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Influence of autocatalytic coating bath parameters on the formation of copper over surface treated boron carbide particles

J. P. Deepa, T. P. D. Rajan*, C. Pavithran, B. C. Pai

National Institute for Interdisciplinary Science and Technology, CSIR, Trivandrum-695019, India

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ABSTRACT

The functional and structural applications of boron carbide (B_4C) for neutron shielding and engineering sectors are limited due to brittleness and low temperature oxidation; however its use is enhanced by the synthesis of its composites. During composite synthesis, the interfacial compatibility of boron carbide with the matrices can be improved by the formation of metallic coatings. The present study aims at formation of autocatalytic copper coating over surface treated B_4C particles with varying bath parameters and evaluating its influence on coating morphology and uniformity. An effective coating of copper over alkali treated boron carbide was obtained at pH12 and a bath temperature of 30 °C. Above pH 12 as well as higher bath temperatures of 50 and 75 °C leads to predominant co-deposition of metallic copper clusters within the reaction bath. SEM observations of coated boron carbide particles show the formation of copper clusters in the size range of 200–400 nm. The morphology of Cu coating changes from cauliflower-like structure to angular shape with increase in bath temperature and pH. The Debye–Scherrer crystal size calculation shows that copper crystallite size vary from 17 to 25 nm.

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1. Introduction

Boron carbide (B_4C) is one of the potential functional ceramics which possess high neutron absorption cross-section, therefore primarily used as neutron shielding materials. The conserved hardness even at elevated temperature along with good chemical stability, wear and corrosion resistance makes it as a potential strengthening material in various sectors [1]. B_4C has a complex structure consisting of B_{12} icosahedra and three carbon intericosahedral framework which provides it with exceptional thermo-mechanical and electro-chemical properties. The presence of ^{10}B isotope without long-lived nuclides and γ -radiation emission and good chemo-mechanical characterizes makes it as a strong competitor in diverse sectors like nuclear, defense, medicine and space as neutron absorbent shield/detector, wear-resistant ceramics, lightweight body armor, blasting nozzles, high temperature thermoelectric devices, field emission device, etc. [2–10]. In the present diverse requirement of nuclear energy in various sectors and the prime requirement of non-radioactive reaction products with minimal decay problems increase the demand for B_4C as control/shutoff

rods, neutron sensors, human and instrument shielding against neutrons, nuclear/neutron poison and in nuclear material storage/disposal [11].

The demand for nuclear reactors and waste disposal tanks from lead-free radioactive shielding and protecting materials with high neutron absorption cross section and lower X-ray scattering coefficient lead to development of B_4C reinforced components. However, its potential applicability further gets increased due to the existence of changeable semi-conductivity from p to n-type depending on the wide composition and structure variation provided by single phase stable boron-to-carbon atomic ratio from B_4C to $B_{10.4}C$ as very high-temperature thermoelectric material for energy conversion [12]. The reduced structural applicability of B_4C in nuclear industry was due to crack propagation in hot-pressed pellets caused by low ductility, extreme susceptibility to brittle fracture, high vapor pressure and interfacial problems [1,4,11,13]. The poor sinterability and low ion diffusion mobility further shrink its application even at lower metal-ceramic processing temperatures [14]. The low melting thin boric oxide layer present on B_4C particles hinders the densification during sintering [4].

Utilization of B_4C for viable structural application can be enhanced by the formation of cermets and composite materials with metals, ceramics and polymers either in bulk or reinforced form. Metallic coating on boron carbide improves the interfacial characteristics and sinterability during the formation of B_4C reinforced metallic composites. Electroless or autocatalytic reduction, a potential technique for

* Corresponding author. Tel.: +91 471 2515327; fax: +91 471 2491712.

E-mail addresses: deepsjp@gmail.com (J.P. Deepa), tpdrajan@rediffmail.com (T.P.D. Rajan).

forming metallic coating over ceramic particles from a stabilized metastable metal ion complex reaction bath containing pH modifiers and accelerators in presence of a reducing agent containing. The coating nature, formation, adhesion and morphology on the substrate surface depend mainly on bath parameters like bath constituents, pH, temperature and time as well as surface properties, cleaning procedures and additives. Similarly the coating substrate surface characteristics also have greater effect on the formation of the coating. The previous studies on electroless coating of copper on other ceramic particles have shown that the bath parameters play a vital role in the uniformity and adhesion of coating onto the particle surface [15–17]. In the present work the effect of coating bath parameters such as varying pH and temperature on copper coating adhesion, uniformity and morphology over surface treated B₄C particles was investigated. The coated particles were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS).

