İÇİNDEKİLER/CONTENTS

Co-Mn/TiO₂ catalyst to enhance the NaBH₄ decomposition
.....................................................................................................................................................Gözde Özsaçmacı, Çetin Çakanyıldırım, Metin Gürü 1

Boron-substituted bioceramics:A review
.....................................................................................................................................................Bengi Yılmaz, Zafer Evis 6

DIN 1.2842 çeliğinin borlanması ile oluşan borür tabakası üzerine borlama sıcaklık ve süresinin etkileri
........................................................................................................................................................Polat Topuz 15

Boron isotopes enrichment via continuous annular chromatography
.....................................................................................................................................................Gonca Sağlam, Ahmet R. Özdural 20

Microwave-assisted direct synthesis of boronated alkanolamine succinic anhydride esters as potential surfactants for various application
........................................................................................................................................................Arun K. Chattopadhyay, Troy Gaona, Beth Bosley 28

Bor bileşiklerinin alev geciktirici ve yüksek sıcaklığa dayanıklı pigment olarak uygulanabilirliği
........................................................................................................................................................Duygu Yılmaz Aydın, Metin Gürü, Barış Ayar, Çetin Çakanyıldırım 33

Resin type and resin diameter effect on the adsorption of boron isotopes
.....................................................................................................................................................Gonca Sağlam, Zeynep Aktosun, Gülşah Özçelik, Ahmet R. Özdural 40

Characterization of W₂B nanocrystals synthesized by mechanochemical method
........................................................................................................................................................Mustafa Barış, Tuncay Şimşek, Hakan Gökmeşe, Adnan Akkurt 45
ABSTRACT
Developing catalyst to create a feasible system for NaBH₄ hydrolysis would increase the widespread use of clean energy producing fuel cell system. However, transfer difficulties such as; three phase reaction mechanism and reactant-side product solubility problems limit the promising proper-
ties of the hydrolysis systems. In this study Co₁₋ₓMnx bimetallic catalyst was produced and adhered on TiO₂ support by co-reducing method. Opti-
timum NaOH concentration for the catalyst and reaction conditions was determined before the studies. In the experiments it was proved that only 40 mg of Co₀.₇Mn₀.₃/TiO₂ catalyst is highly active to decompose NaBH₄ at 20 °C. SEM-EDX results revealed that the catalyst homogeneity and ac-
tive sites existence are valid after reaction. Released hydrogen was col-
lected by inverse burette apparatus and maximum hydrogen generation rate was calculated as 43.6 mL H₂ s⁻¹ g⁻¹ catalyst at 20 °C. Investigations resulted that the reaction obeys first order kinetic on the basis of NaBH₄ and the activation energy is 38.7 kJ.mol⁻¹.

ARTICLE INFO
Artlice history:
Received 14 January 2016
Received in revised form 21 February 2016
Accepted 21 February 2016
Available online 24 March 2016

Keywords:
Bimetallic catalyst,
Hydrolysis,
NaBH₄

1. Introduction
Environmental and waste problems might be stated as the hardest task addressed to scientists for feasible solutions. Waste problems can be mainly divided in to two categories; first waste materials produced due to the production necessities and the second matters (mostly gases) trashed by energy produc-
tion processes. Concisely, industry and transportation are named as the main sources of pollution. Energy production methods for both of these sectors must not be interrupted however it is believed a revolution is needed to update these methods to more environment-
list and economic form. That would double the low yield of interior combustion engine and makes its waste tens of times less. Fuel cell (FC) technologies are seems to be the best candidate to take the duty, however a few problems retards the widespread use. Continuously hydrogen feeding to FC anode side is one of the technical problems since the current stor-
age alternatives are not able to meet the expectations [1]. At this point metal borohydrides are lifesaving. Especially NaBH₄ is known as the most applicable one with its 10.8 wt% hydrogen capacity.

Catalytic hydrolysis of NaBH₄ in alkaline medium of-
fers advantageous reactant spent fuel composition for recycling process and possibility of wide range of ac-
tive metal utilization. Noble Pt, Pd, Ir, Rh, Ru [2] and non-noble metals Co, Ni, Fe, Cu, Mn, Mo [3-6] can be utilized solely or in alloy like structures for NaBH₄ dehy-
drogenation. Rapid catalytic decomposition of NaBH₄ should be suppressed by increasing the reaction me-
dium pH value. For that purpose NaOH is introduced to reaction medium. It has two distinct advantageous apart from other hydroxides, first economic point of view and second no risk to give cation exchange re-
action with NaBH₄. In the literature many concentra-
tion values are advised for NaOH between 2-30 wt% (%10 [5], %2.5-30 [7], %2 [8]). Effect of NaOH amount differs according to the catalyst and support type [9]. Thus pioneer experiments should be performed to be sure about the optimum NaOH concentration.

Decomposition of NaBH₄ is favorable in the pres-
ence of supported catalysts. There are many ma-
terials to be used as support material such as: acti-
vated carbon, Al₂O₃, TiO₂, diatomite, zeolites, etc. Aim of support material usage may be explained in
a few captions; (a) Separation of the used catalyst become easy, (b) Support-precursors engagement may increase the catalytic effect, (c) Catalyst may be designed in any 3 dimensional shape (d) Support provides broad surface area that is necessary to achieve high hydrogen generation rates (HGR). The proper selection of support provides catalyst to retain its specific properties, such as porosity, surface area, dispersion, selectivity, and activity. The morphology and pore size of the selected support materials play an important role in enhancing the catalyst’s stability and performance. TiO$_2$, due to its nontoxicity, long-term photostability, and high effectiveness, has been widely utilized in mineralizing toxic and nonbiodegradable environmental contaminants. TiO$_2$ possesses good mechanical resistance and stabilities in acidic and oxidative environments. These properties make TiO$_2$ a prime candidate for catalyst support.

Dehydrogenation process of NaBH$_4$ shows quite differences depending on the catalyst materials and reaction conditions. Kinetic studies performed report that the reaction order of the dehydrogenation can differ from negative [10] to positive values. Mostly reactions obey first order [8, 11] while a few are zeroth order [12, 13]. Negative reaction order means decreasing kinetics with NaBH$_4$ amount. Actually this behavior is valid for all the catalyst type if the NaBH$_4$ concentration is kept high because of its and NaBO$_2$ limited solubility. Role of the catalyst is decreasing the activation energy. Decrease in the activation energy would let the reaction yield further even the reaction temperature is unchanged. The activation energy variation of the performed studies is summarized by Rakap et al. between 27-76 kJ/mol [5].

In this study Co-Mn bimetallic catalyst is produced by impregnation technique on TiO$_2$ support. Hydrolysis condition, behavior and kinetic data of the produced catalyst are reported for different reactant ratios and temperatures.

2. Materials and methods

CoCl$_2$.6H$_2$O and MnCl$_2$.4H$_2$O were provided by Sigma-Aldrich with 98% and 99% purity, respectively. Hexadecyltrimethylammonium bromide (CTAB, CH$_{16}$(CH$_3$)$_2$N(Br)(CH$_3$)$_3$) was provided by Sigma-Aldrich with 98% purity and utilized as surfactant.

2.1. Catalyst preparation

The Co$_{x}$Mn$_{1-x}$ bimetallic catalysts were synthesized at four different mole ratios (x=0, 0.1, 0.3 and 0.5) in the presence of surfactant (CTAB). Amounts of CoCl$_2$.6H$_2$O and MnCl$_2$.4H$_2$O were calculated and dissolved in 5 mL of distilled water. Then solution trickled on 200 mg TiO$_2$ support in a way that results 20wt% Co$_{x}$Mn$_{1-x}$ on support. 75 mg of CTAB was added to the precursors and solution was stirred for 10 min. Then, 3 mL of aqueous solution of the reducing agent NaBH$_4$ (1.632 mmol) was added drop wise to the solution. The solution was then strongly shaken and stirred for 5 more min to uniformly form the black particles suspension. Reactor content was centrifuged at 6000 rpm for 5 min to put aside the particles, subsequently solid residue was washed with deionized water. Centrifugal and washing processes were repeated for 3 times. Catalyst particles were dried in vacuum-oven which, operates at 50 °C and under 150 mmHg pressure.

2.2. Catalyst testing

100 mg of NaBH$_4$ and 70 mg of NaOH are weighed and dissolved in 5 mL of distilled water. 40 mg of Co$_{x}$Mn$_{1-x}$/TiO$_2$ catalyst was put in the dehydrogenation reactor whose two outlets are designed to feed the alkaline NaBH$_4$ solution and to transfer produced hydrogen to the inverse burette. Reactor temperature was set to 20 °C with 0.1 °C accuracy for all experiments. Before introducing the alkaline NaBH$_4$ solution, reactor and its content is rested for 15 minute to provide thermal equilibrium and check for the risk of leakage. Dissolved NaBH$_4$ and NaOH were introduced in reactor and hydrogen product was collected in the measured burette and volume versus time data were reported. Temperature increase of the reactor due to the exothermic reaction of hydrolysis was neglected since the reactor contents are very dilute and the decomposition reaction is slightly exothermic.

