caused residual copper-enriched liquid to be squeezed back out of the preform, thereby yielding a 99.6% dense ZrC_y/WC/W-based composite with little residual copper. Image analyses yielded a phase content of 48.8 vol% $ZrC_{0.676}$, 26.4 vol% WC, 20.3 vol% tungsten, and 4.5 vol% copper-rich phase. This phase assemblage was also consistent with carbon analysis, X-ray diffraction analysis, and the observed weight change. Because the preform remained rigid during the course of the pore-filling displacement reaction, the shape was retained with little change (−0.08 to +1.3%) in external dimensions.

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LOW-TEMPERATURE FABRICATION OF DENSE, NEAR NET-SHAPED TUNGSTEN/ZIRCONIUM CARBIDE COMPOSITES WITH TAILORED PHASE CONTENTS BY THE PRIMA-DCP PROCESS

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ABSTRACT

Refractory metal/carbide composites can possess unique and attractive combinations of properties for aerospace and other applications. A novel process for fabricating dense, near net-shaped refractory metal/carbide composites at modest temperatures has recently been demonstrated: the PRIMA-DCP process (Pressureless Reversible Infiltration of Molten Alloys by the Displacive Compensation of Porosity). In this paper, the PRIMA-DCP process is used to synthesize W/ZrC-bearing composites with tailored phase contents. Porous, but rigid WC-bearing preforms were pressureless infiltrated with a Zr-Cu liquid at 1200-1300°C. Upon infiltration, the Zr in the liquid underwent a displacement (oxidation-reduction) reaction with WC to yield a solid mixture of ZrC and W. The reaction-induced increase in internal solid volume was accommodated by the prior pore volume of the rigid preform ("displacive compensation of porosity"). As the solid products filled the pores, the unreacted liquid was extruded back out of the preform ("reversible infiltration"), so that dense composites were produced with little change in the external dimensions. By varying the W:WC ratio of the preforms, composites with tailored phase contents (i.e., varied amounts of ZrC) could be produced.

INTRODUCTION

The high melting point (3410±20°C) and exceptional high-temperature properties (low vapor pressure, high modulus and strength, good creep resistance) of tungsten have made this refractory metal, and alloys based on this metal, attractive for use in a variety of aerospace components, such as rocket nozzles, heat shields, combustion chamber liners, hot gas valves, and other parts [1-5]. However, commercially pure tungsten and tungsten-based alloys are also

relatively heavy (i.e., densities are in the range of 17.1-19.3 g/cm^3) and can be difficult to produce in complex shapes at low cost [1-4]. Refractory, tungsten-bearing composites that are lighter than conventional tungsten-based alloys, and that can be more readily fabricated into desired shapes, could be attractive for advanced aerospace applications.

Composites of tungsten with refractory carbides (e.g., TiC, ZrC, HfC, NbC, TaC) can exhibit an attractive combination of chemical, thermal, and mechanical properties. For example, consider composites of tungsten and zirconium carbide, ZrC. Zirconium carbide is a high-melting (up to 3420°C), hard (up to 2900 kg/mm^2) compound with a density that is nearly 1/3 of that for tungsten (ρ[ZrC] = 6.63 g/cm^3) [6-8]. Tungsten and zirconium carbide are chemically and thermally compatible. That is, these phases: i) do not react to form stable intermediate compounds, ii) exhibit limited mutual solid solubility, iii) possess similar thermal expansion coefficients[1], and iv) are relatively good thermal conductors at high temperatures[2] [1,3,4,9-13]. Composites of W and ZrC can also possess improved mechanical performance relative to monolithic W or ZrC. W-rich composites can be quite resistant to fracture above about 400°C (i.e., above the brittle-to-ductile transformation temperature of tungsten) [1,4]. For example, Song, et al. reported that composites with 80 vol% W/20 vol% ZrC possessed flexure strengths of 979 MPa at 1200°C [14]. On the other hand, ZrC-rich composites should exhibit enhanced creep resistance relative to tungsten or tungsten-rich alloys above 2000°C (i.e., above the typical recrystallization temperatures for W and W-rich alloys) [3-5,7,15].

Dense, refractory W/ZrC composites with relatively complicated (non-axisymmetric) shapes may be produced by hot pressing or hot isostatic pressing (e.g., at $\geq$2000°C) followed by machining [3,14]. However, given the relatively high costs associated with such high-temperature, labor-intensive batch processing, alternative fabrication routes capable of yielding dense, near net-shaped composites at lower temperatures and at ambient pressure (i.e., for continuous processing) would be strongly preferred.

A novel reactive-infiltration process for fabricating dense, near net-shaped carbide/refractory metal composites at modest temperatures ($\leq$1300°C) has recently been demonstrated at Ohio State University [16-18]. This process, referred to as the PRIMA-DCP method[3], involves the pressureless infiltration of a low-melting metallic liquid into, and reaction with, a porous, rigid, ceramic-bearing preform. The metallic liquid contains an element that can undergo a

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[1]Average linear CTE values from 25°C to 2700°C range from 4.5X10^{-6}/°C to 9.2X10^{-6}/°C for W and 4.0X10^{-6}/°C to 10.2X10^{-6}/°C for ZrC [12,13].

[2]W and ZrC possess thermal conductivities of 105±10 W/m-K and 40±10 W/m-K, respectively, from 1000-2200°C [3,4,10,11]

[3]Pressureless Reversible Infiltration of Molten Alloys by the Displacive Compensation of Porosity

displacement (oxidation-reduction) reaction with a ceramic phase in the preform. Because the displacement reaction is designed to yield a larger volume of solid product(s) than is consumed, the original pore volume in the preform becomes filled with the new solid during reaction ("displacive compensation of porosity"). The increase in internal solid volume causes the low-melting metallic liquid within the infiltrated rigid preform to be extruded back out ("reversible infiltration"), so that a dense, refractory composite that retains the preform shape and dimensions is produced. Recent work with the PRIMA-DCP process demonstrated that dense, ZrC/WC/W-based composites could be produced within 1-2 h by the pressureless infiltration of a Zr-Cu liquid into, a partial reaction with, porous WC preforms at 1200-1300°C [16]. The resulting carbide-rich composites contained little residual copper (only 5.9 vol%), and retained the shapes and dimensions of the starting preforms (i.e., the average dimensional changes were less than 1%).

The objective of the present paper is to demonstrate the feasibility of using the PRIMA-DCP process to produce dense, near net-shaped, fully-reacted ZrC/W-based composites with a range of ZrC contents at ≤1300°C.

EXPERIMENTAL PROCEDURE

Two types of porous preforms were prepared: i) WC preforms (for ZrC-rich composites) and ii) W/WC preforms (for W-rich composites). The molar W/WC ratio in the latter preforms was varied from 0.59 to 5.8. The tungsten carbide (Aldrich Chemical Co., St. Louis, MO) and tungsten (Johnson Matthey, Ward Hill, MA) were obtained as powders with particle sizes of <10 μm and <12 μm, respectively, and purities in excess of 99.9%. For some of the W/WC preforms, nickel powder (≤3.0 μm, 99.9% purity, Johnson Matthey) was introduced (5-10 wt%) as a sintering aid [19]. The powders were mixed in a mortar and pestle with 5 wt% of an aqueous 4 wt% solution of polyvinyl alcohol (Grade Airvol 205, Air Products and Chemicals, Inc., Allentown, PA). The preforms were produced in the shape of disks (1.3 cm dia. X 3.5 mm thick) by uniaxial pressing of the powder/binder mixtures at a peak stress of 84 MPa. The binder was then removed by heating at 400°C for 4 h in flowing Ar. The preforms were then annealed in flowing argon for either 0.5 h at 1100°C (for Ni-doped specimens) or for 2 h at 1750°C (for Ni-free specimens).

The porous WC-bearing preforms were infiltrated with a Zr_2Cu liquid (T_{fusion} = 1025°C [20]). A 1 kg ingot of Zr_2Cu was produced by induction melting of a copper rod (2.5 cm dia. x 5.9 cm thick, 99.9% purity) and zirconium sponge (0.8-19 mm dia. pieces, 99.6% purity, Johnson-Matthey, Inc., Ward Hill, MA) within a magnesia crucible (10.2 cm dia. x 15.2 cm high, Ozark Technical Ceramics, Inc., Webb City, MO). Prior to melting, the Zr-Cu charge was sealed in an argon atmosphere within a silica enclosure. Induction melting/stirring was conducted

with a 60 kV power supply for 4 minutes. The melt was then allowed to cool to room temperature within the argon atmosphere. The composition of the cast ingot was determined by inductively-coupled plasma spectroscopic analysis (Optima 3000 ICP-OES, Perkin-Elmer Corp., Norwalk, CT) to be 67.5 at% Zr/32.5 at% Cu (i.e., close to the Zr_2Cu composition). XRD analyses of the ingot yielded diffraction peaks for only the Zr_2Cu phase.

Prior to a given reactive infiltration experiment, pieces of the solid Zr_2Cu ingot were placed above a disk-shaped preform inside a magnesia crucible (Ozark Technical Ceramics, Inc.). The molar ratio of Zr_2Cu:WC used in each experiment was 1.5-1.6:1, which was in excess of the amount required for complete consumption of the WC. After purging the tube furnace with flowing Ar for 2-3 h, the Zr_2Cu-covered preforms were heated at 7°C/min to 1200-1300°C for 1-8 h. The specimens were then cooled at 7°C/min under the flowing argon atmosphere. The phase content and microstructure of the resulting specimens were evaluated with x-ray diffraction (XRD) analyses (i.e., using Cu-Kα radiation and a scan rate of 0.5°C/min) and scanning electron microscopy (Model XL-30 SEM, Philips Electron Instruments, Eindhoven, The Netherlands).

RESULTS & DISCUSSION

Consider the following displacement reaction between molten zirconium, {Zr}, and solid tungsten carbide:

$$\{Zr\} + WC(s) = ZrC(s) + W(s) \qquad (1)$$

The standard Gibbs free energy change for this reaction at temperatures above the Zr melting point (1852±2°C) is strongly negative (e.g., $\Delta G°_{rxn}(1900°C) = -144.8$ kJ/mole), so that a WC preform infiltrated with Zr(l) should spontaneously react to yield a solid mixture of ZrC and W [21,22]. Alternately, by using a low-melting, Zr-rich alloy instead of pure Zr(l), this reaction may be conducted at temperatures well below the zirconium melting point. The Zr_2Cu composition chosen for the present work is particularly attractive as this compound melts congruently at only 1025°C (i.e., more than 800°C lower than pure Zr) [20,22]. Furthermore, the Gibbs free energy change of reaction (1) for the case where {Zr} is present in molten Zr_2Cu remains strongly negative at modest temperatures (e.g., $\Delta G_{rxn}(1200°C) = -136.8$ kJ/mole) [21,23]. The residual liquid copper generated upon removal of the zirconium from the Zr_2Cu liquid by reaction (1) can not form stable compounds with ZrC or W. Copper also has minimal effect on the melting point of tungsten (a decrease of only about 8°C) [24]. Indeed, copper additions to tungsten have been used for transpiration cooling and to enhance the thermal conductivity, ductility, and toughness of W-based components used in rocket nozzles and combustion chambers [3,4,25].

