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Original Research Paper

Synthesis and room temperature coating of nano ZrB₂ on copper using mechanical roll-millingUğursoy Olgun^{a,*}, Mustafa Gülfen^a, Hasan Göçmez^b, Mustafa Tuncer^b^a Department of Chemistry, Faculty of Arts and Sciences, Sakarya University, Sakarya, Turkey^b Department of Materials Science and Engineering, Faculty of Engineering, Dumlupınar University, Kütahya, Turkey

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ABSTRACT

In this study, ZrB₂ was prepared from ZrOCl₂·8H₂O, H₃BO₃ and citric acid by using the gel method. The gel was dried at 400 °C and then it was calcined at 1500 °C. The prepared 0.5–1 μm ZrB₂ powder was encapsulated into the Cu tube. For the purpose of coating ZrB₂ on Cu metal, the roll-milling of ZrB₂ particles inside the cylindrical Cu tube has been performed at room temperature. The prepared ZrB₂ coating on Cu was analyzed by using FE-SEM, EDS, XRD, electrical resistivity and CV measurements. The final ZrB₂ particle size on the surface of the coating layer was below 100 nm, and the coating thicknesses were about 15–20 μm. The long nanofiber like ZrB₂ structures was observed. The coating of nano ZrB₂ on Cu was achieved by using this novel roll-milling process which is an environmental friendly, low cost and practical technique.

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1. Introduction

Zirconium diboride (ZrB₂) has many interesting high performance material properties for large variety of industrial applications [1]. It is used as the sunlight absorber in concentrated power generation units [2]. It is a ultra-high temperature ceramic material with a melting temperature of 3245 °C [1,3–5]. In addition to its resistance to the high temperatures, ZrB₂ exhibits good chemical stability and the anticorrosive properties [3]. The ZrB₂ containing materials are commonly used in the extreme chemical and thermal environments associated with hypersonic flight, atmospheric re-entry and rocket propulsion applications.³ Unlike many typical ceramic materials, ZrB₂ possesses surprisingly high electrical conductivity (>10⁶ S/m) comparable to those of the metals [6–8]. It shows thermal conductivity of about 57.9 W/m·K at room temperature [9–11]. In the literature, it was also reported that the bulk resistivity of ZrB₂ is 9 × 10^{−8} Ω m [12]. Due to these electrical and thermal properties, ZrB₂ is used for the fabrication of conductive devices [1,13]. Furthermore, ZrB₂ has high hardness (8 mohs) and low thermal stress resistivity [14].

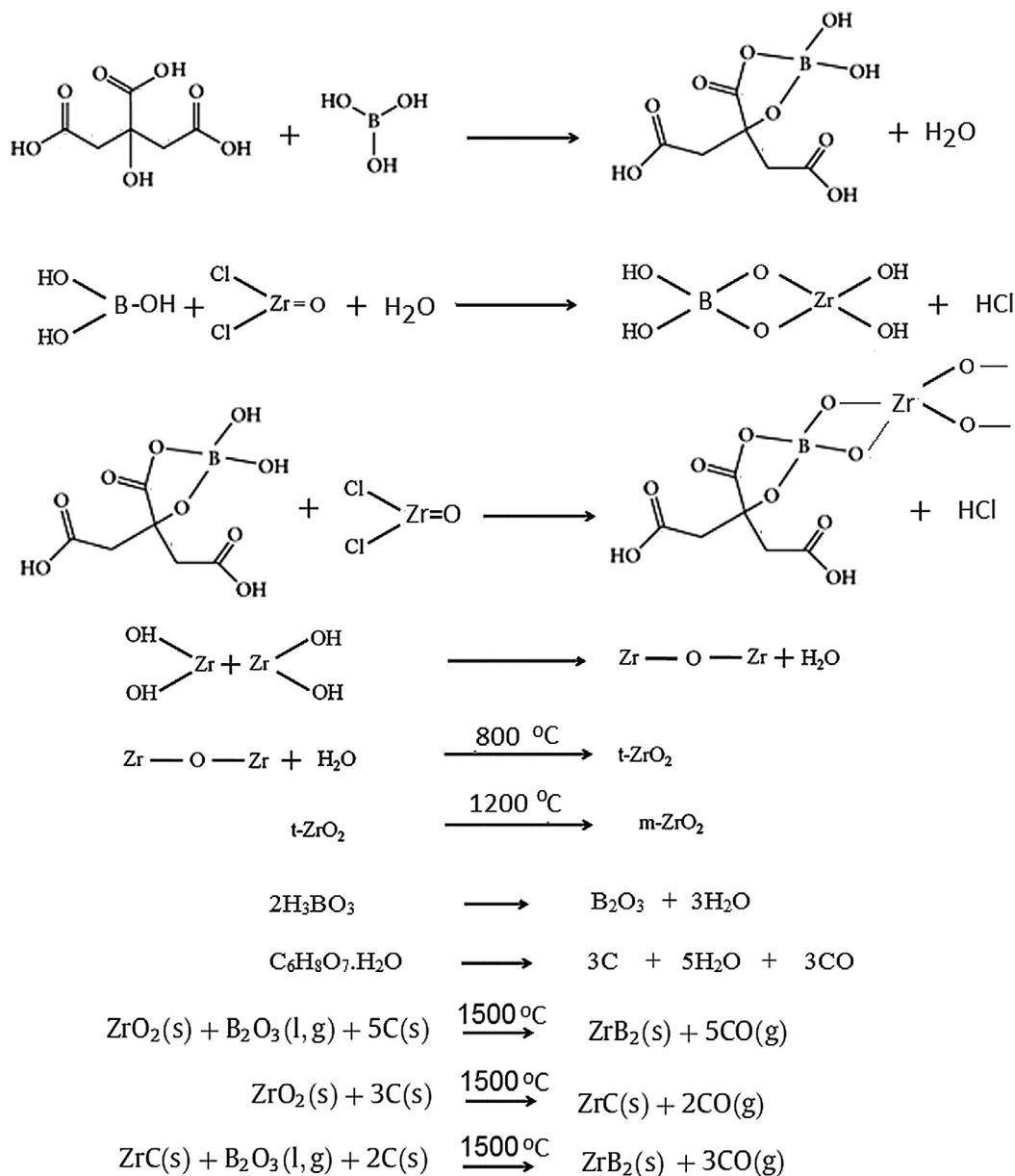
Copper metal has high electrical and thermal conductivity, good corrosion resistance at ambient temperature, excellent malleability/workability and reproducibility. However, it has relatively poor mechanical properties such as hardness and wear resistance. Some