2.3. Kinetics of the catalyst

In order to determine the kinetic data of the catalysts, similar method explained for catalyst testing was applied. Reactor temperature was arranged between 20-60°C by 10 °C increasing steps to calculate the activation energy by Arrhenius equation. A temperature controlled oil bath was utilized to provide reaction condition with 0.1°C accuracy. Reaction rate order was investigated on the NaBH$_4$ basis. For this purpose, 0.263, 0.526, 1.053 and 1.579 M, 5 mL of NaBH$_4$ was decomposed at 20 °C. In each of the experiments 40 mg 20wt% Co$_{x}$Mn$_{1-x}$/TiO$_2$ catalyst was used and the amount of hydrogen released was continuously recorded.

3. Results and discussion

3.1. Effect of NaOH concentration

Alkaline reaction medium is always used to suppress and control the sudden hydrolysis kinetics. Competition between OH$^-$ and the BH$_4^-$ ions slows down the hydrolysis. However the mechanism is not clear all the time. Concentration of the NaOH can make radical changes on the reaction. Thus a series of hydrolysis test were performed to decide the optimum NaOH amount. 100 mg of NaBH$_4$ is decomposed in the presence of 40 mg Co$_{0.5}$Mn$_{0.5}$/TiO$_2$ catalyst in each of the
Results, are drawn in Figure 1, depicts on its logarithmic scale that the optimum NaOH concentration is around 0.35 M (1.4 wt%) NaOH if the hydrogen generation rates are considered. Similarly, Yuan and coworkers are also reported the optimum NaOH concentration for Co-Mn-B catalyst as 1-5 (wt)% [4].

3.2. Hydrolysis tests

100 mg NaBH₄ is hydrolyzed each time in the presence of 40 mg CoₓMnᵧ/TiO₂ supported bimetallic catalyst. SEM-EDX analysis given in Figure 2 shows that even after hydrolysis process catalyst is still keeping its chemical and physical properties. EDX mapping indicates the active sites which are the composition of Co and Mn are homogenously adhered on the surface. Co and Mn catalyst alloy is close to the outer surface (in the range of EDX electron gun) and ready for another hydrolysis experiment. The elements of side product NaBO₂ are also strongly visible on the surface as seen in oxygen and sodium mapping. Accumulation of these elements eventually ends the activity of the catalyst. Low solubility of the side product NaBO₂ is the main reason of that harmful deposition. In order to avoid coverage of side product excess amount of water usage may be a temporary solution for small scale devices. NaBH₄ decomposition product hydrogen was collected by inverse burette. Hydrogen levels in the burette were recorded versus time at 20 °C. Temperature rise of the reaction exponentially increases the rate therefore temperature should be arranged to able to follow gas release properly. HGR for the catalyst with different Co:Mn content are depicted in Figure 3. Inactivity of sole Mn catalyst is the most interesting part of the graph. In the periodic table, Mn is on the left of iron and it is at the edge of non-noble catalytic elements. However Co-Mn alloy perform better HGR than that of Co catalyst could do solely. The addition of small amounts of Mn to a Co/TiO₂ catalyst affects the catalytic performance by increasing the activity and suppressing the byproducts. These variations in the catalyst selectivity are due to Mn promotion effects that influence the final catalyst active site distribution, playing a role under reaction conditions. In Table 1, HGR values which were calculated between a certain time intervals are given. Initial 30 seconds and time required to release 85% of total hydrogen are selected as the first and last points for HGR calculation. In Figure 3 it is clear that the Co₀.₇Mn₀.₃/TiO₂ catalyst result in the maximum performance. Co is the most active non-noble element for NaBH₄ decomposition and its activity can be increased further by alloying with suitable elements. Alike elements can be alloyed according to Hume-Rothery rules in metallurgy science. It is interesting to see the same elemental behavior and validity of these rules in catalyst synthesis.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>HGR, mL g⁻¹ s⁻¹</th>
<th>g_catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co₀.₇Mn₀.₃/TiO₂</td>
<td>43.6</td>
<td></td>
</tr>
<tr>
<td>Co₀.₅Mn₀.₅/TiO₂</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>Co₀.₇Mn₀.₃/TiO₂</td>
<td>21.1</td>
<td></td>
</tr>
<tr>
<td>Co₀.₉Mn₀.₁/TiO₂</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Co₀Mn₁/TiO₂</td>
<td>0.2</td>
<td></td>
</tr>
</tbody>
</table>

The life cycle of the Co₀.₇Mn₀.₃/TiO₂ catalyst was tested in 5 distinct tests. HGR and cumulative hydrogen

![Figure 1. Effect of alkalinity (on logarithmic scale) on hydrogen generation rate (20 °C, 100 mg NaBH₄, 40 mg Co₀.₅Mn₀.₅/TiO₂).](image1)

![Figure 2. Elemental distribution over catalyst surface (20 wt% Co₀.₅Mn₀.₅/TiO₂).](image2)
amount obtained are compared. Results are indicating that no detectable activity change occurs on the surface after 5 runs. That encourages using the catalyst for long term periods. However, reactant concentration and catalyst washing-rinsing procedures mainly affect the results and detailed investigations considering these parameters should be performed.

Kinetic calculation of the catalysts was done according to the rate equation given below. Firstly NaBH₄ concentration effect on the rate equation was determined. In 5 mL alkaline solution four different molar concentration of NaBH₄ were decomposed in the presence of constant amount of Co₀.₅Mn₀.₅/TiO₂ catalyst. Initial values of decomposition were recorded as shown in Figure 4. Increasing the reactant molarity results higher initial rates. If the reaction rate is assumed as first order on the basis of NaBH₄ concentration gives a straight line and the slope is close to one. Thus the reaction can be accepted to happen according to the first order rate law. First order reactions depended on reactants concentration. If the bulk is dilute, amount of reactant on the (inner and outer) surface decrease because of the poor adsorption mechanism. In other word, in such condition, adsorption process is the rate limiting due to Langmuir-Hinshelwood approach.

Temperature dependence of HGR is studied between 20-50 °C as given in Figure 5. Gas volume of captured hydrogen is used to compute the decomposed NaBH₄ mole numbers and they graphed versus time to create the inset of Figure 5. Increasing HGR values, as the temperature raises, is not a surprise according to the Arrhenius equation given below. Where k is the reaction rate constant, kₒ is the frequency constant, T is the absolute temperature, R the ideal gas constant and Eₜ is the activation energy of the decomposition. Arrhenius equation in which logarithm of reaction rate constant (slopes of inset in Figure 5) against reciprocal of absolute temperature is plotted in Figure 6 and the activation energy was found as 38.7 kJ/mol.

\[ \ln(k) = \ln(k_o) - \frac{E_t}{RT} \]
4. Concluding remarks

In this study it was found that the TiO$_2$ supported Co-Mn bimetallic catalyst is beneficial to develop the NaBH$_4$ hydrolysis systems. Experimental studies revealed that, 5 mL, 0.526 M NaBH$_4$ and Co$_{0.7}$Mn$_{0.3}$/TiO$_2$ catalyst is able to reach up to 43.6 mLH$_2$.s$^{-1}$.g$^{-1}$ catalyst hydrogen generation rate at 20 °C. SEM-EDX analysis depicted that the catalyst surface keeps its activity and proper active site distribution even after hydrolysis process. Kinetic data were collected at different temperatures and NaBH$_4$ concentrations. Results indicate that the Co$_{0.5}$Mn$_{0.5}$/TiO$_2$ catalyst activation energy is 38.7 kJ.mol$^{-1}$ and the reaction fits to first order rate on the basis of NaBH$_4$. Mass transfers of the reactant-product are thought to be the limiting step of the process. These findings would be beneficial to develop the hydrogen generating systems to feed devices like fuel cells. However water management (which decrease the system energy density) and scale-up problems still need further investigations.

Acknowledgements

The financial support of this study is from Hitit University Project number MUH03.13.005 is gratefully acknowledged.

References


ABSTRACT

Biomaterials can be designed by imitating and taking inspiration from the forms and compositions of natural tissues. The inorganic component of the hard tissues; bone, dentin and enamel, is hydroxyapatite (Ca\(_{10}\)(PO\(_4\))\(_6\)(OH)\(_2\)) containing various trace elements that are important in biochemical reactions of bone metabolism. Boron is considered as an essential element for human physiology and it has many biologic effects especially on hard tissues. As it is in the natural hard tissues, substitution of boron into the structure of hydroxyapatite or other bioceramics, such as calcium phosphates and bioglasses, could enhance angiogenesis and osteogenesis of the damaged tissue. This review covers briefly the recent and very recent works on preparing numerous bioceramic, bioglass and glass-ceramic systems containing boron.

1. Introduction

The definition of the term biomaterial is “a substance that has been engineered to take a form which, alone or as part of a complex system, is used to direct, by control of interactions with components of living systems, the course of any therapeutic or diagnostic procedure, in human or veterinary medicine” [1]. Biomaterials can be divided into different groups according to their structural, chemical, and biological characteristics. They are classified as ceramics, glasses, metals, polymers and composites likewise to the general material classification. In addition, biopolymers, self-assembled systems, nanoparticles, carbon nanotubes and quantum dots are also the parts of the biomaterial family.

Bioceramics are the group of biomaterials that are used for the repair and reconstruction of diseased or damaged parts of the musculoskeletal system. They can be bioinert (alumina, zirconia), resorbable (tricalcium phosphate (TCP)), bioactive (hydroxyapatite (HA), bioactive glasses, and glass-ceramics), or porous for tissue ingrowth (HA-coated metals, alumina) [2]. Bioactive ceramics are capable of direct bonding to living tissues without causing the formation of a fibrous tissue layer at the interface. In contrast, bioinert ceramics are biologically inactive and have no ability to bond to the surrounding living tissue; therefore they are mostly encapsulated by a fibrous tissue with variable thickness. Consequently, bioactive bioceramics are more suitable when new bone tissue growth and mechanical support are needed. Resorbable bioceramics are preferred for filling in gaps to be replaced by normal bone.