The phases generated upon the infiltration and reaction of the Zr_2Cu liquid into a porous WC preform at 1300°C for 8 h are shown in the XRD pattern in Fig. 1a. The presence of diffraction peaks for W and ZrC, and the absence of peaks for WC, Zr_2Cu, or other Zr-Cu compounds (e.g., $Cu_{10}Zr_7$, $Cu_{51}Zr_{14}$, Cu_8Zr_3, Cu_5Zr, CuZr) are consistent with complete consumption of the WC in the starting preform. Secondary and backscattered electron images of a polished cross-section of such a specimen are shown in Figs. 2a-c. The secondary electron image reveals a dense microstructure with a small amount of isolated, fine pores. The backscattered electron images reveal two major phases (i.e., bright particles and a grey matrix phase) and a minor phase (i.e., a relatively bright phase outlining some of grey grains in the matrix; see Fig. 2c). Energy dispersive x-ray (EDX) analyses indicated that the relatively bright particles are comprised of tungsten, whereas the grey matrix phase is zirconium carbide (i.e., the major phases seen in Figs. 2b and 2c are consistent with the XRD pattern in Fig. 1a). The x-ray map shown in Fig. 2d indicates that the minor phase surrounding some of the ZrC grains is Cu-rich. This phase possessed a tan color in an optical microscope, which was consistent with copper. Image analyses of the backscattered electron images indicated that this specimen was comprised of 45.1 vol% zirconium carbide, 45.9 vol% tungsten, and 9.0 vol% copper. The absence of diffraction peaks for copper phase in the XRD pattern of Fig. 1a is likely to be due to the relatively small amount of this phase in the specimen.

The WC preform for the specimen shown in Fig. 2 possessed a density of 7.58 g/cm^3, which corresponds to a porosity of 51.6% (the theoretical density of WC is 15.67 g/cm^3) [8]. The volume change associated with the complete conversion of WC into a solid mixture of ZrC and W is +101% (i.e., the solid volume nearly doubles) [8]. Hence, the total pore volume within this preform was sufficient to accommodate the volume increase resulting from complete consumption of the WC by reaction (1). Prior work at OSU has shown that preforms with less than 50% porosity require times well in excess of 8 h at 1300°C to achieve complete reaction of the WC [16]; that is, if the pore channels become plugged with new solid prior to complete consumption of the WC, then an appreciably longer time is required to complete the reaction. Because the pore volume for the specimen in Fig. 2 was largely filled by the reaction-formed ZrC and W, most of the excess, unreacted (Cu-rich) liquid was squeezed back out of the specimen. Residual, solidified Cu-rich phase trapped within the specimen can be seen in Fig. 2c. Because the lightly-sintered preform remained rigid during the course of the reaction, the external dimensions of the specimens remained essentially unchanged (i.e., the average dimensional changes were less than 1%).

The ZrC content of a fully-reacted, PRIMA-DCP-derived composite should be proportional to the WC content in the original preform. Hence, in order to vary the ZrC content, preforms containing a mixture of W and WC were prepared with

varied W:WC molar ratios (from 0.59 to 5.8). Nickel was also introduced to these W-bearing preforms as a sintering aid to reduce the temperature required to obtain a rigid (yet porous) preform. An XRD pattern obtained after infiltration and reaction of the most tungsten-rich preform for 4 h at 1250°C is shown in Fig. 1b. Again, the presence of diffraction peaks for ZrC and W, and the absence of peaks for WC and Zr-Cu compounds, was consistent with complete consumption of the WC phase. As expected, the peak height ratio for the most intense W reflection (at about $2\theta = 40.3$ degrees) to that for the most intense ZrC reflection (at about $2\theta = 33.1$ degrees) is significantly stronger for this specimen than for the specimen shown in Fig. 1a. Diffraction peaks for nickel were also detected in Fig. 1b. Secondary and backscattered electron images of a polished cross-section of this specimen are shown in Figs. 3a and 3b, respectively. These images reveal a dense specimen with three distinct phases: relatively large bright particles, finer dark particles, and a grey matrix phase. EDX analyses indicated that the bright particles were tungsten (polishing scratches can be seen running across the relatively soft tungsten grains in the secondary electron image in Fig. 3a). The fine dark particles and grey phase in Figs. 3a and 3b were too fine to allow for unambiguous identification by EDX analyses. However, x-ray maps for Zr, Ni, and Cu (Figs. 3c-e) reveal that the zirconium content is highest, and the nickel and copper contents are lowest, in regions where the dark particles are concentrated. Since the only zirconium-bearing phase detected in the sample by XRD analyses was ZrC, the fine dark particles are presumed to be ZrC. Comparison of the XRD pattern in Fig. 1b with the x-ray maps also indicates that the grey matrix phase is a nickel-rich alloy. Using these phase assignments, image analyses indicated that this specimen consisted of 60.5 vol% W, 17.2 vol% ZrC, and 22.3 vol% Ni-rich alloy.

The bulk density of the W/WC-bearing preform used to produce the specimen in Fig. 3 was 10.41 g/cm^3, which corresponds to a relative density of about 59.0%. Because the molar W:WC ratio for this preform was 5.8:1, the complete consumption of WC in this specimen can be described by the reaction:

$$\{Zr\} + 5.8W(s) + WC(s) = ZrC(s) + 6.8W(s) \qquad (2)$$

The increase in internal solid volume associated with this reaction is about 18.6%; that is, the preform porosity (41.0 vol%) was well in excess of that required to accommodate the increase in solid volume due to reaction (2). Upon infiltration, the nickel added to this preform could dissolve into the Zr_2Cu liquid (i.e., the liquidus temperature for Ni-doped Zr_2Cu ranges from 880°C to 1025°C for compositions with up to 30 at% Ni [26]). Because the reaction-induced volume increase was much less than required to fill the prior pore volume in this preform, the unreacted components of the liquid (nickel and copper) could not have been

completely extruded back out of the specimen upon completion of the reaction. Hence, more of this unreacted Ni-bearing metal solidified within this specimen upon cooling.

CONCLUSIONS

The feasibility of using the PRIMA-DCP process to fabricate dense, near net-shaped W/ZrC-bearing composites with a range of phase contents at 1200-1300°C has been demonstrated. Porous, rigid WC preforms and W/WC-bearing preforms were produced by light sintering of powder compacts. Nickel doping was used in some cases to reduce the temperature for initial stage sintering of the preforms from 1750°C to 1100°C. The rigid preforms were then pressureless infiltrated with a Zr_2Cu liquid at 1200-1300°C. Upon infiltration, the Zr in the liquid underwent a displacement reaction with the WC to yield a solid mixture of ZrC and W. Porous WC preforms were converted into dense composites comprised of 45.1 vol% ZrC, 45.9 vol% W, and 9.0 vol% Cu at 1300°C. Ni-doped, W/WC-bearing preforms were converted into dense composites comprised of 60.5 vol% W, 17.2 vol% ZrC, and 22.3 vol% Ni alloy within 4 h at 1250°C. These ZrC-rich composites retained the shapes and dimensions of the porous WC preforms to within a few percent. Further work is underway to determine whether such near net-shaped, ZrC-bearing composites can be fabricated within shorter times (<1 h) at ≤1200°C.

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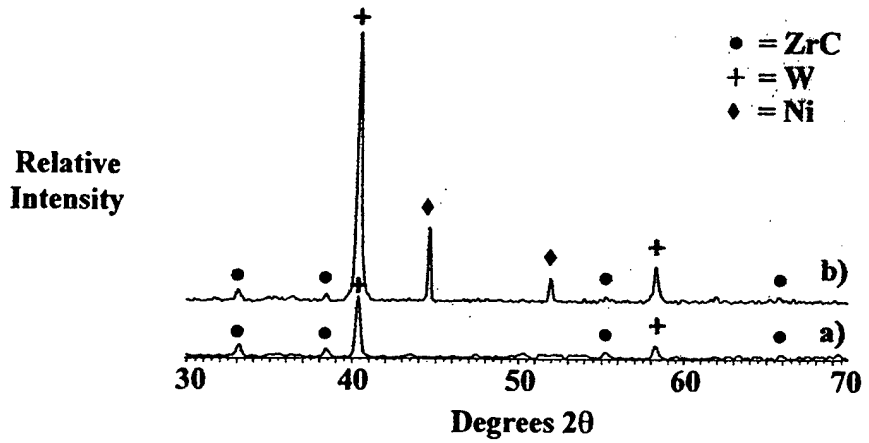


Figure 1. XRD patterns from PRIMA-DCP-derived composites prepared by reactive infiltration of $Zr_2Cu(l)$ into: a) a porous WC preform at 1300°C and b) a porous, Ni-doped W/WC preform at 1250°C (molar W:WC ratio = 5.8:1).

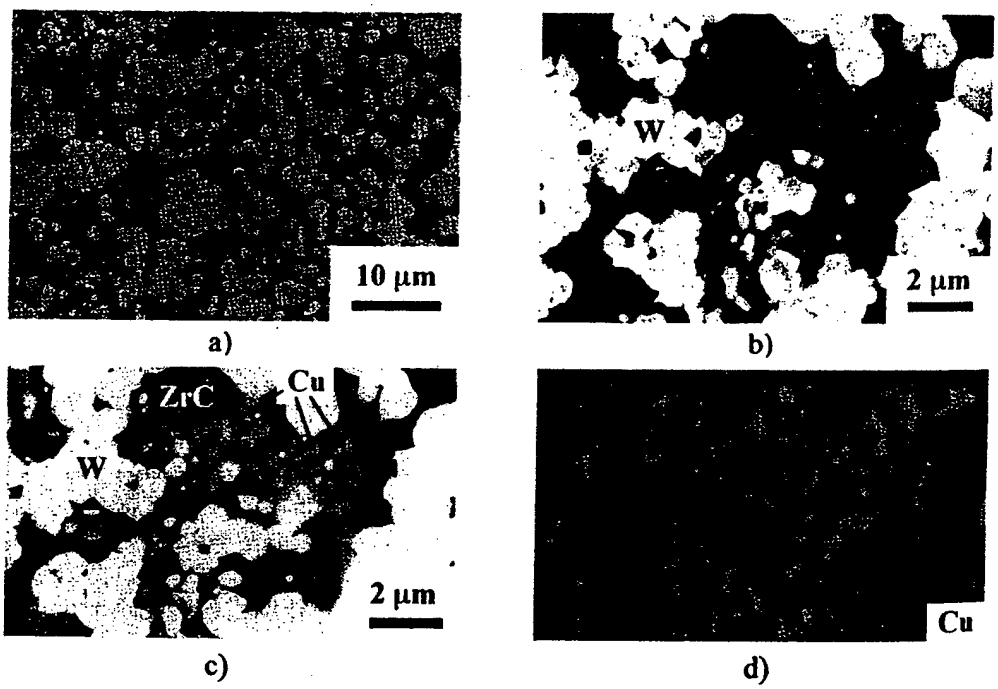
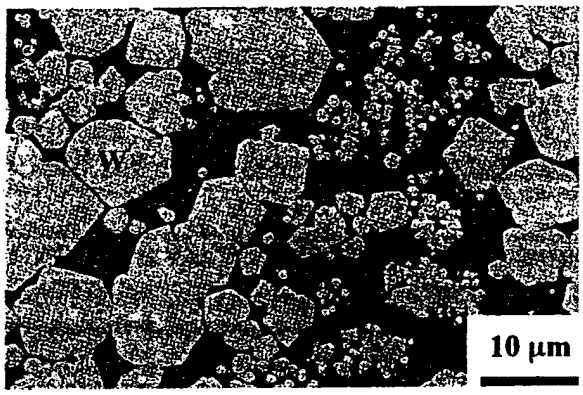


Figure 2. a) Secondary and b), c) backscattered electron images of a polished cross-section of a ZrC/W-bearing composite produced by reactive infiltration of $Zr_2Cu(l)$ into a porous WC preform at 1300°C. A Cu x-ray map associated with the high-contrast image in c) in shown in d).



