

Corrosion Behavior of Metal-Ceramic Composites

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ABSTRACT

Zirconium carbide/zirconium boride ceramic composites were melt processed in an inert atmosphere using a combination of zirconium alloys and boron carbide particulates. UNS R60702 (commercially pure zirconium, CP Zr) and UNS R60705 (Zr-2.5Nb) were utilized in this study. Corrosion test coupons were cross sectioned from the as-fabricated materials. Microstructural and phase characterization of the composites were accomplished by optical and scanning electron microscopy, energy dispersive spectroscopy and X-ray diffraction. The corrosion behavior of these composite materials was evaluated in accordance with ASTM G59-97 and ASTM B117-18. The erosion characteristics were determined in accordance with ASTM G75-15.

Key words: Metal-Ceramic Composites, Melt Processing, Composites, Zirconium, Zirconium Carbide/Zirconium Diboride Composite, Marine Applications, Microstructure

INTRODUCTION

Zirconium-based composites (ZBC) with zirconium diboride (ZrB_2) platelets, zirconium carbide (ZrC) spheroids, and residual zirconium (Zr) have been previously investigated.^{1,2} These materials are prepared through the melt processing of Zr metal with boron carbide (B_4C) resulting in the aforementioned phases. The amount of residual Zr can be controlled and altered through the ratio of initial B_4C to Zr. Increasing the amount of residual Zr can be used to impart improved mechanical properties such as fracture toughness.^{1,2}

Zr-based composites offer the potential for significant enhancements in wear and corrosion resistance in the context of marine pumps, pipes and heat exchangers compared to traditionally used alloys. For instance, commonly used alloys for marine applications, such as copper-nickel and aluminum-bronze, demonstrate decent resistance to corrosion. However, copper-based alloys exhibit high erosion rates when substantial quantities of sand are present.^{3,4} On the other hand, Zr alloys develop hard, adherent passive oxide films that provide corrosion protection and wear resistance for the base metal in a wide range of acidic and basic aqueous solutions. This same surface oxide layer is utilized in erosion-

corrosion applications where a combination of corrosion resistance and wear resistance is required in the presence of abrasive slurries. Previously, titanium-based composites were also examined for potential marine applications.⁵

Zr-based composites with niobium (Nb) additions (ZNBC) could potentially enhance ZBC behavior since Nb is highly corrosion resistant and strengthens Zr. Previous work demonstrated that small additions of Nb to ZBC improve wear behavior; however, no work has investigated the combined wear behavior and corrosion resistance of ZBC with Nb additions.^{6,7}

EXPERIMENTAL PROCEDURE

Several batches of ZBC and ZNBC composites were produced using a refractory crucible. Either a pure UNS R60702 (commercially pure zirconium, CP Zr) billet or UNS R60705 (Zr-2.5Nb) billet was placed on top of a predetermined grit size B₄C preform. The proportions of reactants were based on stoichiometry, and each impression contained a mass ratio of 6:1±0.05 of Zr to B₄C. The refractory crucible was then placed into a vacuum-pumped furnace and heated in an inert gas environment to 2000°C, where it was held for 2 hours until the reaction completed. The resulting top surface of the metal-matrix composite coupon was metallographically prepared to a 1 µm finish. The surfaces of the samples were then analyzed using optical microscopy, scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). Vickers microhardness tests were performed on the surface of the metal-matrix composite in order to obtain the microhardness of each phase in the composite. Electrochemical testing was performed on the coupons according to ASTM G59-97(2014) using a 3.5 wt% NaCl solution against a saturated calomel reference electrode (SCE) and a platinum mesh counter electrode.⁸ Linear Polarization Resistance (LPR) scans and Potentiodynamic Polarization (Tafel) scans were conducted using a scan rate of 0.167 mV/s. SEM images were obtained for each sample before and after electrochemical testing in order to observe the effects of corrosion on the composite surface. Miller abrasion testing was conducted on a ZBC and ZNBC coupon according to ASTM G75-15(2015).⁹

RESULTS

Micrographs of the as-processed ZBC and ZNBC samples were obtained using scanning electron microscopy (SEM). Figure 1 shows a side-by-side comparison of the ZBC and ZNBC micrographs acquired at the same magnification to illustrate the noticeable difference in grain size.