The composition and features of various bioceramics are given in Table 1. Calcium phosphate (CaP) family, especially HA, is the main member of bioceramics that can be used for repair of bone defects, e.g. for joint or tissue replacement, applied as coatings for metal implants to improve biocompatibility of the surface, and function as a resorbable temporary framework. They can also find use in drug delivery systems.

The most widely used CaP compounds in medical area are HA and TCP. All CaPs have different characteristics. For example, monocalcium phosphate monohydrate (MCPM) is the most acidic and the most soluble at almost all pH values, dicalcium phosphate (DCP) is the most stable at low pH, tetracalcium phos-
phosphate (TetCP) is the most soluble below a pH of 5 and the most basic, and HA is the most stable in aqueous solutions and the most biocompatible one in the CaP family [5].

The history of the use of CaPs in healthcare starts in 20th century. TCP was first applied in vivo by Albee and Morrison in 1920 [6]. It was in 1952 that Ray et al. [7] implanted HA in rats and guinea pigs to compare synthetic HA with fresh autogenous and frozen bone in filling various skeletal defects. HA has been used as a bioactive and biocompatible coating material on metallic implants since the publication of first clinical results by Furlong and Osborn in 1991 [8]. Calcium phosphate cement (CPC), which sets to HA when moistened, was first formulated by Brown and Chow [9] in 1985 and this water setting cement was a new form of CaPs for the treatment of bone defects especially in craniofacial and maxillofacial areas.

Table 1. Compositions and features of various bioceramics [3,4]

<table>
<thead>
<tr>
<th>Name</th>
<th>CaP Formula</th>
<th>Feature/Application/Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ca/P Family</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCPA monocalcium</td>
<td>Ca(HPO₄)₂</td>
<td>Soluble in water</td>
</tr>
<tr>
<td>phosphate anhydrous</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MCPP monocalcium</td>
<td>Ca(HPO₄)₂·H₂O</td>
<td>Soluble in water; cement powder</td>
</tr>
<tr>
<td>phosphate monohydrate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DCPD dicalcium</td>
<td>CaHPO₄·2H₂O</td>
<td>Cement powder</td>
</tr>
<tr>
<td>phosphate dehydrate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DCPA dicalcium</td>
<td>CaHPO₄</td>
<td>Cement powder</td>
</tr>
<tr>
<td>phosphate anhydrous</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OCP octacalcium</td>
<td>Ca₅(PO₄)₃·5H₂O</td>
<td>Transient intermediate phase; reaction product</td>
</tr>
<tr>
<td>phosphate anhydrous</td>
<td></td>
<td>in cement setting; powder</td>
</tr>
<tr>
<td>ACP amorphous calcium phosphate</td>
<td>1.50</td>
<td>Amorphous; transient intermediate phase; powder</td>
</tr>
<tr>
<td>β-TCP tricalcium</td>
<td>Ca₃(PO₄)₂</td>
<td>Resorbable; sintered body (dense and porous), powder</td>
</tr>
<tr>
<td>phosphate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-TCP tricalcium</td>
<td>Ca₃(PO₄)₂</td>
<td>Cement powder</td>
</tr>
<tr>
<td>phosphate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcium deficient</td>
<td>Ca₃(PO₄)₂OH</td>
<td>Low or moderately crystalline; decomposes above 700°C; low crystalline material is resorbable</td>
</tr>
<tr>
<td>HA hydroxyapatite</td>
<td></td>
<td>Low to highly crystalline; sintered body (dense or porous), powder, coating, composite, fiber; low crystalline material is resorbable; highly crystalline material is nonresorbable and osteoconductive</td>
</tr>
<tr>
<td>+TCP tetracalcium</td>
<td>Ca₅(PO₄)₃</td>
<td>Cement powder</td>
</tr>
<tr>
<td>phosphate</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Others</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y-TZP yttria-stabilized tetragonal zirconia</td>
<td>Y₂O₃·ZrO₂</td>
<td>Sintered body (dense)</td>
</tr>
<tr>
<td>Aluminum oxide</td>
<td>Al₂O₃</td>
<td>Sintered body (dense)</td>
</tr>
<tr>
<td>(alumina)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Titanium oxide</td>
<td>TiO₂</td>
<td>Sintered body (dense)</td>
</tr>
<tr>
<td>(titania)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicon nitride</td>
<td>Si₃N₄</td>
<td>Sintered body (dense)</td>
</tr>
<tr>
<td>Silicon carbide</td>
<td>SiC</td>
<td>Sintered body (dense)</td>
</tr>
<tr>
<td>Carbon</td>
<td>C</td>
<td>Fiber</td>
</tr>
<tr>
<td>Bioactive glasses system</td>
<td>SiO₂·P₂O₅·Na₂O·CaO</td>
<td>Bulk</td>
</tr>
<tr>
<td>Silicon oxide</td>
<td>SiO₂·P₂O₅·Na₂O·CaO·MgO</td>
<td>Bulk</td>
</tr>
<tr>
<td>Bioactive glass-ceramics system</td>
<td>SiO₂·P₂O₅·CaO·Al₂O₃</td>
<td>Bulk</td>
</tr>
<tr>
<td>Apatite-Wollastonite (A-W)</td>
<td>SiO₂·P₂O₅·Na₂O·K₂O·CaO·MgO (Ceravital)</td>
<td>Bulk</td>
</tr>
</tbody>
</table>
called apatites [12]. More generally, the term apatite includes a large class of minerals and synthetic compounds represented by $M_{10}(A\text{O}_4)_X$. $M$ is most often an alkaline earth ion, the tetrahedral group is generally (PO$_4$) and X is usually a hydroxide, halide, oxide or sulfide ion [13].

The channel site in the HA structure is occupied by OH$^-$ but when the other substituting ions F$^-$ or Cl$^-$ fully occupies this site the apatite becomes fluorapatite and chlorapatite, respectively. Apatite is more prone to accept chemical substitutions compared to most other minerals. Ion substitutions affect the structure of apatites and change their mineral properties, such as solubility, hardness, brittleness, strain, thermal stability, and optical properties [14].

In addition, anions, such as AsO$_4^{3-}$, SO$_4^{2-}$, CO$_3^{2-}$, SiO$_4^{4-}$ can replace PO$_4^{3-}$, and many cations, such as K$^+$, Na$^+$, Mn$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Zn$^{2+}$, Sr$^{2+}$, Ba$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Y$^{3+}$, and trivalent ions of rare-earth elements can substitute for Ca$^{2+}$ (usually in trace concentrations) [14]. Therefore, it is possible to design and develop advanced HA biomaterials for certain specific applications with the use of the ability to exchange various ions in this structure [15].

Boron is one of the dopant elements that attract the attention of biomaterial scientists due to its natural functions in human hard tissues. This paper aims to review the recent studies on substitution of boron into the structure of bioceramics with a main focus on calcium phosphates. From the studies in the literature, it can be said that current research on boron doping into the structure of bioceramics has shown some promises of enhancing the service characteristics of these biomaterials.

2. Boron and hard tissues

Boron (B, atomic number 5) is the first element in Group IIIA and the only nonmetal in the family. It exhibits the bonding and structural characteristics of both metals and nonmetals. In nature, boron does not occur in its elemental form [16]. It reacts with oxygen to form boric acid (H$_3$BO$_3$). Boron occurs naturally in the form of borates, such as borax, which are the salts or esters of boric acid and they are the compounds that contain or supply boric oxide (B$_2$O$_3$).

The Babylonians were believed to use borax for working gold over 4000 years ago and Egyptians were thought to use for mumifying, medicinal and other metallurgical applications. However, the first use of tinkar (i.e., Na$_2$B$_4$O$_7$.10H$_2$O, the mineral borax) dates back to the 8th century around Mecca and Medina, and it was brought there (and to China) by Arab traders. The use of borax by European goldsmiths dates to about the 12th century. [17]. The element boron was first isolated by Joseph Louis Gay-Lussac, Louis Jacques Thénard, and Humphry Davy separately in 1808 [18]. Currently, boron is largely produced in Turkey and the USA, and is used in a wide range of products, including glass, detergents, fire retardants, fibers to reinforce plane fuselages and body armor, and superhard materials [19].

The history of boron in biological systems is relatively recent and starts with its acceptance as an essential nutrient for plants. Boron was considered as necessary to complete the life cycle of plants after the reports by Warington in 1923 and Sommer and Lipman in 1926. It is now known as a constant constituent of foods of plant origin due to its structural role in plant cell walls [20]. Boron is also accepted as an essential trace element to human health, mainly for wound healing functions and bone health [21].

Boron has many biological effects, such as (1) actions on reproduction and embryogenesis, (2) improvement of wound healing and response to injury or infection, (3) modifications of calcium and bone metabolisms (4) beneficial effects on central nervous function, (5) effects on the presence or function of vitamin D and hormones, including thyroid hormone, insulin, estrogen and progesterone [20, 22]. It is known to interact with calcium, vitamin D and magnesium, all of which play a role in bone metabolism [23]. At the molecular level, it was reported that boron enhances RNA transcription in the isolated placental nuclei and stimulates mRNA translation, especially those encoding growth factors involved in angiogenesis and wound repair [22].