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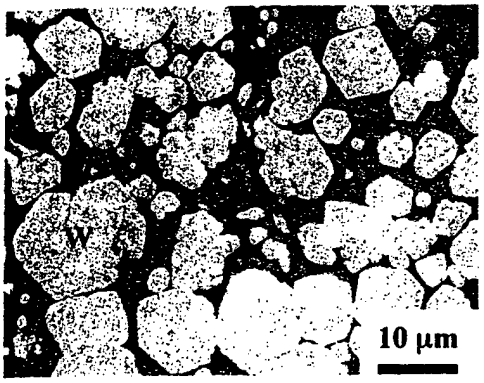

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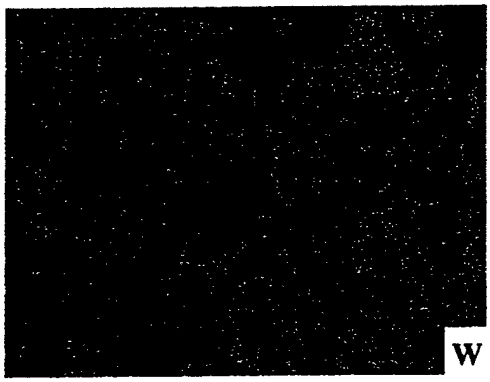

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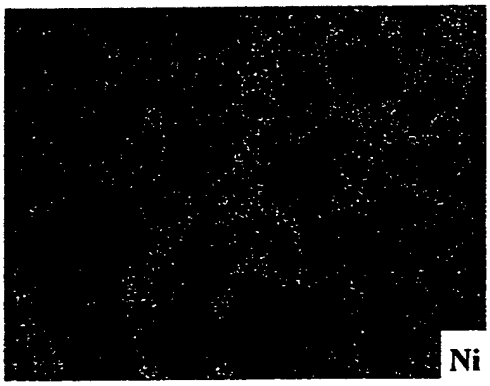

e)

Figure 3. a) Secondary and b) backscattered electron images of a polished cross-section of a W/ZrC-bearing composite produced by the reactive infiltration of $Zr_2Cu(l)$ into a porous, Ni-doped W/WC preform (molar W:WC ratio = 5.8:1) at 1250°C. X-ray maps of W, Zr, and Ni associated with the backscattered electron image in b) are shown in c)-e), respectively.

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RAPID, LOW-TEMPERATURE FABRICATION OF VERY-HIGH-MELTING ZrC/W-BEARING COMPOSITES BY THE PRIMA-DCP PROCESS

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Abstract

The PRIMA-DCP method is a novel, near net-shape, low-temperature, and rapid alternative to traditional methods for processing ultra-high-melting carbide/refractory metal composites. In this paper, the PRIMA-DCP process has been used to produce dense ZrC/W-bearing composites via the pressureless infiltration and reaction of Zr-Cu liquid with porous WC preforms. The Zr in the liquid underwent a displacement (oxidation-reduction) reaction with the WC to yield ZrC and W. The sum of the molar volumes of the reaction products, ZrC and W, was about twice the molar volume of the reactant, WC. This reaction-induced increase in internal solid volume was used to quickly fill the pores within the WC preforms at temperatures (1200-1300°C) well below the melting point of the resulting ZrC/W-bearing composites (≥2620°C). Such *in-situ*, reaction-induced densification caused the non-reactive, Cu-rich liquid to be largely squeezed out of the reacting body. Thus, copper acted as an attractive transient processing agent, by lowering the reactive infiltration temperature (e.g., the melting point of $CuZr_2$ is about 800°C lower than for pure Zr) and subsequently leaving the specimen. The influence of processing time on the microstructure and phase content of the resulting composite materials was evaluated.

Introduction

Zirconium-carbide-bearing composites can be attractive for a variety of advanced aerospace and nuclear applications [1-6]. Such composites, when reinforced with refractory metals or ceramic platelets, have been shown to possess excellent levels of strength, toughness, and erosion resistance [1-3]. However, the application of such composites has been severely hampered by the lack of rapid, low-temperature, and near net-shape fabrication processes. Such alternative fabrication routes would be strongly preferred to the conventional processing of these composites, which has relied upon either high temperature (≥2000°C) hot pressing (uniaxial or isostatic) of powder mixtures or the infiltration and reaction of high-melting zirconium metal with carbide powder beds (e.g., with porous B_4C at 1850-2000°C) [1-3]. Alternative processes that can produce dense ZrC/refractory metal composites at much lower temperatures, at ambient pressure, and with complicated (non-axisymmetric) shapes, while avoiding the use of extensive, costly diamond machining, are needed.

A novel process for fabricating dense, near net-shaped, carbide/refractory metal composites at relatively low temperatures (≤1300°C), the PRIMA-DCP method[1], has recently been demonstrated [7,8]. This process involves the pressureless infiltration of a low-melting metallic liquid into, and reaction with, a porous, rigid, ceramic-bearing preform. The metallic liquid contains an element that can undergo a displacement (oxidation-reduction) reaction with a carbide, nitride, boride, or oxide phase in the preform [7-9]. Because the displacement reaction is chosen to yield a larger volume of solid product(s) than is consumed, the original pore volume in the preform becomes filled with the new solid(s) during reaction. This increase in internal solid volume also forces residual metallic liquid back out of the composite body ("reversible infiltration"). Hence, a dense, refractory composite can be produced that retains the shape and dimensions of the original preform, and that contains minimal residual infiltrant metal [7,8].

The objective of the present paper is to demonstrate the feasibility of using the PRIMA-DCP process to produce dense, near net-shaped, ZrC/W-bearing composites in short times at low temperatures (i.e., ≤30 minutes at ≤1300°C).

Experimental Procedure

ZrC/W/WC-based composites were produced via the infiltration and reaction of Cu-Zr liquid with porous, bar-shaped WC preforms. Tungsten carbide (99.9% purity, 10 μm average size: Aldrich Chemical, St. Louis, MO) was mixed in a mortar and pestle with 5 wt% of an aqueous 4 wt% solution of polyvinyl alcohol (Grade Airvol 205, Air Products and Chemicals, Inc., Allentown, PA). The preforms were produced in the shape of bars (11 mm length X 9.5 mm width X 2.5 mm thick) by uniaxial pressing of the powder/binder mixtures at a peak stress of 240 MPa. The binder was then removed by heating at 400°C for 4 hours in flowing Ar. The preforms were then partially sintered (i.e., to allow for necking between WC particles) under vacuum for 2 hours at 1700°C.

The porous, rigid WC preforms were infiltrated with a Zr_2Cu liquid (T_m = 1025°C [10]). A 1 kg ingot of Zr_2Cu was produced by induction melting of a copper rod (2.5 cm dia. x 5.9 cm thick, 99.99% pure, Atomergic Chemetals, Farmingdale, NY) and zirconium sponge (0.8-19 mm dia. pieces, 99.6% pure, Johnson-Matthey, Inc., Ward Hill, MA) within a magnesia crucible (99.4% pure, 96% dense, Ozark Technical Ceramics, Inc., Webb City, MO). Prior to melting, the Zr-Cu charge was placed within a silica enclosure that was repeatedly evacuated and backfilled with Ar. Induction melting/stirring was then conducted with a 60 kV power supply for 4 minutes. The melt was allowed to cool to room temperature within the silica

[1]Pressureless Reversible Infiltration of Molten Alloys by the Displacive Compensation of Porosity

vessel. The composition of the ingot was determined by inductively coupled plasma spectroscopic analysis (Optima 3000 ICP-OES, Perkin-Elmer Corp., Norwalk, CT) to be 67.5 at% Zr/32.5 at% Cu (i.e., close to the Zr_2Cu composition). XRD analyses of the ingot yielded a diffraction pattern consistent with the Zr_2Cu phase.

Prior to a given reactive infiltration experiment, pieces of the solid Zr_2Cu ingot were placed above a bar-shaped preform inside a magnesia crucible (99.4% pure, 96% dense, Ozark Technical Ceramics, Inc.). The molar ratio of Zr_2Cu:WC used in each experiment was 1.5-1.6:1, which was in excess of the amount required for complete consumption of the WC. After purging the tube furnace with flowing gettered Ar (titanium getter, Oxy-gon Industries, Epsom NH) for 2 hours, the Zr_2Cu-covered preforms were heated at 7°C/minute to 1300°C for 0.5 to 8 hours. The specimens were then cooled at 7°C/minute under the flowing argon atmosphere. The phase content and microstructure of the resulting specimens were evaluated with x-ray diffraction (XRD) analyses (i.e., using Cu-Kα radiation and a scan rate of 0.5°C/minute) and scanning electron microscopy (SEM, Model XL-30, Philips Electron Instruments, Eindhoven, The Netherlands). Microchemical analyses were conducted with a Si/Li detector (EDAX International, Mahwah, NJ) attached to the electron microscope. Image analyses (Clemex Vision version 3.0.027 software, Langueuil, Quebec, Canada) of backscattered electron images were also conducted to determine the phase contents of reacted composites.

Results and Discussion

The formation of ZrC/W-bearing composites by the PRIMA-DCP process can occur by the following displacement reaction between zirconium dissolved in the Zr-Cu melt, {Zr}, and solid tungsten carbide:

$$\{Zr\} + WC(s) = ZrC(s) + W(s) \quad (1)$$

The Gibbs free energy change of reaction (1) for the case where {Zr} is present in molten Zr_2Cu is strongly negative at modest temperatures (e.g., $\Delta G_{rxn}(1200°C)$ = -136.8 kJ/mole) [11,12]). The solid products of this reaction, ZrC and W, possess a combined volume that is 101% larger than the molar volume of the WC reactant [13]. As discussed above, such a reaction-induced increase in internal solid volume results in pore filling and extrusion of the Cu-enriched liquid back out of the specimen. Hence, copper acts as a low-temperature, fugitive solvent for zirconium. Furthermore, any residual solid copper left in the composite can not form stable compounds with ZrC or W and has minimal effect on the melting point of tungsten (i.e., a decrease of only about 8°C) [14].

