Corrosion Science 80 (2014) 402–407

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Ultra-high temperature oxidation of a hafnium carbide-based solid solution ceramic composite

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ARTICLE INFO

Article history:
Received 30 May 2013
Accepted 29 November 2013
Available online 4 December 2013

Keywords:
A. Ceramic
C. High temperature corrosion
C. Oxidation

ABSTRACT

Hafnium carbide-based solid solution ceramics with yttria additions were consolidated via hot pressing utilizing chromium carbide as a transient liquid sintering agent. Selected samples were oxidized at temperatures exceeding 2200 °C under high velocity airflow to determine their potential for service in ultra-high temperature environments. Cross-sectional examination revealed a complex multi-layer scale comprising a highly porous exterior region, a dense multi-phase interior region, and an oxygen- and carbon-containing interlayer consisting of nanocrystalline graphite in an amorphous or nanocrystalline oxide matrix. Outward diffusion of mobile cations is speculated to play an important role in establishing the observed scale morphology.

1. Introduction

The discovery and development of ultra-high temperature (i.e., greater than 2000 °C) oxidation-resistant materials is expected to enable many future technologies such as protective coatings for hypersonic and propulsion-related aerosurfaces [1,2]. Few known materials possess the requisite refractoriness to withstand such temperatures, let alone the simultaneous corrosive action of oxidizing species. Investigators in this field have expended great effort to form an understanding of the effects of chemical composition and processing-microstructural relationships on the oxidation behaviors of two classes of relatively oxygen impermeable materials: silica/silicate-formers and iridium/rhenium-based compounds [3]. Due to the onset of active oxidation (i.e., wherein the primary oxidation products are gaseous rather than condensed phases) silica/silicate-formers are unsuitable for extended exposures to ultra-high temperatures [4–7], while the cost and scarcity of iridium/rhenium-based compounds makes their widespread use impractical.

The search for viable alternatives has led to an interest in hafnium-bearing materials (e.g., HfC, HfB_2, Hf-based alloys, etc.) whose primary oxidation product hafnia is amongst the most refractory oxides [8–11]. Under certain conditions, the oxidation of hafnium carbide-based materials has been observed to produce an oxygen- and carbon-containing interlayer between the unoxidized carbide and oxide scale [2,12–16]. Oxidation kinetics studies seem to indicate that this oxide–carbide interlayer constitutes a diffusion barrier whose diffusion coefficient is at least an order of magnitude lower than that of hafnia under similar conditions of temperature and oxygen partial pressure [15].

Thermodynamic arguments impose strict limits on the equilibrium oxygen partial pressure at the oxide–carbide interface depending on the local carbon activity. For example, the four-phase mixture embodied by the net reaction $HfO_2 + C = O_2(g) + HfC$ would only be in equilibrium at an oxygen partial pressure of 4.6×10^{-11} atm at 2200 °C, assuming all solid phases exist in their pure, crystalline states at unit activity [17]. Thus, an effective secondary oxygen barrier (e.g., in the form of a protective overlayer) may also be requisite for the chemical stability of the interlayer.

Notwithstanding issues surrounding thermochemical instability of silica/silicate-formers, potential lessons from the oxidation scale morphology of state-of-the-art HfB_2/SiC ceramic composites might be applied to the design of oxidation-resistant hafnium carbide-based ceramics. For example, the oxidation scale formed upon HfB_2/SiC consists of a porous hafnia framework that lends mechanical integrity to the scale in high shear environments, infilled by a hafnium- and boron-containing silicate liquid that acts as the basis for protection against oxygen ingress, sealing cracks and pores while allowing the escape of back-pressured product gases [18–21]. This self-healing aspect is a highly sought after feature for protective coatings enabled by the inclusion of a flowable but not overly inviscid phase [22,23].

In this preliminary investigation, we sought to develop an ultra-refractory analogue to the 'porous framework/liquid infill' morphology of HfB_2/SiC oxidation scales via the introduction of several additional components to a hafnium carbide-based solid solution

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0010-938X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.corsci.2013.11.049

ceramic whose oxidation products might serve to induce limited liquid formation. Chromium carbide (Cr_3C_2) was identified as a promising transient liquid phase sintering agent to facilitate the formation of homogeneous solid solutions [24,25]. The peritectic decomposition of pure Cr_3C_2 into a carbon-saturated chromium liquid and free carbon is known to occur at 1826 °C and, more importantly, available ternary C–Cr–Hf, C–Cr–Ti, and C–Cr–Ta phase diagrams indicate the existence of eutectic compositions with substantial carbide solubilities along the pseudo-binary joins of Cr–HfC, Cr–TiC, and Cr–TaC [26]. Since these constituent metal oxidation products possess far lower melting points than their unoxidized carbide counterparts, anticipated solidus depression resulting from chromium substitution into the hafnium-carbide based solid solution ceramic composite was not considered to be overly disadvantageous. Here we report on the synthesis and ultra-high temperature oxidation behavior of a hafnium carbide-based solid solution ceramic composite consolidated via hot pressing utilizing Cr_3C_2 as a transient liquid phase sintering agent.