The accumulation of boron in bone is significantly greater than those found in blood or soft tissues and the concentrations depend on the intake [24, 25]. Boron level in human bone tissue of one individual is 0.90 ppm [25]. Although no estimated average requirement or adequate intake levels have been determined for boron, based on animal data, the tolerable upper intake level is set for an adult at 20 mg/day [26]. In a study where the subjects were instructed to take daily either a 3 mg/day boron supplement or a placebo, it was shown that even this amount of dietary boron intake can cause a slight increase in bone mineral density [27].

A boron-deficient diet (0 vs 3 mg/kg) leads to decreased weight gain, femur strength, and femur concentrations of the minerals associated with the organic matrix: copper, iron and magnesium in rats. In addition, the vertebral microarchitecture was also altered by boron supplementation, in such a way that trabecular thickness of boron-supplemented rats was found to be greater than that of boron-deficient rats [28]. Another study on the effect of boron on the concentrations of mineral elements associated with the bone organic matrix noted that the amount of zinc and potassium in tibia was increased by boron supplementation [29].
One study reports the altered periodontal alveolar bone modeling and remodeling due to an inhibition of bone formation in mice that were treated with a boron-deficient diet (0.07 vs 3 mg/kg diet for nine weeks) [30]. Another study revealed that boron supplementation (50 mg/kg body weight B in 96 h) resulted in significantly increased bone mineral density, maximum breaking force of femur and compression strength of tibia in rabbits fed with a high energy diet [31]. Boron intake (3 mg/kg daily for 40 days) was reported to have a positive effect on bone regeneration of the midpalatal suture in response to expansion in rabbits [32]. Boron supplementation in long-term diet as 5 mg sodium borate/kg was noted to increase the serum osteocalcin concentrations in gilts which can be assumed as a measure of increased osteoblast activity or bone remodeling [33].

In addition, in vitro cell studies showed that boron is a dose-dependent regulator on the osteoblastic cells. Hakki et al. [34] performed cell viability tests on pre-osteoblastic cells (MC3T3-E1) with different concentrations of boron in the cell culture media. It was shown that addition of boron at a concentration of 1000 ng/ml or above decreased cell survival rate in short time period (at 24 h), while there was no statistically significant difference in different boron concentrations when compared to untreated control group in long term. They also observed remarkable regulation in favor of osteoblastic function for collagen type I, osteopontin, bone sialoprotein, osteocalcin and Runx2 mRNA expressions in B-treated groups. The levels of bone morphogenic proteins (BMPs) were increased at 0.1, 1, 10 and 100 ng/ml B concentrations. Similarly, the proliferation and osteogenic differentiation of MC3T3-E1 cells was shown to be affected by the release of boron from a chitosan scaffold with boric acid-doped chitosan nanoparticles (diameter of approx. 175 nm) by Gümüşderelioğlu et al. [35]. The alkaline phosphatase (ALP) activity, which is the early stage marker of osteogenic differentiation, was shown to increase on scaffolds containing boron encapsulated nanoparticles.

### 3. Boron-substituted calcium phosphates

Based on the knowledge that boron has many physiological effects beneficial to bone growth and maintenance, it has been applied as a dopant element in CaPs. Anions, such as borate, may replace negatively charged PO₄³⁻ groups and/or OH sites in the HA lattice and this affects physicochemical, biological, functional, and surface features of HA and in turn its performance as a biomaterial. The electrostatic interactions and chemical bonding between the biomaterial and body proteins and solubility of substituted apatite would also be affected.

B-substituted HA particles were synthesized by the wet chemical processing method and a subsequent thermal treatment was applied at the temperature ranging from 700-1200°C by Hayakawa et al. [36]. Nuclear magnetic resonance (NMR) studies showed that no B atom was incorporated into HA lattice structure by this method without heat-treatment. When a heat-treatment above 900°C was applied to the particles, a chemical reaction took place resulting in the formation of B-substituted HA particles accompanied by the formation of β-TCP phase which transforms to α-TCP at 1200°C. The Ca/P ratio of 0.4 wt% B containing HA was 1.60 before and after being heat-treated, which means B-substituted HA was calcium-deficient compared with stoichiometric HA (Ca/P=1.67).

Barheine et al. [37] also used NMR to investigate the structural model of borate containing CaP prepared by a high-temperature solid state reaction sintering process. The material consisted of HA and a disordered borate containing CaP phase. The crystalline HA did not accommodate the borate groups and all borate units were located in CaP. The various BO₃³⁻ units were shown to be randomly distributed in the phosphate network of CaP phase.

On the other hand, borate groups, such as BO₃³⁻ and BO₂⁻, were shown to partially substitute both PO₄³⁻ and OH sites in HA [38]. A borohydroxyapatite (BHA) with nominal stoichiometry Ca₉₋ₓ[(PO₄)ₓ(BO₃)ₙ][BO₂]ₓ(OH)₁₋₂ₓ was proposed by Ternane et al. [38]. When P/B ratio = 7.22, borate groups are introduced the apatitic lattice. This suggested that borate group can enter into the HA lattice with an amount dependent manner. This substitution leads to a decrease in lattice parameter a (when x=0, a=9.4180Å and x=1, a=9.3760Å) and increase lattice parameter c (when x=0, c=6.8840Å and x=1, c=6.9122Å). It was also shown that when the amount of boron is increased to a concentration over P/B ratio = 7.22, this yields secondary phases as Ca₉(BO₂)ₙ and CaO. Similarly, Barheine et al. [39] prepared BHA by a high-temperature solid-state reaction processing method. They also reported that the lattice parameter a decreased, while the lattice parameter c and unit cell volume increased with the increasing B content. The length of a-axis was reported as 9.406Å in HA and 9.389Å in phase pure BHA (analyzed P/B ratio=6.10). The length of c-axis was 6.882Å in HA and 6.927Å in phase pure BHA.

In another study of Ternane et al. [13], the assignments for infrared (IR) and Raman spectra of a pure oxyboroapatite were provided. Table 2 summarizes the bands in the IR and Raman spectra of oxyboroapatites. The previously reported assignments for the BHA were also for both triangular BO₃ groups and linear BO₂ groups. The bands at 1304, 1253, 1208 and 784, 771, 755 cm⁻¹ were attributed to the antisymmetric stretching v₁ and the symmetric bending v₂ modes of the BO₃ groups. The weak peaks at 2002 cm⁻¹ and 1932 cm⁻¹ were at-
tributed to the antisymmetric stretching $\nu_3$ mode of the BO$_3^-$ groups, respectively [38]. However, Güler et al. [41] did not detect BO$_3^-$ substitution in the IR analyses of BHA which was synthesized by the solid-state reaction of colemanite as a primary reactant for both Ca and B source. The amount of B was found as 0.195 mol by using a spectrometric method. Therefore, they concluded that since only BO$_3^-$ group replaced partially with the PO$_4$ groups, the assigned chemical formula could be as Ca$_{10}$[(PO$_4$)$_{6.07}$ (BO$_3$)$_{2.02}$] (OH)$_2$.

Table 2. Infrared and Raman wave numbers and assignments for oxyboroapatite [13,40].

<table>
<thead>
<tr>
<th>Assignment</th>
<th>IR (cm$^{-1}$)</th>
<th>Raman (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$(BO$_3^-$)</td>
<td>2002, 1932</td>
<td></td>
</tr>
<tr>
<td>$\nu_1$(BO$_3^-$)</td>
<td>1304, 1250-1252, 1208</td>
<td></td>
</tr>
<tr>
<td>$\nu_1$(PO$_4^{3-}$)</td>
<td>1090, 1050, 1044</td>
<td>1076, 1049, 1030</td>
</tr>
<tr>
<td>$\nu_1$(PO$_4^{3-}$)</td>
<td>962</td>
<td>962</td>
</tr>
<tr>
<td>$\nu_1$(BO$_3^-$)</td>
<td>912</td>
<td></td>
</tr>
<tr>
<td>$\nu_1$(BO$_3^-$)</td>
<td>784, 772, 755</td>
<td></td>
</tr>
<tr>
<td>$\nu_1$(PO$_4^{3-}$)</td>
<td>671, 602, 570</td>
<td>608, 593, 581</td>
</tr>
<tr>
<td>$\nu_1$(PO$_4^{3-}$)</td>
<td>472</td>
<td>448,431</td>
</tr>
</tbody>
</table>

Not only the structure, but the morphology, optical properties and dielectric properties of the BHA are also dependent on the amount of B-doped into the lattice. The change in size, UV shielding properties and dielectric constant with the amount of dopant element in BHA, which was produced by using sol-gel method, were studied by AlHammad [42]. It was stated that absorbance and reflectance of BHA increased gradually while the dielectric constant decreased with increasing boron concentration.

The structural and mechanical changes of the biphasic mixture of B-doped HA (BHA) and β-TCP of varying BHA/β-TCP ratios after sintering at variable temperatures of 1000, 1100 or 1200 °C for 2 h has previously been studied [43]. The amount of β-TCP in the needle-like nano-size biphasic mixture was reported to increase with the increasing amount of boron in the precipitation stage or increasing the sintering temperature. B-doping was shown to increase the decomposition of HA into β-TCP. However, as the boron content increases, the sinterability, density and microhardness of the B-doped mixture decreased.