applications, like contacts in electrical switches necessitate the improvements in the mechanical properties without much loss of electrical and thermal conductivities [15]. The melting point of Cu is 1085 °C and the hardness is 3.0 mohs [16]. Copper does not react with water but it does slowly react with atmospheric oxygen to form a layer of brown-black copper oxide which protects the underlying copper from more extensive corrosion. A green layer of copper carbonate can often be seen on copper metal due to the corrosion. Among the metals, copper and its alloys with superior electrical and thermal conductivities are widely used in many different environments and the industrial applications [16].

In the literature, there are some studies about ZrB₂/Cu composites and coatings [16,17]. Jin et al. [18] studied the electroforming technique for the preparation of ZrB₂-Cu composite coatings. The dispersion plating of ZrB₂ was carried out by Norasetthekul et al. [14] in Cu plating baths, resulting in a new electrical contact material. The copper-ZrB₂ composite was prepared via powder metallurgy processing by combining mechanical mixing and hot pressing process at temperature of 950 °C [19]. The copper matrix composite with ZrB₂ particles was also prepared by using mechanical methods and laser melting process [20]. The ZrB₂ ceramics and ZrB₂ containing composites are prepared by various methods, including hot pressing, spark plasma sintering, pressureless sintering and electroforming [5,18]. There are some previous studies in the literature about the ZrB₂ coatings on different substrate materials. Commonly, physical vapor deposition, plasma spray and chemical vapor deposition techniques were utilized for the prepa-

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Scheme 1. Citric acid gel formation and calcination reactions for ZrB₂ production.

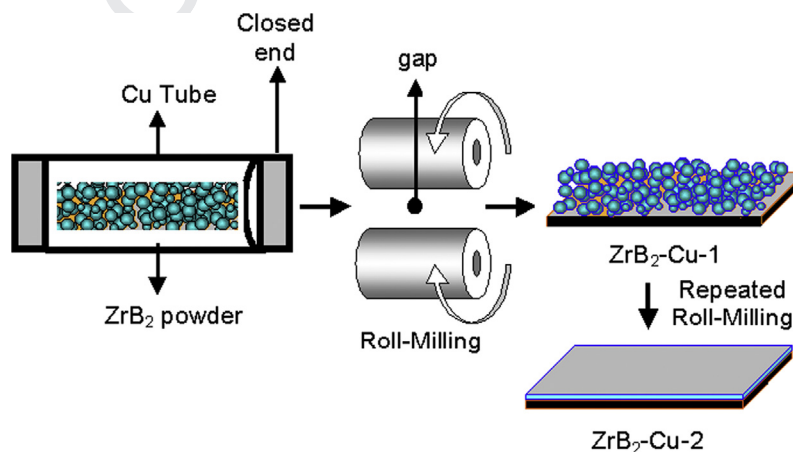


Fig. 1. ZrB₂ coating on Cu metal using the roll-milling process [37].

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