Although previous studies [7,8] have focused on reaction times up to 8 hours, the PRIMA-DCP process is sufficiently rapid as to yield dense microstructures in substantially less time. The microstructure of a composite specimen produced in the present work by reaction for 30 minutes is shown in Fig. 1. This composite contained residual tungsten carbide particles coated with layers of reaction-formed tungsten. The coated particles were embedded within a matrix comprised of zirconium carbide. Isolated pockets of a minor copper-rich phase were also occasionally observed (not seen in Fig. 1). Image analyses indicated that this composite was comprised of 17.8±2.7 vol% W, 40.4±7.3 vol% WC, and 41.8±5.1 vol% of the ZrC-rich matrix. The progress of the displacement reaction (1) as a function of time at 1300°C was tracked by measuring the volume fraction of the reaction products (tungsten and zirconium carbide) by XRD (Fig. 2). No clear trend was observed in the amounts of ZrC and W produced with an increase in reaction time from 0.5 to 8 hours. In other words, the quantity of reaction products formed within 30 minutes was similar to that formed after 8 hours at 1300°C. For all reaction times, diffraction peaks from Cu-Zr compounds ($CuZr_2$, $Cu_{10}Zr_7$, $Cu_{51}Zr_{14}$, Cu_5Zr [10]) were

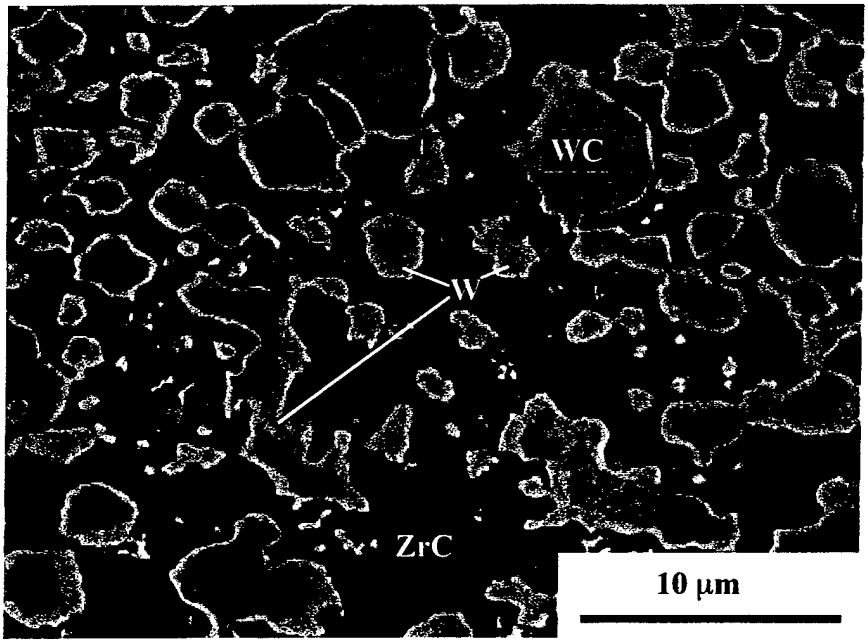

Figure 1: Backscattered electron image of a polished cross-section of a composite produced by the reactive infiltration of $CuZr_2$(l) into porous WC(s) at 1300°C for 30 minutes.

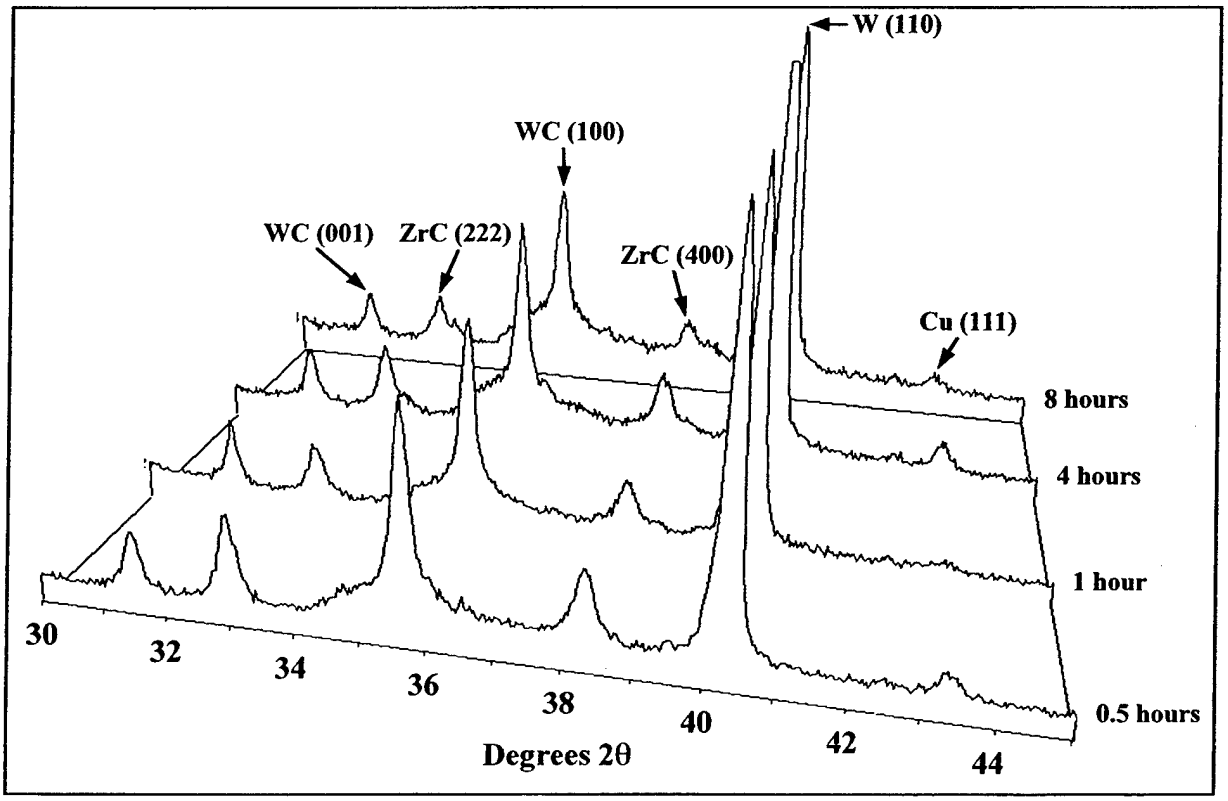

Figure 2: X-ray diffraction powder patterns of samples after reaction at 1300°C for 0.5 to 8 hours.

absent in Fig. 2, whereas the major (111) diffraction peak for pure copper (which has negligible solid solubility of zirconium [10]) was present. This indicated that the available internal supply of zirconium was quickly exhausted after infiltration. This observation corresponds well with thermodynamic calculations, which predict that a WC preform infiltrated with a Zr-Cu liquid should spontaneously react at 1300°C to form ZrC and W until only about 0.092 at% Zr remains within the Zr-Cu melt [11,12].

The rapid consumption of Zr within the specimens at 1300°C occurred as the pores became filled with more voluminous ZrC and W. There is an approximate doubling of solid volume associated with the complete conversion of WC into a solid mixture of ZrC and W. (i.e., the volume change is +101%) [13]. Consequently, rigid WC preforms need to possess porosities of ≥50.2% in order for complete WC consumption to occur prior to or just at the point of complete pore filling. However, the WC preforms in the present work possessed densities of 8.76-9.22 g/cm^3, which corresponded to porosities of only 44.1-41.2 vol% (the theoretical density of WC is 15.67 g/cm^3) [13]. Hence, the pores within these WC preforms became sealed prior to complete consumption of the WC by reaction (1). The limited amount of zirconium present within the remaining liquid in the specimen was quickly consumed (i.e., within 30 minutes at 1300°C). Because such pore sealing inhibited further long range migration of zirconium from the bulk liquid into the specimen, the phase content and microstructure of the composite specimens remained largely unchanged for times of 0.5 to 8 hours. In other words, the phase content of the PRIMA-DCP-derived composites was relatively insensitive to reaction time, for times longer than 0.5 hours.

The infiltration and reaction-induced densification of WC preforms in times as short as 12 minutes at 1200°C has also recently been achieved. Image analysis of this sample yielded a phase content that was similar to that for specimens held at 1300°C for ≥30 minutes. The dimensional and volume changes associated with the reaction of this sample were 1.12% and 2.27%, respectively. The average dimensional and volume changes of the 1300°C series of samples were 1.45% and 4.18%, respectively. Hence, the near net-shape feature of the PRIMA-DCP process was observed over a range of reaction times at 1200-1300°C. Such reaction temperatures are well below the solidus temperatures of ZrC/WC/W composites (≥2620°C) [15]. These results demonstrate that dense, near net-shaped, carbide/refractory metal composites can be produced by the PRIMA-DCP method in relatively short periods of time at modest temperatures (i.e., within 30 minutes at 1200-1300°C).

Conclusions

The feasibility of using the PRIMA-DCP process to fabricate dense, near net-shaped carbide/refractory metal composites at modest temperatures and in short times has been demonstrated. Molten Zr_2Cu infiltrated and underwent a displacement reaction with porous WC preforms at 1200-1300°C and ambient pressure to yield dense ZrC/WC/W-based composites within 30 minutes. The zirconium available for reaction within the infiltrated specimens was quickly consumed as the WC was replaced with more voluminous ZrC and W (i.e., as the prior pores became filled with new solid). The reaction-induced filling of pores served to block the influx of additional reactant. Consequently, the phase contents and microstructures of samples reacted at 1300°C for 30 minutes were similar to those of samples reacted for up to 8 hours. The near net-shape aspect of the PRIMA-DCP process, which alleviates the need for final machining, was realized for short and long reaction times (e.g., the dimensional and volume changes after reaction for 12 minutes at 1200°C were only 1.12% and 2.27%, respectively). Further work is currently underway to determine whether such near net-shaped, ZrC/W-bearing composites can be rapidly fabricated at temperatures below 1200°C.

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

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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 aerospaciales y otras (por ejemplo, erosión y resistencia al creep en conjunto con una resistencia y tenacidad relativamente altas). En este articulo, 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 liquido 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 liquido 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±20°C) refractory metal and also one of the heaviest (ρ[W] = 19.3 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 (ρ[ZrC] = 6.63 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 conductors[1] [1,3,4,10-13]. ZrC/W composites should also exhibit excellent creep resistance at =2000°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 =2000°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 volumi-nous internal network of solid product(s). Dense, fully-reacted composites can thereby be produced with a reten-tion 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 (1000-1300°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%), $MgAl_2O_4$/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 1200-1300°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

[1]Average linear coefficients of thermal expansion from 25°C to 2700°C range from 4.5X10^{-6}/°C to 9.2X10^{-6}/°C for W and 4.0X10^{-6}/°C to 10.2X10^{-6}/°C for ZrC [12,13]. W and ZrC possess thermal conduc-tivities of 105±10 W/m-K and 40±10 W/m-K, respectively, from 1000-2200°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 powder[2] (=3.0 μm, 99.9% purity) was added as a sintering aid [23]. After blending with 5-10 wt% of an aqueous polyvinyl alcohol solution[3], 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-Kα radiation and a scan rate of 0.5°C/min), scanning electron microscopy[4], 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 displace-ment reaction with solid tungsten:

$$Zr(l) + WC(s) = ZrC(s) + W(s) \qquad (1)$$

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±2°C [26]).

[1]Johnson Matthey, Ward Hill, MA
[2]Aldrich Chemical Co., St. Louis, MO
[3]Air Products and Chemicals, Inc., Allentown, PA
[4]Model XL-30 FEG-SEM, Philips Electron Instruments, Eindhoven, The Netherlands

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

$$\{Zr\} + WC(s) = ZrC(s) + W(s) \qquad (2)$$

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 $5.0X10^{-6}$ 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 tempera-tures 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, $Zr_2Cu(l)$ 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:

$$0.5\{Zr_2Cu\} + WC(s) = ZrC(s) + W(s) + 0.5\{Cu\} \qquad (3)$$

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].

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 unambi-guous 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, Zr_2Cu, 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.