As stated before, the substitution of borate groups occurs on PO$_4$ and OH sites, predominately the first. Therefore, it is also possible to co-dope the ions of other elements together with B, especially cations which can be replaced with Ca$^{2+}$, into the HA lattice without creating a competition between boron and other dopant element. The cations, such as Eu$^{3+}$ [44] and Ce$^{3+}$ [45], were previously doped into BHA separately to change the luminescent properties of BHA.

From the bioengineering point of view, concepts such as biocompatibility and bioactivity, are equal or more important than the structure and physico-chemical properties of a material, thus they need to be deeply investigated. Çiftci et al. [46] examined the adhesion, proliferation and differentiation of B-substituted nano HA with human bone marrow derived mesenchymal stem cells (MSCs). They reported that the adhesion and proliferation rates of MSCs were higher than controls while adipogenic and osteogenic differentiation potential remained unchanged.

In addition to using B as a dopant element into HA or various other CaP-based systems, it is also possible to design composites that include both bioceramics and boron compounds. There are recent studies on B-containing composites. Ali et al. [47] used boron nitride nanotubes (BNNTs) as a reinforcement additive for HA and β-TCP. Atilla et al. [48] prepared composites consisting of nano-sized hexagonal boron nitride (hBN) and HA. They reported that implantation of these composites to rats resulted in statistically increased serum B levels experimental groups compared to healthy group.

### 4. Other boron-substituted bioceramics

In addition to the use of B as a dopant or component in the composites consisting of the CaPs, it also finds use in other bioceramics, especially glasses. Concerning the borophosphate compounds, glasses were investigated more widely. The physico-chemical properties of calcium borophosphate glasses, with the composition of (1-x)Ca(PO$_4$)$_2$–x(B$_2$O$_3$) where x=B/P ≤6, are previously studied [49]. The presence of BO$_3^-$ was observed to increase the glass transition and crystallization temperatures, density and microhardness, while it decreased the solubility in water and the cut-off wavelength in the UV region.

A more complex system with other substitutions was proposed as (50-x)PO$_4$–20CaO–20SrO–10Na$_2$O–xB$_2$O$_3$ with x = 0, 1.25, 2.5, 3.75 and 5 mol% B$_2$O$_3$[50]. An increase in B$_2$O$_3$ led to an increase in the density, the refractive index and glass transition temperature and a decrease in the molar volume. Small amounts of B$_2$O$_3$ reduced the glass dissolution rate but the presence of B$_2$O$_3$ only slightly affected the dissolution rate of the glass at high concentrations.

HA and borophosphate glasses were previously combined to form a ternary system with the formula of (1-x)((NaPO$_4$)$_x$)/(Na$_2$B$_2$O$_7$)$_{2-x}$)XCa$_{1-x}$(PO$_4$)$_x$OH where x is the molar fraction of Na$_2$B$_2$O$_7$ in the binary system and X is molar amount of HA [51]. The changes in physical and chemical properties were investigated in terms of addition of HA rather than considering boron as the main effector. When HA-free system was compared with the ternary system, HA was considered to improve most of the physical and chemical properties of the boron containing glass system, such as micro-hardness and water resistance.
Another glassy state borophosphate was prepared with selenium (Se) in different %mol SeO₂ amounts to form xSeO₂(100−x)(48P₂O₅−50CaO−2B₂O₃) system [52]. The Se ions replaced dominantly with the B units. The electronic density of the bonding state of the B, P and O atoms was shown to be modified by SeO₂ content. Copper (Cu) is another element which is studied in combination with B-containing bioceramics. In order to take the advantage of the angiogenic characteristic of Cu, B-containing bioactive glass-based scaffolds [53] and borosilicate glasses [54] were enriched with Cu.

The changes in the physical and chemical characteristics of bioglasses by the addition of certain ions influence the in vitro and in vivo properties. Haro Durand et al. [55] investigated the in vitro angiogenic effects of the ionic dissolution products (IDPs) from 2 wt% B₂O₃ doped 45S5 borosilicate glass (BG) system (SiO₂−CaO−NaO−P₂O₅). It was reported that the IDPs from B-doped BG stimulated the proliferation and migration of human umbilical vein endothelial cell (HUVEC). In addition, in vitro HUVEC tubule formation and secretion of interleukin 6 (IL6) and the basic fibroblast growth factor (bFGF) was enhanced. It was noted that the controlled and localized release of boron ions from BGs could stimulate angiogenesis and osteogenesis. A more recent study [56] showed that the ionic dissolution products released from the B-doped BGs stimulate angiogenesis also in vivo.

Unlike 45S5 glasses, the borate and phosphate glasses dissolve uniformly and borate glass reacts much faster than the 45S5 silicate glasses, when they are soaked in a phosphate rich solution to form HA [57]. A borophosphate glass with the mol% composition as 25Na₂O−25CaO−5P₂O₅−45B₂O₃ started to form HA in four days in this solution. It was faster when compared to the osteoconductive NaCaPO₄ (rhenane) crystal phase [58]. In another study, B-containing glass-based scaffold coated with degradable poly(3−lactic acid) were tested in simulated body fluid (SBF). The test showed that a HA layer was deposited on uncoated and coated scaffolds again on four days of immersion [59]. The degradation rate is another important factor together with the rate at which the bioactive glass converts to HA. It is also related with rate at which the degradation products are released. As an example, the amount of B released from a borate-based bioactive glass scaffold into a phosphate solution was reported to increase rapidly during the first 24 h, reaching a value equal to ~20% of the boron content of the starting material after an immersion time of 360 h [60]. This rate is important in the early cellular response to the high concentration of degradation products.

A new calciumsilicate borate (Ca₃(SiO₄)₃(BO₃)₃) ceramic was recently prepared by using a conventional solid-state reaction [61]. As stated before, CaO–SiO₂ based glass materials are already known to exhibit bioactivity. Similar to above mentioned studies, when BO₃ groups were added into the lattice, a greater in vitro HA-forming ability was obtained in SBF. This is attributable to the released BO₃ ions which could improve the supersaturation of the SBF and enhance the nucleation of HA.

The scaffolding materials for bone tissue engineering should be osteoconductive. Mesoporous bioactive glass serves a greater surface area and allows osteoblast adhesion, proliferation, and differentiation due to its structure. By using a boron-containing mesoporous bioactive glass scaffold as a dexamethasone drug-delivery system, Wu et al. [62] obtained a controllable release of boron ions. The scaffold significantly improved the proliferation of primary osteoblasts and expression of bone-relative genes Collagen I and Runx2.

5. Concluding remarks

This paper aimed to provide a brief overview about the biological approach to the use of boron element. The data reviewed here provides evidence of the increasing interest with recent advances in substitution of boron into the structure of ceramic, glassy or combined biomaterial systems due to its close relationship with the hard tissues. These boron containing materials can be used in any application like their un-doped forms, such as bone substitutions, implant coatings or components, dental materials and drug delivery vehicles. However, the physicochemical properties, e.g. structure, composition, dissolution rate, density, crystallinity, hardness, strength etc., would be changed depending on the amount of boron and this in turn affect the biological response especially biocompatibility and bioactivity of the resulting material. It is also possible to combine the known angiogenetic and osteogenetic properties of boron with the various properties of functional ions of other elements, such as anti-bacterial and anti-cancer and/or growth factors and drugs.

References


[12] Hughes J. M., & Rakovan J., The crystal structure of apatite, Ca$_5$(PO$_4$)$_3$(F,OH,Cl), Reviews in Mineralogy and Geochemistry, 48 (1), 1-12, 2002.


[61] Pu Y., Huang Y., Qi S., Chen C., Seo H. J., In situ hydroxyapatite nanofiber growth on calcium borate silicate ceramics in SBF and its structural characteristics, Materials Science and Engineering: C, 55, 126-130, 2015.


*Sorumlu yazar: polat.topuz@gedik.edu.tr

---

**ARTICLE INFO**

Artıcle history:
Received 19 January 2016
Received in revised form 11 March 2016
Accepted 11 March 2016
Available online 24 March 2016

Keywords:
90MnCrV8, fluidized bed furnace, boronizing, boron phases, thermal expansion

---

**ABSTRACT**

In this study, DIN 1.2842 Steel located in cold work tool steels class was boronized. The boride layer changes depending on the boronizing time and temperature formed on the surface of steel were examined and aimed to determine the optimum boronizing temperature and time for this type of steel. About the boronizing experiments, 850 °C, 950 °C and 1050 °C were selected and 1 and 4 hours were determined for each temperatures. The experiments were carried out with the pack boronizing method using EKabor 1™ boronizing agent in indirect heated fluidized bed furnace. Prior to experiments, which is planned to be used 90MnCrV8 steel was analyzed obtained with the aid of optical emission spectrometer and test samples were prepared in identical dimensions. The sectional areas of the boronized samples were prepared for the metallographic study, XRD analysis, microstructure images, hardness measurements, layer thicknesses and layer morphologies were examined separately in order to determine the changes on boronized layer formed on the samples. The realization of all these investigations result, the boronizing temperature led to the separation between the phases constituting boride layer rather than the boronizing time and in this case, as reported in literature; to the conclusion that the difference between the thermal expansion coefficients of the boride layer which is constituting FeB and Fe₂B were reached.
1. Giriş

Bor, periodyik tablonun IIIA grubunda B simgesi ile gösterilen, atom numarası 5, atom ağırlığı 10,81 olan geçç ELEMENTILIR. Bor atomunun yarıçapı 0,098 nm ve erime sıcaklığı 2092 °C'dir. Bor elementinin yoğunluğu 2,33 ± 0,02 g/cm³, değerlik elektron sayısı "3", ve iyon yarıçapı 0,023 nm'dir [1,2]. Bor tablatta serbest halde olmayıp boratalar halinde bulunmaktadır [3]. Diğer yaklaştık 230 çeşit bor minerali vardır. Çeşitli metalden veya metal elementlerle yapıtı bölümlerin göstergi farklı özellikler, endüstride birçok bor kullanımının olasılığına olanak sağlamaktadır. Bor bileşiklerinin elektrik iletkenliği azdır, ancak saf bor iletkendir. Kristalize bor görünüm ve optik özelliklerini açısından elmasa benzer ve neredeyse elmas kadar serttir [2,4,5,6].