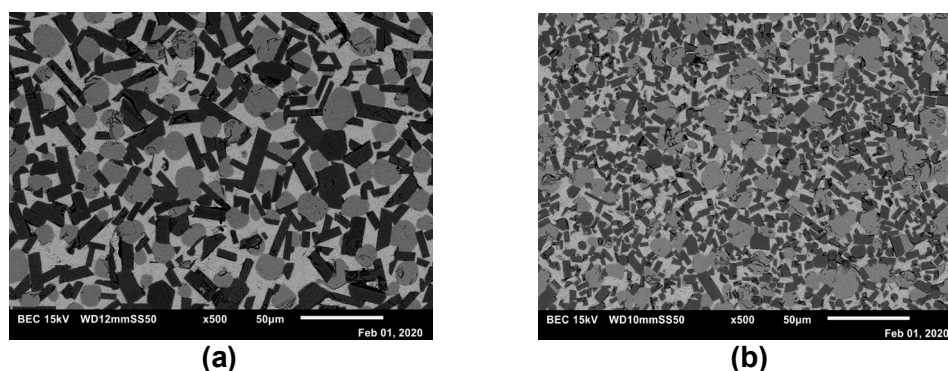


Figure 1: Backscattered electron micrographs of as-processed (a) ZBC and (b) ZNBC (500x)

The backscattered electron micrographs of ZBC before and after corrosion testing are shown in Figure 2a and Figure 2b, respectively. The microstructure of the ZBC in both Figure 2a and Figure 2b illustrates the presence of residual Zr, ZrB₂ platelets and ZrC spheroids. The G59-97(14) electro-

chemical evaluation did not result in significant changes in the microstructure and morphology of the ZBC.

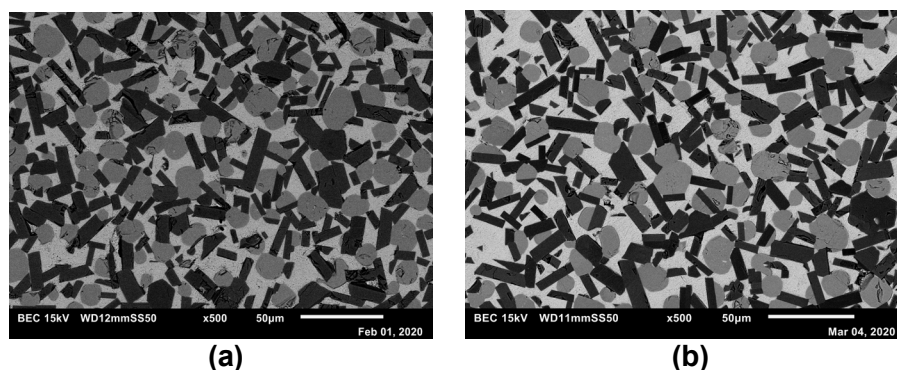


Figure 2: Backscattered electron micrograph of ZBC (a) before and (b) after corrosion tests (500x)

Elemental maps using energy dispersive spectroscopy (EDS) of the ZBC samples were obtained to determine the distribution and elemental composition of the present phases. The elemental maps of the ZBC after corrosion tests are shown in Figure 3. These maps indicated the presence of the residual Zr surrounding the ZrC spheroids and ZrB₂ platelets. Likewise, the elemental map of boron (B) in Figure 3 indicated a strong presence of B in the ZrB₂ platelets. The elemental map of carbon (C) indicates its presence in the ZrC spheroids. The elemental maps did not indicate a significant change in chemical composition following the G59-97(2014) electrochemical evaluation. The presence of phases and elemental maps were consistent with existing literature.^{1,2}

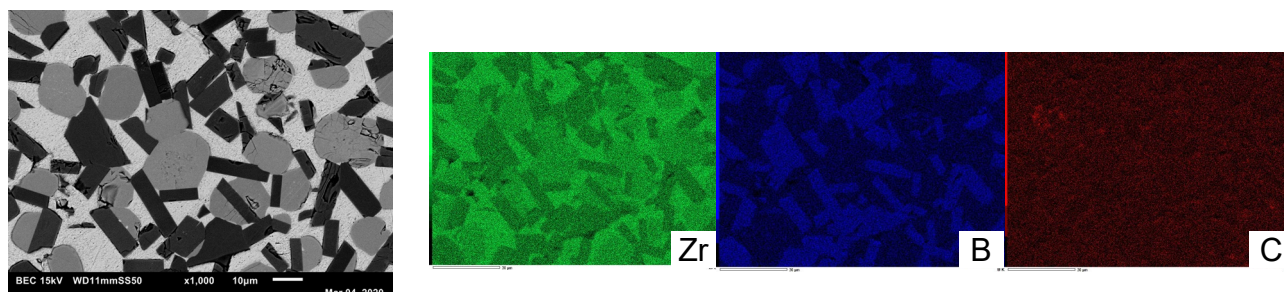


Figure 3: Elemental maps of Zr, B and C for ZBC after corrosion tests (1000x)

Micrographs of the polished ZNBC samples were taken before and after corrosion testing using scanning electron microscopy (SEM). The backscattered electron micrographs of ZNBC before and after corrosion testing are shown in Figure 4a and Figure 4b, respectively. The microstructure of the ZNBC in Figure 4a and Figure 4b illustrates the presence of residual Zr, ZrB₂ platelets and ZrC spheroids. The G59-97(2014) corrosion test did not result in significant changes in the microstructure and morphology of the ZNBC.