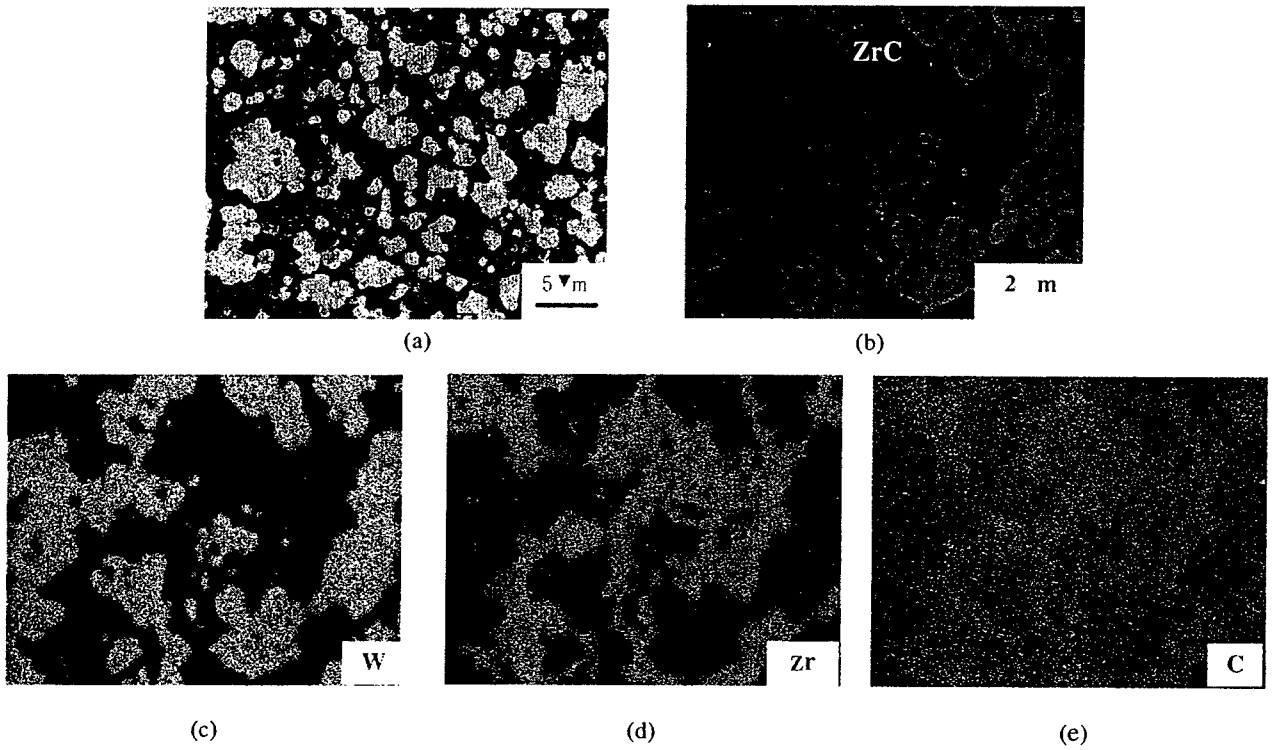


Fig. 1. a) Secondary electron image, and b) backscattered electron image with associated x-ray maps for c) W, d) Zr, and e) C obtained from a polished cross-section of a ZrC/W composite produced by the reaction casting of $Zr_2Cu(l)$ into a porous WC preform at 1300°C.

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].

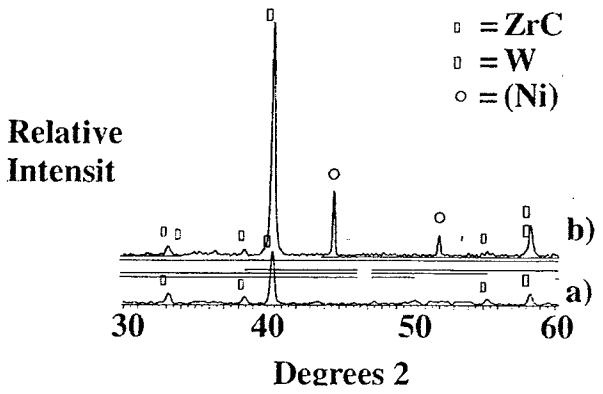


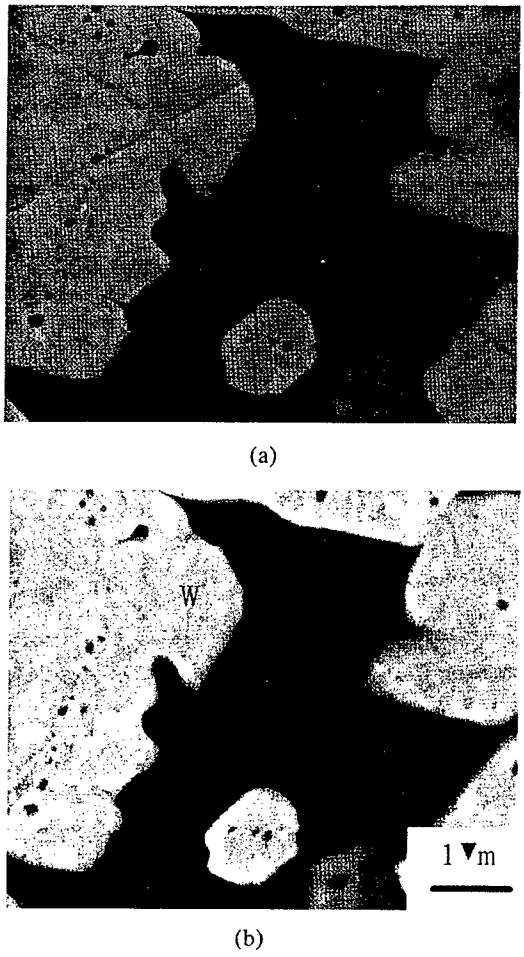
Fig. 2. XRD patterns of ZrC/W-bearing composites produced by the reaction casting of Zr_2Cu(l) into: a) a porous WC preform at 1300°C and b) a porous, Ni-doped W/WC preform at 1250°C.

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:

$$0.5\{Zr_2Cu\} + WC(s) + xW(s) = ZrC(s) + (1+x)W(s) + 0.5\{Cu\} \quad (4)$$

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 thesephases 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.



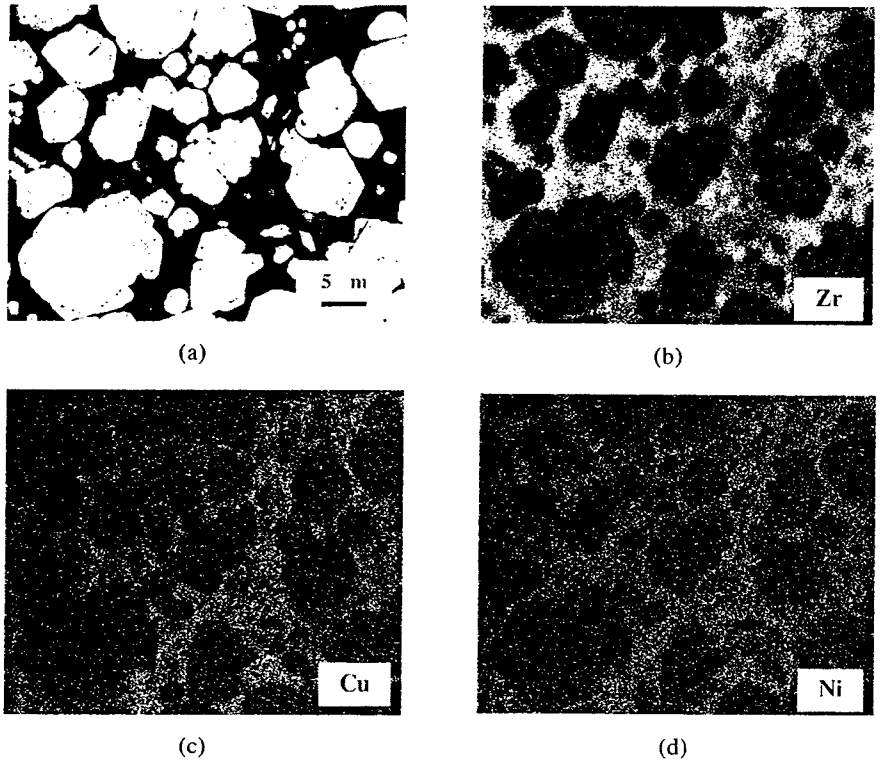
(a)

(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%.



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

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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NOWA GENERACJA MATERIAŁÓW KOMPOZYTOWYCH WYTWARZANYCH METODĄ PRIMA - DCP

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słowa kluczowe: PRIMA-DCP, kompozyty, węgliki metali żaroodpornych, WC, ZrC

Streszczenie: W pracy przedstawiono nową generację materiałów kompozytowych wytwarzanych metodą PRIMA–DCP (Pressureless Reversible Infiltration of Molten Alloys by the Displacive Compensation of Porosity). Metoda ta, umożliwiając uzyskanie kompozytów o skomplikowanych kształtach z węglików metali żaroodpornych w stosunkowo niskich temperaturach (1373 - 1573 K) i krótkim okresie czasu (1 - 2 h), stanowi dobrą alternatywę dla dotychczas stosowanych procesów klasycznych. Poszczególne etapy produkcji kompozytów metodą PRIMA-DCP omówione zostały na przykładzie wytwarzania kompozytów W-ZrC, przeznaczonych do zastosowań w niezwykle wysokich temperaturach (2773 K) i agresywnych środowiskach, np. w silnikach odrzutowych i rakietowych jako dysze, zawory i elementy komory spalań.

New generation of composite materials fabricated by PRIMA-DCP method

Abstract: In the present paper the new generation of composite materials fabricated by PRIMA-DCP method (Pressureless Reversible Infiltration of Molten Alloys by the Displacive Compensation of Porosity) is demonstrated. The PRIMA-DCP method enabling the fabrication of composites with relatively complicated shapes from the refractory carbides at modest temperatures (1373 - 1573 K) within short period of time (1 - 2 h), is a good alternative for used up to now other classical processes. The feasibility of using the PRIMA-DCP process have been demonstrated on the example of W-ZrC bearing composites, which are attractive materials to use at high temperature and aggressive environments, e.g. in jet and rocket engines, as a nozzles, liners and other aerospace components.

1. Wstęp

Niezwykle szybki rozwój wszystkich praktycznie gałęzi nowoczesnej techniki oraz pojawianie się nowych dziedzin technologii, stwarza coraz wyższe wymagania stosowanym materiałom konstrukcyjnym, zwłaszcza w odniesieniu do ich własności żarowytrzymałych i żaroodpornych. Dotyczy to przede wszystkim przemysłu lotniczego, motoryzacyjnego, chemicznego i maszynowego. Wzrost wydajności oraz sprawności określonych urządzeń i maszyn wymaga bowiem z reguły podwyższania temperatury, ciśnienia i szybkości przepływu gazów i par, co w konsekwencji oznacza gwałtowny wzrost zagrożenia materiału konstrukcyjnego zniszczeniem [1, 2]. Szczególnie trudne warunki pracy materiałów konstrukcyjnych występują w najnowszych silnikach rakietowych i odrzutowych oraz w przemyśle motoryzacyjnym [3] - [5]. Ponieważ materiały te pracują równocześnie pod obciążeniem (dysze i zawory silników rakietowych i odrzutowych, łopatki turbin, instalacje wysokociśnieniowe), muszą one oprócz wysokiej żaroodporności posiadać także odpowiednie własności żarowytrzymałe. W tym zakresie nowoczesna metalurgia posiada znaczne osiągnięcia, w obrębie których jednym ze szczytowych sukcesów są materiały kompozytowe zbudowane z metali żaroodpornych i ich węglików [3], [6].