Akışkan yatak, akışkan özellik gösteren akışkan-katı karışım ihtiva eder. Akışkan yatakın özellikleri, asta halan havada beslemeli dikey silindirlik şekilli bir uniteidir, diğer isil işlem kaynaklarına oranla pek çok avantajlıdır. Çalışır halde iken, aynı kaynayan sivi boyunca benzemektedir, bu da hızlı bir şekilde, her yönde eşit bir isı transferi sağlamaktadır. Akışkan yatakın fırınlar ucuz işlem maliyeti ve güvenli kullanıyla sağlamlaktadır.

Şekil 1’de borlama deneylerinde kullanılan numunele- rin borlama öncesi ve sonrası görüntüleri yer almaktadır ayrıca Çizelge 1’de borlama deneyleri öncesi optik emisyon spektrometresi yardımıyla elde edilen kimyasal analiz sonucu yer almaktadır. Borlama işlemleri için 850 °C, 950 °C ve 1050 °C sıcaklıklar ile 1 ve 4 saat işlem süreleri uygulanmıştır.

**Malzeme cinsi** | **Alaşım elementleri (% kütlesi)**
--- | ---
DIN 1.2842 | C | Mn | Si | Cr | Ni | V | W
(90MnCrV8) | 1,02 | 2,01 | 0,24 | 0,22 | 0,01 | 0,09 | 0,04

**Çizelge 2.** Deneylerde kullanılan DIN 1.2842 çeliğinin sertlik ölçümü

| Malzeme cinsi (DIN) | Sertlik (HV 0,1) |
--- | ---
1.2842 | 198 |

3. **Sonuçlar ve tartışıma**

Borlama deneyleri tamamlanan numunelerin yüzeyinde oluşan borür tabakalarının morfolojileri, tabaka kalınlıkları ve sertliklerinin tespiti amacıyla metalografik inceleme için numuneler hazırlanmıştır. Mikroskop altında alınan görüntüler Şekil 2, 3 ve 4’te yer almaktadır.

**Mikro yapı görüntülerin**

**Malzeme cinsi** | **Borlama sıcaklığı (°C)** | **Borlama süresi (saat)** | **Borür tabaka kalınlığı (µm)**
--- | --- | --- | ---
1.2842 | 850 | 1 | 44,4 ± 11,4
(90MnCrV8) | 950 | 4 | 103,9 ± 5,3
1.2842 | 1050 | 1 | 101,2 ± 5,8
(90MnCrV8) | 1050 | 4 | 230,4 ± 10,4

**Çizelge 3.** DIN 1.2842 malzemesi boru tabakalarının ortalamama kalınlıkları

**Çizelge 4.** DIN 1.2842 malzemesi boru tabakalarının ortalamama sertlikleri

Mikro yapı görüntülerin elde edilip, tabaka kalınlıkları ölçulen numunelerin daha sonra sertlik ölçümleri Vickers Sertlik ölçüm yöntemiyle 100 g ağırlık kullanılarak gerçekleştirilmiştir. Numunelerin dış yüzeyinden içeriye doğru 20, 50, 150 ve 280 µm aralıklarla alınan sertlik değerleri Çizelge 4’te yer almaktadır.

**Çizelge 5.** Borur tabakasını oluşturan fazların tespiti amaci ile XRD ölçümleri yapımı, sonuçlar Şekil 5, 6 ve 7’de verilmiştir.
Şekil 5. 850 °C’de 1 saat borlanmış DIN 1.2842 çeliğinin XRD analizi

Şekil 6. 950 °C’de 1 saat borlanmış DIN 1.2842 çeliğinin XRD analizi

Şekil 7. 1050 °C’de 1 saat borlanmış DIN 1.2842 çeliğinin XRD analizi

İşletilen deneylerde, borlama sıcaklığı ve zamanın artışına bağlı olarak borür tabakası kalınlığı da artmaktadır. Çeliklerde oluşan bor tabakasının genellikle FeB ve Fe₂B’den oluşan çift fazlı bir tabaka olduğu bilinenmektedir. Gerçekleştirilen XRD analizleri sonucunda FeB ve Fe₂B fazlarının yanı sıra, kullanılan çelik için içerisinde bulunan yüksek Mangan miktarı dolayısıyla MnB, Mn₂B ve diğer demir esaslı malzemelerde de rastlanan FeB₄ fazına da rastlanmıştır. Demir esaslı malzemelerin borlanması sonucu oluşan iki fazlı bor tabakasını oluşturutan fazlardan FeB, içeriği demir miktarının yüksek olması sebebiyle nü-}

mune'nin dış (yüzeyi) bölgesinde oluşan FeB fazının hemen altında bulunmaktadır ve bu iki faz testere dişı gibi bir oluşumla birbirlerine kentelenerek bor görünmesini oluşturmuştur [18]. 850 °C’de, 1 ve 4 saat süre ile aynı ayrı gerçekleştiren deneylerde oluşan bor tabakalarında zamanın artışına bağlı olarak tabakaların kalınlaştığı görülmektedir. 950 °C ve 1050 °C’de yine 1 ve 4 saat süre ile aynı gerçekleştiren deneylerde tabakaları oluşturan FeB ve Fe₂B fazlarının arasında ayrılmalar olduğu görülmektedir. Sıcaklığın artışına bağlı olarak bu ayrırmalar daha da genişlemektedir. Eşit mesafelerden alınan sertlik değerlerine bakıldığında en dışta FeB fazından ana matrise doğru inildikçe sertliğin azaldığı görülmektedir.

Sıcaklık ve zamanın artışına bağlı olarak borür tabakasının kalınlığının artması beklenen bir durumdur. 950 °C ve 1050 °C’de gerçekleştiren deneyler sonucunda, fazlar arasındaki ayrılmaların varlığı, bu sıcaklıklara olan DIN 1.2842 çeliği için uygun borlama sıcaklıklar olup olmadığı görülmektedir. Fazlar arasındaki bu ayrırmaların temel nedeni, FeB ve Fe₂B fazlarının farklı termal genleşme katsayılara sahip olmaları ve FeB’un, Fe₂B’a göre daha gevrek bir yapıya sahip olmasıdır.

4. Değerlendirme

Geçirilen deneyler sonucunda, zamanın artışından daha ziyade sıcaklığın artışının tabakaları oluşturutan fazların ayrılmalarında etkili olduğu görülmüştür. Bu durum, sıcaklığın artışına daha kolay bir şekilde ayrılmaları olan yorumlanabilir. Aynı zamanda, üç farklı sıcaklıkta borlanmış olan DIN 1.2842 soğuk iş takım çelik için en uygun borlama sıcaklığının, bu 3 sıcaklık içinde 850 °C olduğu görülmüştür.

Kaynaklar


**Abstract**

Boron has two stable isotopes namely $^{10}$B and $^{11}$B isotopes. The large cross section of $^{10}$B isotope for thermal neutrons is used for reactor control in nuclear fission reactors. The thermal neutrons absorption cross sections of pure $^{10}$B and $^{11}$B are 3837 and 0.005 barns respectively. In the literature, amongst others, batch elution chromatography techniques are reported for $^{10}$B isotope enrichment. This work focuses on continuous chromatographic $^{10}$B isotope separation system via continuous annular chromatography (CAC) where isotope enrichment from boric acid solution is studied. CAC is slurry packed with commercially available n-methyl glucamine functionalized boron-specific anion exchange resin (Diaion CRB03 - Mitsubishi). The nominal height of AISI 316 stainless steel pipe outer and inner cylinders of CAC is 200 cm. The outside diameter of column is 20 cm and inside diameter of inner column is 14 cm. The liquid level above the top of the resin is monitored with an ultrasonic sensor. Its level is kept between the set values by air injection from the top of the column. For this purpose, the liquid level signals received from the ultrasonic sensor is fed to a proportional controller unit so as to adjust the column head pressure by regulating air injection pressure and its flow rate. Dilute aqueous nitric acid solutions were used as the eluent. Eluent $^{10}$B and $^{11}$B isotope ratios are measured by ICP-MS spectrometer (Perkin Elmer, ELAN 9000). It is determined that depending on the operation parameters $^{10}$B isotope ratio can be increased over 27% in a single pass mode operation of the present CAC apparatus.