2. Experimental procedure

Boron carbide particles with average particle size of 20 μm procured from Boron Carbide (India) Ltd. were used in the present study. Surface pre-treated particles under optimized acidic and alkaline condition were sensitized using 0.044 N acidic SnCl₂ solution followed by activation using 0.0001 N acidic PdCl₂ solution under ultrasonic agitation [18]. The ultrasonic agitation improves the size and density of Pd on particle surface, thereby enhancing the coating metal adhesion by increasing the number of anchoring points on the particle surface. The surface activated particles were introduced into autocatalytic reduction bath containing metastable Cu⁺² complexes and alkaline HCHO reducing agent. The reduction was carried out by formate ion (0.7 ml) reducing solution containing 0.08 N Cu-salt (CuSO₄) complexed with 0.176 N Rochelle salt (excess complexing agent was used to prevent untimely precipitation). The effect of bath temperature and pH variation on the surface coating of copper over boron carbide was studied. The pH of the bath was monitored continuously by the pH meter and the bath pH was maintained using alkali replenishment.

EL copper coating was executed by varying the pH from 10 to 12 ± 0.05 for 2 h under temperatures of 30, 50 and 75 ± 1 °C. The coating morphology and uniformity were characterized using scanning electron microscopy (JEOL, Japan), energy dispersive X-ray spectroscopy (Hitachi, Japan) and X-ray diffraction (PANalytical, Netherlands) using CuKα radiation in the 2θ angles ranging from 20° to 80°.

3. Result and discussion

Boron carbide physical appearance changes from shiny black to brownish black to reddish brown depending on the amount of surface copper deposition. Fig. 1 shows the XRD patterns of boron carbide particles with varying surface conditions of (a) as received, and surface treated with (b) acid and (c) alkali conditions. The major peaks in the XRD patterns corresponding to B_xC and varying stoichiometric ratio of boron and carbon peaks represented as B_xC containing B_{9.28}C, B_{3.57}C, B₁₂(BC₂) and B₁₂(BC₂)_{0.76}(B₃)_{0.24} etc. An inevitable peak corresponding to free carbon during the commercial synthesis of B₄C from the carbothermal reduction of boron trioxide was also seen along with base peaks. The reduction in intensity of B_xC peak along with inevitable carbon peak on surface cleaning and other treated B₄C particles were reflected in XRD pattern (Fig. 1b and c). The earlier studies showed that continuous treatment removes inevitable free carbon, less adhered, fine and less stable B_xC phase from particle surface in comparison with untreated particles.

From the SEM micrographs (Fig. 2a), the angular characteristics of B₄C with ≈ 20 μm size having fine containments are well observed. The reduction of surface containments under acid (Fig. 2b) and alkali

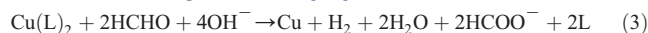
(Fig. 2c) surface pretreatment can improve the adhesion of coating. Earlier studies show better surface cleaning and effective copper adhesion on surface pre-treated B₄C particles [18]. Hence, EL copper coating was carried out on the acid and alkali surface pre-treated particles.

3.1. Acid surface treatment

The XRD pattern of acid pre-treated and copper coated B₄C particles under ambient condition at pH varying from 10 to 12 is shown in Fig. 3. At pH11 the detectable peaks corresponding to copper and its oxides appear along with base peaks of boron and carbon. Very low pH (below 9) and temperature do not provide effective coating over particles. The presence of copper oxide peaks in the XRD pattern on the coated particles indicates the formation of Cu(OH)₂ within the reaction bath, which gets converted to oxides during drying to some extent and a partly due to reaction with entrapped oxygen molecules within reaction bath or with atmospheric oxygen when exposed. The following reaction occurs when Cu(II) reacts with the excess hydroxide ion in the reaction bath and during drying it gets converted to CuO crystals.



At pH below 11, the higher potential energy required for the dissociation of metal ion and lower negative reduction potential leads to the excessive deposition of metallic coating on highly activated energetically favored anchoring points. The overall reaction happening in electroless bath is given below [19].



where 'L' is the complexing agent.

With increase in pH to 12, the higher metal ion release and increased Brownian movement within the reaction bath increases the uniformity of coating on highly activated regions. At pH12 high alkalinity favors the formation of more Cu(OH)₂ and it gets reduced to its oxides depending upon the availability of adsorbable oxygen.

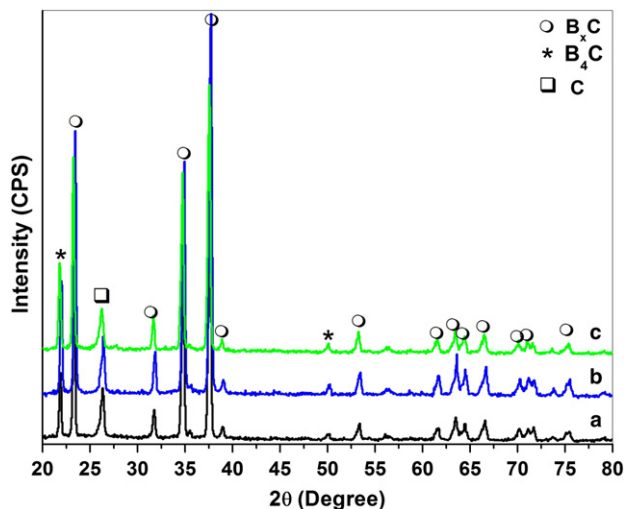


Fig. 1. XRD pattern of (a) as received (b) acid treated, and (c) alkali treated B₄C particles.

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