Materiały kompozytowe, w skład których wchodzą czyste metale żaroodporne lub związki międzymetaliczne oraz węgliki, charakteryzują się unikalnymi i niezwykle atrakcyjnymi własnościami mechanicznymi i termicznymi [3] - [6]. Tego typu kompozyty w porównaniu z litymi metalami czy związkami międzymetalicznymi posiadają na ogół większą twardość, sztywność, odporność na ścieranie i pełzanie (szczególnie w podwyższonych temperaturach). Z drugiej natomiast strony wykazują wysoką, charakterystyczną dla materiałów ceramicznych, wytrzymałość na pękanie i odporność na szoki termiczne. Dodatkową zaletą jest ich niski ciężar właściwy, przez co są szczególnie atrakcyjnymi materiałami dla przemysłu lotniczego. Materiały kompozytowe zawierające w swym składzie fazę ceramiczną były do tej pory produkowane przy użyciu technik odlewniczych. Otrzymywano je mianowicie dzięki odlewaniu półstałej mieszaniny metali i rozdrobnionego

materiału ceramicznego do kokili [7], lub dzięki odlewaniu stopionego metalu na zawierającą materiał ceramiczny porowatą pastylkę [8-10]. Niestety, metody te ze względu na znaczny stopień komplikacji procesu i koszt związany z odlewaniem metali żaroodpornych nie są zbyt atrakcyjne w przypadku wytwarzania na masową skalę kompozytów, wykonanych z metali i węglików o wysokiej temperaturze topnienia. Metody te nie nadają się również do produkcji kompozytów o dużej zawartości fazy ceramicznej. Należy także podkreślić, że wady z jakimi produkowane są kompozyty przy użyciu wymienionych metod odlewania, takie jak zniekształcenia kształtów i wymiarów, pociągają za sobą stosowanie precyzyjnej i kosztownej obróbki mechanicznej w celu odpowiedniego wykończenia powierzchni wytwarzanych elementów. Kompozyty zbudowane z metali żaroodpornych i ich węglików można otrzymać również przez spiekanie w wysokich temperaturach (T > 2273 K) i pod wysokim ciśnieniem pastylek wykonanych ze sprasowanych materiałów wyjściowych [11]. Niemniej jednak duże trudności techniczne oraz wysokie koszty, na jakie napotyka się przy produkcji wymienionymi metodami kompozytów zawierających w swym składzie węgliki metali żaroodpornych, powodują konieczność opracowania i wdrożenia nowego procesu ich produkcji. Takim procesem wydaje się być metoda PRIMA-DCP (Pressureless Reversible Infiltration of Molten Alloys by the Displacive Compensation of Porosity), opracowana w Ohio State University, USA [12-13]. Metoda ta umożliwiając uzyskanie kompozytów o skomplikowanych kształtach z węglików metali żaroodpornych w stosunkowo niskich temperaturach i krótkim okresie czasu, stanowi atrakcyjną alternatywę dla dotychczas stosowanych procesów metalurgicznych.

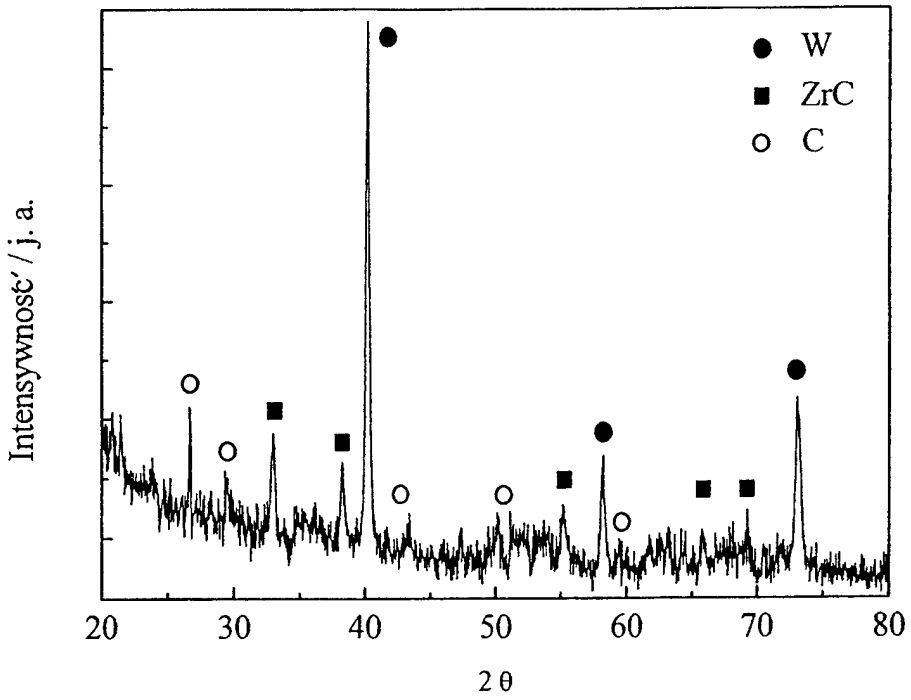
Proces wytwarzania kompozytów z metali żaroodpornych i ich węglików metodą PRIMA-DCP składa się z dwu faz [13]. W pierwszej fazie, wykonana z węglika metalu żaroodpornego (np. z węglika wolframu) przez prasowanie pastylka o odpowiednio dobranej zawartości porów otwartych, poddawana jest bezciśnieniowej infiltracji ciekłego stopu metali. W skład występującego w fazie ciekłej stopu wchodzi wysokotopliwy metal mogący reagować z materiałem pastylki (np. Zr) oraz jeden lub więcej pierwiastków (Cu, Ag) nie reagujących z materiałem pastylki, a powodujących jedynie obniżenie temperatury topnienia stopu w porównaniu z temperaturą topnienia czystego metalu wysokotopliwego. Przy odpowiednio dobranym składzie stopu można obniżyć temperaturę topnienia nawet o około 1000 K. W drugim etapie wytwarzania kompozytów z metali żaroodpornych i ich węglików metodą PRIMA-DCP dochodzi do reakcji podstawienia (utleniania-redukcji) pomiędzy reaktywnym składnikiem stopu, a węglikiem, z którego wykonana jest pastylka. Zarówno materiał pastylki, jak i metal reaktywny stopu są dobierane w taki sposób, aby w wyniku reakcji podstawienia sumaryczna objętość produktu reakcji w stanie stałym była większa od objętości substratu w występującego w stanie stałym. W wyniku reakcji podstawienia dochodzi zatem do zapełniania porów pastylki przez produkty tej reakcji. Stopniowe zapełnianie porów przez produkty reakcji powoduje, że nie reaktywny ciekły składnik stopu jest wypierany z powstającego kompozytu. W rezultacie z pastylki o odpowiednio dobranej porowatości, powstaje praktycznie nieporowaty kompozyt o wysokiej gęstości względnej, zawierający w swym składzie metal żaroodporny pastylki i węglik metalu będącego reaktywnym składnikiem stopu. Tak wytworzone kompozyty mają zatem kształty i wymiary użytych w procesie pastylek.

Celem niniejszej pracy jest przedstawienie procesu wytwarzania kompozytów zbudowanych z wolframu i węglika cyrkonu metodą PRIMA-DCP .

2. Metodyka badań i dyskusja wyników

Jako materiału wyjściowego do sporządzenia pastylek potrzebnych do wytworzenia kompozytów zbudowanych z wolframu i węglika cyrkonu metodą PRIMA-DCP, użyto węglika wolframu w postaci sproszkowanej, o wielkości ziaren mniejszej od 10 μm i czystości 99.9 % firmy Aldrich Chemical Co. W celu poprawy jakości pastylek otrzymywanych podczas prasowania, do sproszkowanego węglika wolframu dodawano w ilości 5 % wag. wodnego roztworu alkoholu poliwinylowego o stężeniu 4 % wag. Po dokładnym wymieszaniu obu składników, prasowano je w prasie jednoosiowej pod ciśnieniem 300 MPa, otrzymując pastylki o średnicy 13 mm i grubości 3 mm. Po sprasowaniu, pastylki wygrzewano w temperaturze 673 K przez 4 godziny w atmosferze argonu (o czystości 99.998 %), w wyniku czego usuwano z nich alkohol poliwinylowy. W dalszej kolejności pastylki z WC poddawano procesowi spiekania w temperaturze 1673 K w ciągu 4 godzin w atmosferze argonu. W wyniku procesu spiekania otrzymywano próbki WC o gęstości względnej około 55 %. Potrzebny do przeprowadzenia reakcji z węglikiem wolframu cyrkon (o czystości 99.6 %, firmy Johnson-Matthey, Inc.) mieszano z miedzią (o czystości 99.9 %, firmy Johnson-Matthey, Inc.) w takim stosunku, aby otrzymać stop Zr_2Cu, a następnie przetapiano oba składniki w tyglu z MgO (Ozark Technical Ceramics, Inc.) w temperaturze 1473 K przez 2 godziny w ochronnej atmosferze argonu. Rentgenowska analiza fazowa (XRD) otrzymanego stopu wykazała, że w jego skład wchodzi jedynie faza Zr_2Cu. Następnie kawałki stopu Zr_2Cu układano na płasko położonej pastylce WC znajdującej się w tyglu wykonanym z tlenku magnezu. Stosunek molowy Zr_2Cu/WC był tak dobierany aby zapewnić całkowity stopień przereagowania WC i wynosił około 1.5/1. Tak przygotowany zestaw umieszczano w piecu. Przed reakcją wymiany piec był przepłukiwany strumieniem argonu przez 2 godziny w celu usunięcia tlenu. Następnie podgrzewano piec z szybkością 7 deg/min do żądanej temperatury reakcji (zwykle 1473 - 1573 K). Po osiągnięciu stałej temperatury była ona utrzymywana na stałym poziomie przez 2 godziny, a następnie piec chłodzono z szybkością 7 deg/min.

Skład fazowy otrzymanego kompozytu badany był metodą dyfrakcyjnej analizy rentgenowskiej. Analizowano zarówno skład fazowy zewnętrznych powierzchni, jak i wewnętrznych przekrojów otrzymanych po przecięciu kompozytów. Wyniki analiz rentgenograficznych wykazały, że wytworzone kompozyty zbudowane są wyłącznie z wolframu i węglika cyrkonu, rys.1.



Rys.1. Dyfraktogram uzyskany z wewnętrznej powierzchni kompozytu W-ZrC, otrzymanego w temperaturze 1573 K.