**Keywords:**
- Boron isotope enrichment
- continuous annular chromatography
- ion exchange resin
- inductively coupled plasma-mass spectrometry

**Article info**

**Article history:**
Received 29 January 2016  
Received in revised form 14 March 2016  
Accepted 14 March 2016  
Available online 24 March 2016

**Keywords:**
- Boron isotope enrichment
- continuous annular chromatography
- ion exchange resin
- inductively coupled plasma-mass spectrometry

1. Introduction

Chromatography is a widely used and highly selective process of separation, employed in the separation of complex mixtures of which the overall product yield of petrochemicals, sugars, proteins, pharmaceuticals, fine chemicals, flavorings, foods, enantiomers and isomers is governed by the individual yields of discrete operations. It is admitted by several researchers that no other separation method is as powerful and generally applicable as is chromatography [1-4].

Chromatographic separation techniques are also employed in isotope enrichment studies. Atoms of the same element can have different numbers of neutrons and the different possible versions of each element are called isotopes. Helium, Lithium, Boron, Nitrogen, Sulfur, Chlorine are the some elements that have stable isotopes found in different abundance ratios in nature. Common stable isotopes of Boron are; $^{10}$B and $^{11}$B. The naturel abundance of Boron stable isotopes, namely $^{10}$B and $^{11}$B are given as 19.92% and 80.12% respectively [5]. That makes the isotope ratio of $^{19.92/80.12} = 0.2486$.

In a nuclear reactor, fission reaction rate is the function of the thermal neutron number found in the reaction medium. Thus, one of the most important parameter in nuclear reactor design is to prevent the increase in thermal neutron number in reaction medium that can cause uncontrollable fission rate. In other words, regulating thermal neutron number continuously and thus...
avoiding the chain reaction to melt the reactor core. The neutron capture cross section of an isotope of a chemical element is a measure of the probability of neutron capture. It is the effective cross sectional area that an atom of that isotope presents to absorption, and usually measured in barns (b) where 1 barn is defined as $10^{-28}$ m$^2$.

Isotope of boron, $^{10}$B isotope is unique between other thermal neutron capture cross section materials used in nuclear reactors and $^{10}$B isotope has the longest continuous service history of any neutron absorbing material, performing its intended function in high gamma and neutron radiation fields. The neutron capture mechanism of $^{10}$B isotope is shown in Figure 1.

![Figure 1. Boron neutron capture (BNC) mechanism](image)

Thermal neutrons capture cross sections of pure $^{10}$B and $^{11}$B isotopes are 3837 and 0.005 barns [6] respectively. This makes the thermal neutrons capture cross section of $^{10}$B isotope is 767,400 times more than that of $^{11}$B isotope [7, 8]. Therefore, $^{10}$B isotope is an extremely effective neutron absorber playing a crucial role in controlling the reactivity of nuclear fuel rods in nuclear reactors. Furthermore it is an indispensable material for neutron shielding purposes such as anti-activation covering for nuclear waste containment. Besides the importance in nuclear power plant as neutron radiation control, $^{10}$B isotope is also used for boron neutron capture therapy of brain tumors and mela
notic cancers because the formed α-particles and $^7$Li nuclei destroy cancer cells when irradiating a tumor by neutrons and it can be injected into a human organism more easily and safely than other neutron absorbents [9]. While $^{11}$B isotope is an excellent neutron reflector, it is used as an additive to semiconductor grade silicon as a doping agent. Although it does not absorb neutrons, it is used as an additive to steels that are used in the construction of reactors to enhance their heat and radiation resistance.

The main isotope separation processes of boron are: distillation, ion exchange chromatography, gaseous diffusion, gas centrifuge and laser isotope separations. For separation of isotopes of lighter elements, such as boron isotopes, distillation [9] and ion exchange chro-matography techniques are generally considered as industrially viable.

The first experiment on ion exchange separation of boron isotopes was done by Yoneda et al. [10] and they used strong base anion exchange resin in hydroxide form as column packing material. They conclude that the lighter isotope, $^{11}$B isotope was enriched in resin phase and the single stage separation factors which is the ratio of the relative concentration of the desired isotope after processing to its relative concentration before processing, increased from 1.010 to 1.016 for concentrated solutions of boric acid.

Isotopic plateau displacement chromatography is one of the most preferred techniques for isotope enrichment found in literature. Sakuma et al. [11] showed that by using weak base anion exchange resin $^{10}$B isotope can be enriched up to %91 from isotope mixture solution. Fujiy et al. [12] improved an explicit expression for isotope profile in migration bands. The applicability of this expression was proved by experimental results obtained from boron isotope separation chromatography with ion exchange. Oi et al. [13] performed experiments in liquid chromatography by using column packing material of which boron specific resins with n-methyl glucamine as the functional group and observed that column performance change with temperature and resin form. Based on the specific affinity of glucamine type resins to boron ions, Sonoda et al. [14] made experiments in ion exchange chromatography with three different glucamine resins. In these experiments they used columns having 1cm inside diameter and 1 m packing height and conclude that $^{10}$B isotope can be enriched with fractional operation. The results in boron isotope enrichment chromatography using kaolin clay as packing material showed that system can be efficient under 12.0 MPa pressure [15].

Resin regeneration with electrochemical techniques was studied in ion exchange chromatography of boron separation and besides that band movement was investigated both in batch and column operations [16].

In literature, the studies performed with column chromatography, isotope exchange separation factor for boron changes between 1.009 and 1.014 however some researchers conclude that this value can increase to 1.020 [13, 16]. The point that should be taken into consideration is that the column height with other operating conditions is the most important parameter that affects isotope exchange separation factor.

All of these studies are batch processes that isotope enrichment is governed by the individual yields of discrete operations. As it is concluded in several studies it is possible to separate boron isotopes at higher ratios in cascade operations. Nevertheless the disadvantage with these batch preparative operations is the low productivity of enriched boron isotopes due to the low feed.
quantity as well as the dilution effect as an outcome of high quantity of eluent. While theoretically it is possible to increase the boron enrichment productivity with the employment of exceptionally large scale systems in a single pass operation, their operation costs would be extremely high. Thus large scale isotope enrichment is not feasible with conventional preparative chromatographic techniques that small amount of the product is separated per unit volume of stationary phase. For large scale separation and purification applications, continuous chromatographic separation processes, have gained greater interest in the last decades due to its advantages in terms of productivity and efficiency. The continuous annular chromatography (CAC) is a potential and promising downstream process that allows large-scale continuous preparative chromatographic separation and purification of multi-component mixtures. CAC is a process intensified technology that replaces the conventional chromatography columns with a smaller unit for the same separation task and eliminates the drawbacks of conventional chromatographic processes, operating in a batch mode by operating in a continuous mode, increasing the productivity and separation factor.

The concept of CAC was first suggested in 1949 by Professor A.J.P. Martin [17] who shared the 1952 Nobel Prize in Chemistry for the invention of partition chromatography. The state-of-the-art of the CAC was developed at Oak Ridge National Laboratory, USA [18, 19] and first continuous annular chromatograph was constructed by Fox et al. [20]. The CAC apparatus consist of two slowly rotating concentric cylinders forming an annulus into which the stationary phase is packed. The inlets of the mobile phase are uniformly distributed along the annular bed entrance, while the feed stream is stationary and confined to one sector. The rotation of stationary phase packed into annulus, in its vertical axis, the selectively adsorbed species take different helical paths through the bed and can be continuously collected at fixed locations [21, 22]. The retention time of each component and thus the angular displacement from the fixed feed entry will remain constant as long as operating conditions remain constant. Hence the separation process in CAC is truly continuous. One of the world’s leading supplier of nuclear technology, namely Westinghouse Electric Company (USA) has a US patent [23] about isotope enrichment with Pressurized Continuous Annular Chromatography (P-CAC). P-CAC is also applicable technology for the separation of compounds other than isotopes such as hormones, proteins, pharmaceuticals and fine chemicals.

The focus of this work, is to enrich $^{10}$B isotope which has a high neutron capture property when compared to $^{11}$B isotope, thus having a wide and significant use in nuclear energy technology, from boric acid solution with a single pass mode operation of continuous annular chromatography packed with commercially available n-methyl glucamine functionalized boron-specific anion exchange resin.

2. Material and methods

Feed Solution

Aqueous solution of low-sulphated (130 ppm max.) boric acid (Eti Mine Works General Directorate, Turkey) at the minimum purity of 99.9%, is used as the feed solution. The sulphate ions or other potential impurities in the boric acid feed solution do not effect the boron isotope separation process since the chelating type resin is specific for only the adsorption of borate ions in the feed mixture. It is reported that the concentration of boric acid feed solution is an important factor in isotope enrichment. It was reported that isotope separation factor increases with decreasing feed solution concentration [10]. For this reason, dilute solutions of boric acid are used as feed solutions in the experiments.

Eluent

Aqueous solution of HNO₃ (Merck, Germany) is used as eluent solution in the experiments in order to overcome interference problems with ICP-MS instrument. It is reported in the literature that isotope enrichment is possible by use of aqueous solutions of HNO₃ with concentrations lower than 0.1 M. With higher concentrations of HNO₃ solutions, no isotope separation is seen despite the quick desorption of boron in conventional packed beds [14].

Resin Properties

Diaion CRB 03 resin (Mitsubishi Chemical Corporation, Japan) having average particle diameter of 556 µm is chosen as boron specific resin for P-CAC experiments. Diaion CRB 03 is a borate selective anion exchange resin. N-methylglucamine group bonded onto a highly porous cross-linked polystyrene matrix as a functional group, the borate ion makes a very stable complex with the glucamine group, whilst other anions do not react. The boron adsorption mechanism of chelating resin is given in figure 2.