2. Materials and methods

Hafnium carbide (Pure Tech Inc., 99.5%), tantalum carbide (Pure Tech Inc., 99.5%), a 60 mol.% titanium carbide/40 mol.% chromium carbide mixture (Inframat Advanced Materials, 99.9%) and yttria (Alfa Aesar, 99.9%) powders were utilized as-received without further processing. Manufacturer-stated median particle sizes were less than 5 μm which were verified via scanning electron microscopy (SEM). Batch compositions were dry blended (Turbula T2F shaker-mixer) and loaded within a 25.4 mm diameter graphite die designed for a vacuum hot press (Thermal Technologies Inc. Astro model HP20 series). The charge was heated to 1500 °C at which point a pressing load of 30 MPa was applied. This load was maintained upon heating to a maximum processing temperature of 1800 °C and continued to be held until the recorded ram travel was less than 0.001 mm within any 60 s interval. Hot pressed specimens were characterized via X-ray diffraction (XRD) (Scintag Inc. XGEN-4000 with Cu anode), SEM (FEI Quanta 600), energy dispersive spectroscopy (EDS) (IXRF Systems model 550i), Vickers microhardness (Shimadzu HMV), and subjected to Archimedes density determination via water displacement method.

Two compositions were selected for ultra-high temperature testing at the Laser Hardened Materials Evaluation Laboratory (LHMEL) (Wright-Patterson Air Force Base, Dayton, OH). Specimens (approximately 10 mm thick, 25 mm diameter) were mounted in a split two-piece graphite holder under compressive spring loading using four 5 mm diameter zirconia beads as contact points and subjected to laser heating (IPG 10 kW 1.07 μm fiber optic laser) for up to 30 min. The specimen holder was mounted within a subsonic wind tunnel that imposed a 90 m/s air flow across the illuminated surface to simulate the high shear conditions encountered by aerosurfaces.

Oxidized specimens were cross-sectioned, polished, and further analyzed via SEM, Raman spectroscopy (Renishaw RM1000 using 515 nm argon laser excitation), and electron backscatter diffraction (EBSD) (conducted by EBSD Analytical Inc., Lehi, UT). The oxidation scale was also destructively sampled via diamond abrasion with recovered material characterized via XRD (Inel Equinox with Co anode). Finally, compositional data was obtained via wavelength dispersive spectroscopy (WDS) (Cameca SX-100); however, significant quantification error may have been introduced due to the use of available standards that did not closely match specimen composition. As a result, reported WDS-derived values have been truncated to the ones digit and are considered 'semi-quantitatve'.

3. Results and discussion

Preliminary consolidation trials empirically revealed that batch compositions comprising nominally 20 vol.% Cr_3C_2 could allow for substantially complete powder consolidation within 30 min at 1800 °C under 30 MPa pressure. XRD analyses, as represented in Fig. 1, indicated that complete carbide solid solutions were achieved, presumably hastened by the dissolution–reprecipitation action of the transient liquid phase sintering agent. Compositional analyses and selected property data are presented in Table 1 for each test specimen.

Six specimens (three each of two batch compositions) were thus tested at the LHMEL facility under various laser power configurations. Due to the limited number of trials, only three specimens (A1, B1, and B2) were successfully tested under controlled conditions. Each of these three specimens exhibited severe lateral cracks during initial heatup, which we speculate to be due to a combination of thermal shock and compressive failure owing to insufficient compliance of the sample holder against thermal expansion of the specimen.

Specimen A1 experienced a maximum front surface temperature of 2190 °C and exhibited catastrophic surface recession due to excessive liquid formation, presumably associated with the greater tantalum carbide batch content whose primary oxidation product Ta_2O_5 melts at 1872 °C and is not known to form any high melting point tantala-rich compounds with hafnia, titania, chromia, or yttria. As a result, the 'A' (Ta-rich) batch composition was deemed unsuitable for ultra-high temperature applications.

Specimen B1 demonstrated significant surface recession upon experiencing a peak surface temperature of 2350 °C, seemingly exceeding the maximum temperature capability of the 'B' batch composition. Specimen B2 reached an average front surface temperature of 2210 °C with heating profiles for the front and back surfaces shown in Fig. 2 and was observed to form a compact oxidation scale whose structure and composition was analyzed in detail and discussed below.

Cross-sectional examination of specimen B2 revealed an adherent, complex multi-layer oxidation scale consisting of a highly porous outer region and relatively compact interior, including an oxygen- and carbon-containing interlayer between the unoxidized carbide composite and fully oxidized region. Several thin transverse cracks were observed to span the compact interior region (with endpoints indicated by arrows in Fig. 3a). The absence of enhanced oxidative corrosion in the vicinity of the cracks supports the notion that they likely formed upon cooldown. If the oxidation scale and unoxidized specimen together act as would a bilayer structure, and assuming the average linear coefficient of thermal

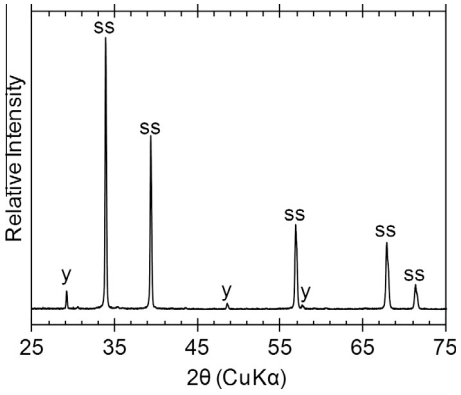

Fig. 1. XRD pattern of specimen B2 post-hot press consolidation at 1800 °C for 40 min. under 30 MPa applied load ($y = Y_2O_3$, ss = solid solution carbide).