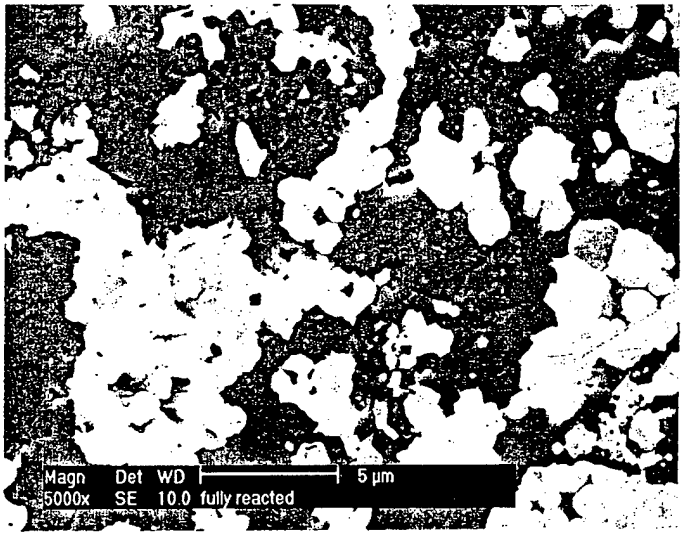
Ponieważ w badanych próbkach nie stwierdzono obecności WC, oznacza to, że węglik wolframu znajdujący się w pastylce całkowicie przereagował z cyrkonem będącym składnikiem stopu, wg następującej reakcji:

$$Zr_{(l)} + WC_{(s)} \rightarrow ZrC_{(s)} + W_{(s)} \qquad (1)$$

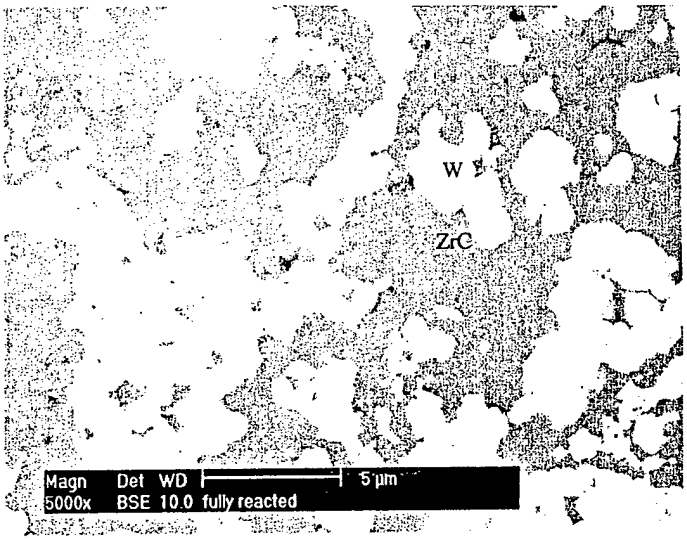
Z drugiej strony, brak obecności miedzi, Zr_2Cu oraz innych związków cyrkonu z miedzią (np. Cu_5Zr, $Cu_{51}Zr_{14}$, Cu_8Zr_3, $Cu_{10}Zr_7$, CuZr) w badanych próbkach świadczy o zapełnianiu porów pastylek głównie przez węglik cyrkonu. Stopniowe zapełnianie porów przez ZrC powoduje bowiem, że nie reaktywny ciekły składnik stopu, czyli miedź, jest wypierany z powstającego kompozytu. Wnioski dotyczące składu fazowego kompozytów, otrzymane dzięki rentgenograficznej analizie fazowej, potwierdzają obserwacje i analizy mikroskopowe, rys. 2. Z przeprowadzonych analiz wynika, że kompozyty zawierają węglik cyrkonu (około 45.1 % obj.), wolfram (około 45.9 % obj.) i miedź (do 9 % obj.). Brak pików odpowiadających miedzi na wykonanych dyfraktogramach wynika prawdopodobnie ze stosunkowo małej jej zawartości w badanych próbkach. Otrzymane kompozyty są praktycznie pozbawione porów, a zmiana ich wymiarów w stosunku do pierwotnych wymiarów pastylek WC, z których zostały wykonane nie przekracza 1 %.

Na szczególną uwagę zasługuje również fakt wysokiej wytrzymałości otrzymanych kompozytów na zginanie (684 MPa w temperaturze 673 K oraz 450 MPa w temperaturze 873 K), w porównaniu do wytrzymałości typowej dla materiałów ceramicznych. W temperaturach wyższych od 723 K kompozyty W/ZrC przestają być kruche i mają własności kowalne. Wytrzymałości badanych kompozytów określano zgodnie z normą C 1161-94 (Standard test method for flexural strength of advanced ceramics at ambient temperature).

(a)



(b)



Rys.2. Przekroje kompozytu W-ZrC, otrzymanego w temperaturze 1573 K w obrazach: a) SE, b) BSE.

3. Podsumowanie

W pracy zaprezentowano metodę PRIMA–DCP umożliwiającą wykonywanie kompozytów o skomplikowanych kształtach z węglików metali żaroodpornych w znacznie niższych temperaturach w porównaniu z temperaturami, jakie dotychczas były stosowane do otrzymania takich materiałów przy wykorzystaniu klasycznych procesów metalurgicznych. Wytworzone kompozyty mają kształty i wymiary odpowiadające pastylkom, z których zostały wykonane, co umożliwia nadawanie im w prosty sposób nawet skomplikowanych kształtów i eliminuje konieczność stosowania czasochłonnej i kosztownej mechanicznej obróbki powierzchni. Wysoka żaroodporność otrzymanych kompozytów oraz ich dobre własności mechaniczne sprawiają, że są one potencjalnymi materiałami przeznaczonymi do zastosowań w niezwykle wysokich temperaturach w przemyśle lotniczym,chemicznym i motoryzacyjnym.

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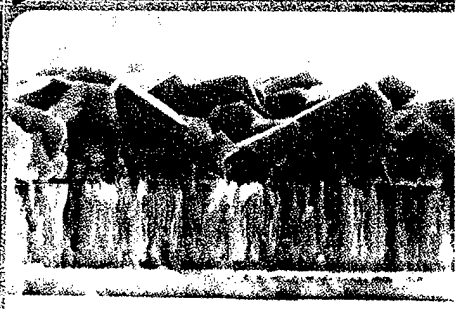

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HETEROGENICZNA REAKCJA WĘGLIKA WOLFRAMU Z CYRKONEM W ŚRODOWISKU CIEKŁEGO Zr_2Cu

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słowa kluczowe: PRIMA-DCP, kompozyty, kinetyka reakcji, WC, ZrC

Streszczenie: W pracy przedstawiono rezultaty badań mechanizmu i kinetyki heterogenicznej reakcji węglika wolframu w środowisku ciekłego Zr_2Cu w zakresie temperatur 1423 – 1673 K. W badanych warunkach miedź nie bierze bezpośredniego udziału w reakcji z WC, a służy jedynie do obniżenia temperatury topnienia cyrkonu. Wskutek reakcji węglika wolframu z ciekłym cyrkonem, na powierzchni WC tworzy się wielowarstwowa strefa produktów reakcji zbudowana z wolframu i węglika cyrkonu. Kinetykę narastania poszczególnych warstw można opisać prawem parabolicznym. Otrzymane wyniki wskazują, że najwolniejszym procesem determinującym szybkość reakcji węglika wolframu z cyrkonem jest dyfuzja węgla po granicach ziaren.

The WC heterogeneous reaction with Zr in environment of liquid Zr_2Cu

Abstract: In the present paper the investigations of the mechanism and kinetics of the WC heterogeneous reaction with liquid Zr at the temperature range of 1423 – 1673 K are presented. At the experimental conditions copper does not react with WC and is used to decrease the melting point of Zr. As a result of heterogeneous reaction, on the surface of WC a multilayered scale composed of W and ZrC is formed. The kinetics of particular layer formation can be described by the parabolic rate law. Obtained results suggest that the slowest step controlling the overall kinetic of displacement reaction is the carbon solid state diffusion through grain boundaries.

1. Wstęp

Kompozyty zawierające w swym składzie metale wysokotopliwe oraz ich węgliki stanowią atrakcyjną grupę potencjalnych materiałów przeznaczonych do zastosowań w przemyśle chemicznym i motoryzacyjnym, a przede wszystkim w przemyśle lotniczym. Szczególnie trudne warunki pracy materiałów konstrukcyjnych, występujące w najnowszych silnikach rakietowych i odrzutowych, w których są one poddawane zarówno działaniu wysokich temperatur jak i obciążeniom mechanicznym powodują, że oprócz wysokiej żaroodporności, materiały stosowane do produkcji dysz i zaworów silników rakietowych lub odrzutowych, łopatek turbin oraz innych elementów komór spalań, muszą posiadać także odpowiednie własności żarowytrzymałe [1] - [3]. Oba te warunki spełniają kompozyty na bazie węglików metali żaroodpornych, które w porównaniu z litymi metalami czy związkami międzymetalicznymi posiadają na ogół większą twardość, sztywność oraz odporność na ścieranie i pełzanie [4], [5]. Z drugiej natomiast strony wykazują wysoką, charakterystyczną dla materiałów ceramicznych, wytrzymałość na pękanie i odporność na szoki termiczne [4]. Niejednokrotnie dodatkową zaletą jest również ich niski ciężar właściwy, przez co są szczególnie atrakcyjnymi materiałami dla przemysłu lotniczego.

Do materiałów nowej generacji mogących znaleźć zastosowanie w przemyśle lotniczym należy zaliczyć przede wszystkim kompozyty zbudowane z wolframu i węglika cyrkonu. Zarówno bowiem wolfram jak i węglik cyrkonu mają bardzo wysokie temperatury topnienia (T_W = 3695 K, T_{ZrC} = 3813 K). Obydwa materiały charakteryzują się również małą prężnością par w zakresie temperatur występujących w gazach wylotowych z dysz rakietowych (T ≈ 2773 K). Ponieważ materiały te posiadają porównywalne wielkości współczynników rozszerzalności termicznej (w przypadku węglika cyrkonu liniowy współczynnik rozszerzalności termicznej zmienia się od temperatury pokojowej do 3000 K w zakresie $4 \cdot 10^{-6}$ deg^{-1} - $10.2 \cdot 10^{-6}$ deg^{-1}, zaś w przypadku wolframu w zakresie $4.5 \cdot 10^{-6}$ deg^{-1} - $9.2 \cdot 10^{-6}$ deg^{-1}), ich stosowanie w wysokich temperaturach powoduje powstawanie na granicy faz W|ZrC relatywnie małych naprężeń mechanicznych. W porównaniu ze stosowanym dotychczas do wyrobu dysz rakietowych czystym wolframem, węglik cyrkonu posiada prawie trzykrotnie mniejszą gęstość (ρ_{ZrC} = 6.63 g/cm^3, ρ_W = 19.3 g/cm^3,) co pozwala na zmniejszenie ciężaru elementów budowanych z kompozytów W-ZrC

bardzo skomplikowane kształty w stosunkowo niskich temperaturach i krótkim okresie czasu, dzięki użyciu do ich wytwarzania metody PRIMA-DCP (Pressureless Reversible Infiltration of Molten Alloys by the Displacive Compensation of Porosity) [7 - 10]. Metoda ta (szczegółowo opisana w publikacji pt. "Nowa generacja materiałów kompozytowych wytwarzanych metodą PRIMA-DCP", zawartej w niniejszym woluminie Inżynierii Materiałowej [10]), polegająca na przeprowadzeniu reakcji podstawiania pomiędzy np. węglikiem wolframu, a ciekłym cyrkonem, będącym składnikiem stopu cyrkonu z miedzią, stanowi atrakcyjną alternatywę dla dotychczas stosowanych procesów metalurgicznych. Proces wytwarzania kompozytów W-ZrC metodą PRIMA-DCP pomimo swojej prostoty nie jest jednak w pełni zrozumiały. Nie jest bowiem znany zarówno mechanizm zachodzenia reakcji pomiędzy węglikiem wolframu, a ciekłym cyrkonem jak i kinetyka tego procesu. Informacje te są natomiast niezwykle potrzebne w celu właściwego zaprojektowania procesu technologicznego wytwarzania kompozytów W-ZrC przy użyciu opisanej metody.

Celem niniejszej pracy jest wyjaśnienie zarówno mechanizmu zachodzenia heterogenicznej reakcji węglika wolframu z ciekłym cyrkonem, będącym składnikiem stopu Zr_2Cu, jak i określenie kinetyki tego procesu w funkcji temperatury i czasu.

2. Procedura eksperymentalna

W ramach przygotowania próbek do badań, z proszku węglika wolframu o wielkości ziaren do 1 μm i czystości 99.9 % at. (Aldrich Chemical Co.) sprasowano pastylki o średnicy 13 mm i grubości 3 mm. W celu poprawy jakości pastylek otrzymywanych podczas prasowania, do sproszkowanego węglika wolframu dodawano w ilości 3 % wag. wodnego roztworu alkoholu poliwinylowego o stężeniu 10 % wag. i po dokładnym wymieszaniu obu składników, prasowano je w prasie jednoosiowej pod ciśnieniem 300 MPa. Tak przygotowane pastylki wygrzewano następnie w temperaturze 673 K przez 4 godziny w atmosferze argonu (o czystości 99.998 %) w celu usunięcia z nich alkoholu poliwinylowego. W dalszej kolejności pastylki z WC poddawano procesowi wstępnego spiekania w temperaturze 1673 K w ciągu 4 godzin w atmosferze argonu pod ciśnieniem atmosferycznym.W wyniku procesu spiekania otrzymywano próbki WC o gęstości względnej około 55 %. W kolejnym etapie pastylki spiekane były izostatycznie przez jedną godzinę w temperaturze 2123 K w argonie pod ciśnieniem 70 kPa, a następnie przez kolejną godzinę w tej samej temperaturze pod ciśnieniem 210 MPa.W rezultacie procesu spiekania pod ciśnieniem, gęstość względna pastylek osiągnęła 99% wartości teoretycznej gęstości węglika wolframu. Tak przygotowane pastylki WC były polerowane na papierach ściernych o zmniejszającej się gradacji (do 800 SiC) i polerowane przy użyciu past diamentowych (o wielkości ziaren od 12 μm do 0.25 μm), aż do osiągnięcia przez próbki lustrzanego połysku. Potrzebny do przeprowadzenia reakcji z węglikiem wolframu cyrkon (o czystości 99.6 %, firmy Johnson-Matthey, Inc.) mieszano z miedzią (o czystości 99.9 %, firmy Johnson-Matthey, Inc.) w takim stosunku, aby po przetopieniu otrzymać stop Zr_2Cu, a następnie umieszczano oba składniki w tyglu z MgO (Ozark Technical Ceramics, Inc.), w którym zawieszano również pastylkę z węglika wolframu. Tak przygotowany zestaw umieszczano w piecu, który przepłukiwano strumieniem argonu przez 2 godziny w celu usunięcia tlenu, a następnie podgrzewano z szybkością 7 deg/min do osiągnięcia żądanej temperatury reakcji (1423 - 1673 K). Po osiągnięciu stałej temperatury była ona utrzymywana przez okres od 1,5 do 24 godzin, a następnie piec chłodzono z szybkością 7 deg/min. Po wykonaniu zgładów z próbek WC poddanych reakcji z ciekłym cyrkonem, badano morfologię oraz grubości poszczególnych produktów reakcji przy użyciu technik mikroskopii elektronowej i dyfrakcji rentgenowskiej.

3. Wyniki badań

W wyniku badań reakcji pomiędzy węglikiem wolframu, a cyrkonem będącym składnikiem ciekłego w temperaturze reakcji stopu Zr_2Cu, okazało się, że na powierzchni pastylek WC dochodzi do powstania ciągłej warstwy wolframu, na której narasta ciągła warstwa węglika cyrkonu:

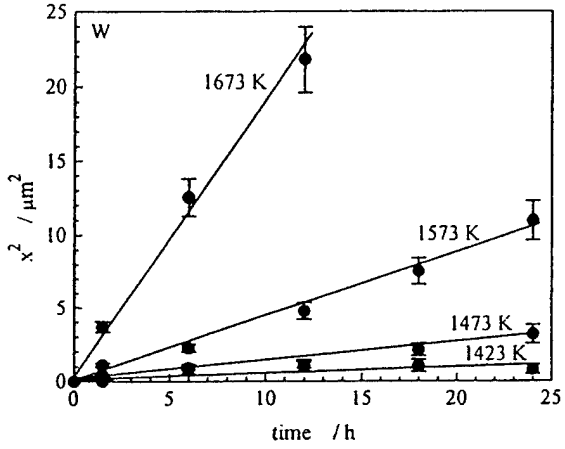
$$WC_{(s)} + Zr_{(l)} \rightarrow W_{(s)} + ZrC_{(s)} \qquad (1)$$

Na rys.1 przedstawiono fragment pastylki węglika wolframu z wyraźnie widoczną warstwą wolframu i węglika cyrkonu. Na uwagę zasługuje fakt, że granica faz pomiędzy węglikiem wolframu, a wolframem jest stosunkowo płaska, co świadczy o równomiernym zachodzeniu reakcji WC z ciekłym cyrkonem. Ponieważ już od początkowych stadiów reakcji opisanej równaniem (1) węglik wolframu jest fizycznie oddzielony od ciekłego stopu poprzez warstwy produktów reakcji, dalsze zachodzenie tego procesu związane jest z dyfuzją atomów węgla z węglika wolframu poprzez warstwę wolframu do węglika cyrkonu. W konsekwencji reakcja pomiędzy węglikiem wolframu, a cyrkonem może być limitowana poprzez jeden z następujących procesów elementarnych: dyfuzję węgla w węgliku wolframu, w wolframie lub w węgliku cyrkonu, dyfuzję cyrkonu w ciekłym stopie Zr_2Cu, albo reakcje chemiczne zachodzące na granicy faz WC|W, W|ZrC lub ZrC|Zr_2Cu. W celu określenia, który z wymienionych procesów elementarnych przebiega najwolniej, a więc limituje szybkość zachodzenia reakcji (1), przeprowadzono pomiary kinetyki powstawania warstw wolframu i węglika cyrkonu w funkcji temperatury. W tym celu po określonym czasie reakcji danej pastylki WC z Zr w stałej temperaturze, mierzono grubości poszczególnych

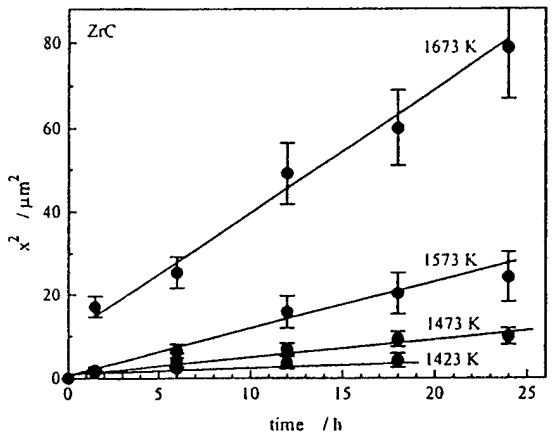
warstw produktów reakcji przy użyciu mikroskopu elektronowego SEM. W wyniku przeprowadzonych pomiarów okazało się, że kinetykę powstawania zarówno warstwy wolframu jak i węglika cyrkonu można opisać prawem parabolicznym, rys.2 i 3, a grubości poszczególnych warstw nie zależą od ich odległości od dolnego brzegu pionowo zawieszonej próbki. Oznacza to, że o szybkości całego procesu decyduje dyfuzja w stanie stałym, a nie dyfuzja w ciekłym stopie [11], czy też reakcje chemiczne zachodzące na poszczególnych powierzchniach badanego materiału. Należy podkreślić, że mierzony ubytek grubości WC związany z zachodzeniem reakcji (1) odpowiada przyrostowi grubości warstw W i ZrC, co świadczy

Rys.1. Poprzeczny przekrój pastylki węglika wolframu po reakcji z ciekłym cyrkonem, przeprowadzanej w temperaturze 1673 K przez 6 godzin.

o znikomym stopniu rozpuszczania się węglika cyrkonu w fazie ciekłej. Wyznaczone eksperymentalnie wartości parabolicznych stałych szybkości powstawania warstw wolframu i węglika cyrkonu zestawione zostały na rys.4 w układzie Arrheniusa. Wyznaczone w wyniku przeprowadzonych pomiarów kinetycznych wielkości energii aktywacji powstawania wolframu i węglika cyrkonu są prawie jednakowe i wynoszą około 255 kJ/mol. Zbliżone wielkości energii aktywacji tworzenia obu warstw w badanym układzie potwierdzają wyciągnięty wcześniej wniosek o braku rozpuszczania się węglika cyrkonu w fazie ciekłej. Opisane badania wykonywane były w temperaturach niższych od 60 % wartości temperatur topnienia poszczególnych związków biorących udział w reakcji (T_W=3695 K, T_{ZrC}=3813 K, T_{WC}=3049 K), a zatem należy oczekiwać, że dyfuzja w fazie stałej zachodzi przede wszystkim wzdłuż granic międzyziarnowych, a nie poprzez defekty sieci krystalicznej. Ponieważ wyznaczone w niniejszej pracy wartości energii aktywacji formowania się wolframu i węglika cyrkonu są znacznie większe od energii aktywacji procesu dyfuzji promieniotwórczego trasera węgla C^{14} zarówno w monokrystalicznym (207 kJ/mol [12]), jak i polikrystalicznym wolframie (169 kJ/mol [13]), dyfuzja węgla poprzez warstwę wolframu nie wydaje się być najwolniejszym procesem determinującym szybkość reakcji WC z cyrkonem. Zbliżone

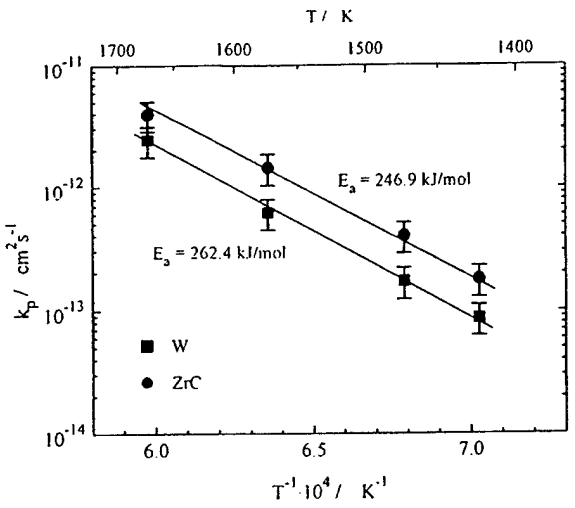


Rys.2. Kinetyka powstawania warstwy wolframu.



Rys.3. Kinetyka powstawania warstwy węglika cyrkonu.

węgla C^{14} wzdłuż granic międzyziarnowych zarówno w węgliku wolframu (288 kJ/mol [14]), jak i węgliku cyrkonu (297 kJ/mol [15]). A zatem najwolniejszym procesem determinującym szybkość reakcji WC z cyrkonem jest dyfuzja węgla po granicach ziaren wymienionych węglików.



Rys.4. Temperaturowa zależność parabolicznych stałych szybkości formowania się warstw wolframu i węglika cyrkonu, powstających w wyniku reakcji węglika wolframu z ciekłym cyrkonem.

4. Wnioski

Na podstawie badań przeprowadzonych w ramach niniejszej pracy można wyciągnąć następujące wnioski:

1. W rezultacie reakcji węglika wolframu z ciekłym cyrkonem powstają ciągłe warstwy produktów reakcji: wolframu i węglika cyrkonu.
2. Kinetyki powstawania ciągłych warstw wolframu i węglika cyrkonu mogą być opisane prawem parabolicznym. Wyznaczone wartości energii aktywacji powstawania zarówno wolframu, jak i węglika cyrkonu sugerują, że najwolniejszym procesem determinującym szybkość reakcji węglika wolframu z cyrkonem jest dyfuzja węgla po granicach ziaren w węglikach.

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