![Figure 2. Chelating mechanism for boron adsorption in n-methyl glucamine functionalized adsorbents](image)

2.1. CAC Apparatus

Figure 3 illustrates the schematic diagram of continuous annular chromatograph (Sinerji Ltd, Turkey) that
consists of two cylinders. The outer and inner cylinder is made of AISI 316 stainless steel and the outer and inside diameters of column are 20 cm and 14 cm respectively. During the experiments P-CAC rotating speed can be regulated between 0.15 – 1.80 rotation/hour. The special step motor is used with computer programming and its sensivity is ± 0.01 rotation/hour. The working pressure is in the range of 0 to 3.0 Bar with 0.01 bar sensitivity which is auto-adjustable. Feed is sent to the column with HPLC pump (Chrom Tech Inc., U.S.A.) of 0-40 mL/min range. Eluent and cleaning solution are fed to the system by use of preparative chromatography pumps (Fluid Metering Inc., U.S.A.) with 0-1240 mL/min flow rate ranges, respectively. The packing height of the column is 168 cm with 72 outlet nozzles.

The head of annular chromatograph is air proof. During the operation, a special pressurization technique is employed for keeping the feed and elution flow rates constant at their setting values regardless of the fluctuations of actual pressure drop in the column during operation that might stem from the small change in bed height i.e. shrinking. This technique is based on monitoring the liquid level at the top of the resin with an ultrasonic sensor. In order to keep the liquid level at its setting value, regulated air is injected from the top of the column. The liquid level signal received from the ultrasonic sensor is fed to a controller unit that adjusts the column head pressure by regulating air injection pressure and its flow rate via proportional control air pressure regulating valve. Proprietary software commands the proportional control valve for regulating head space air pressure so as to maintain the liquid level at the set value within the range of ± 1 mm.

The lower surface of the bed in the annulus is open to the atmosphere. The feed and elution solutions are fed to the system through the entrances on the air-blocker head of the column. At the beginning of each experiment, P-CAC is conditioned as with 0.1 M HNO₃ and washed with large quantities of distilled water.

For boron enrichment from aqueous solutions with N-methylglucamine type resins, it is observed that when pH < 7, adsorption of ¹⁰⁰B isotope to the resin phase is greater than that of ¹¹B and for the case of pH values greater than 11, no enrichment in boron isotopes occur [26]. These researchers suggest that the difference between the tetrahedral coordination geometry of boron complex of ¹⁰⁰B isotope in the resin and the planar trigonal coordination geometry of boron complex in solution phase result in fractionation. The opposite case occurs for ¹¹B. Kakihana et al. [27] reported a similar case for different studies on conventional packed columns. These results are based on experimental results of breakthrough and reverse-breakthrough type stud-
ies in conventional packed columns. Since the feed and eluent are being constantly fed to P-CAC, there are differences on the interaction mechanism of boron isotopes with the resin and liquid phase compared to the studies on batch type conventional column chromatography.

ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) instrument (Perkin Elmer, Model: ELAN 9000, U.S.A.) is used for determination of Boron isotope ratios. ICP-MS instruments are widely used for boron ratio determination because of ease of use and the fact that many samples can be processed quickly [28]. Solutions with 90%, 80% and 70% $^{10}$B/$^{11}$B isotope ratio are prepared by use of primary standard $^{10}$B and $^{11}$B samples. Primary standards used are solid $^{10}$B$_2$O$_3$ (Spectra 2000 Srl, Italy) and $^{11}$B$_2$O$_3$ (Cambridge Isotope Laboratories, U.S.A.). It is seen that there is a very good correlation between these prepared solutions of known $^{10}$B/$^{11}$B isotope ratio and those determined by use of ICP-MS. Since diluted HNO$_3$ solutions (25 mM – 50 mM) are used as eluent, there no interference with the analysis. In all the boron enrichment experiments boric acid with at least 99.9% purity with low sulfate content is used which minimizes matrix effects. Therefore there is no need for matrix effect inspection on $^{10}$B/$^{11}$B isotope ratio analysis. U.S.A. Department of Energy Lawrence Berkeley National Laboratory defines the natural $^{10}$B/$^{11}$B isotope ratio for Boron as 19.92/80.1 = 0.2486 [5]. This natural $^{10}$B/$^{11}$B ratio is defined as 19.9/80.1 = 0.2484 in the software of Perkin Elmer ELAN 9000, U.S.A. is used for determination of Boron isotope ratios. ICP-MS instruments are widely used for boron ratio determination because of ease of use and the fact that many samples can be processed quickly [28].

To overcome any problems associated with the analysis of $^{10}$B isotope enrichment with P-CAC experiment results which may result from ICP-MS instrument, isotope percentage of natural boric acid solution is also analyzed periodically during the analysis. It is seen that expected isotope percentage value of the natural solution is analyzed each time.

![Figure 4a. Run 1. Steady-state $^{10}$B isotope enrichment values at P-CAC outlet streams, feed concentration=0.1 M H$_3$BO$_3$, eluent concentration=0.025 M HNO$_3$, feed flux (mM/cm$^2$.s)/ eluent flux (mM/cm$^2$.s)=0.107](Image)

![Figure 4b. Run 2. Steady-state $^{10}$B isotope enrichment values at P-CAC outlet streams, feed concentration=0.1 M H$_3$BO$_3$, eluent concentration=0.025 M HNO$_3$, feed flux (mM/cm$^2$.s)/ eluent flux (mM/cm$^2$.s)=0.093](Image)

In Figure 4a and 4b, the $^{10}$B isotope percentages are given for each CAC outlet nozzle. During the experiment, for every complete revolution of CAC column, samples are collected cumulatively from each outlet stream of CAC system and it was seen that after the fifth complete revolution of CAC column, system reached the steady-state both for run 1 and 2. From figure 4a it is clearly seen that, between the 14-25 outlet nozzles, 27% $^{10}$B isotope enrichment is achieved. When run 1 and 2 are compared it is clearly seen from figure 4b that when feed to eluent flux ratio decreases, in other words eluent flux increases, the $^{10}$B isotope enrichment decreases to 23% between the 17-21 outlet nozzles due to the low retention time of boron isotopes within the column. On the other hand, from other outlet streams, $^{10}$B % is its natural values of 19.90% for
run 1 and 2. It is obvious that this situation arises from the back-mixing problem within the annular column due to the pressure changes at the outlet of column.

Figure 5a. Run 1. Steady-state boron concentration values at P-CAC outlet streams, feed concentration=0.1 M H$_3$BO$_3$, eluent concentration=0.025 M HNO$_3$, feed flux (mM/cm$^2$.s)/ eluent flux (mM/cm$^2$.s)=0.107

Figure 5b. Run 2. Steady-state boron concentration values at P-CAC outlet streams, feed concentration=0.1 M H$_3$BO$_3$, eluent concentration=0.025 M HNO$_3$, feed flux (mM/cm$^2$.s)/ eluent flux (mM/cm$^2$.s)=0.093

In Figure 5, steady-state boron concentration values are given for each CAC outlet nozzle after the fifth complete revolution of CAC column for run 1 and 2. When investigated with Figure 4, it is seen that boron concentration increases at the region where $^{10}$B per cent increases. On the other hand, at the 14-25 outlet nozzles for run 1 and 17-21 outlet nozzles for run 2, the boron concentration is greater than the boron concentration of the feed stream while the dilution effect of feed stream is taken into consideration.

As a result, from Figures 4a and 5a, it is clearly seen that P-CAC is an effective instrument for $^{10}$B isotope enrichment such that in some eluent collection bottles, $^{10}$B isotope values of 27% are obtained at high concentration values. Regarding the amount of feed separated to 27% isotope ratio, it should be stated that the process is continuous. The data expressed in Figure 4 and 5, is collected during the operation interval between 23 hour – 27 hour, commencing from the experimentation. During which time interval the cumulative volume of injected feed and eluent was 9.24 l. During this time interval of experimentation, $^{10}$B isotope which is enriched to 27% constitutes 7% (v/v) of input stream. These results when compared with natural $^{10}$B isotope ratio of 19.9% indicate the significance of use of P-CAC instrument for continuous chromatographic method of isotope enrichment process.

Sonoda et al. [26], carried out batch studies where they first boron loaded an ion exchange column, containing glucamine functionalized resin under pH > 7.5. Later, carried out reverse breakthrough studies with dilute acidic solutions. They observed fractionation of $^{10}$B isotope in the stationary phase and explained it due to the tetrahedral coordination geometry of the $^{10}$B isotope boron complex in the stationary phase and its planar trigonal coordination geometry in the mobile phase. Whereas, they stated that, regarding $^{11}$B isotope the reverse case holds. Nevertheless our repeated observations with Continuous Annular Chromatography system shows that the mechanism might be different since column pH is always on the acidic side during the operation (competitive simultaneous adsorption and elution of boron isotopes) of the CAC system.

Zhou et al. [29] also investigate the separation performance of continuous annular chromatography technology and in their study, they reached 21.45% $^{10}$B isotope enrichment from boric acid solution with 820 mm continuous annular chromatography by using weak base anion exchange resin, Diaion WA21J.

4. Concluding remarks

In this study, it is determined that $^{10}$B isotope ratio can be increased over 27% in a single pass CAC operation. According to the best of our knowledge, in the open literature, this figure is the highest $^{10}$B isotope enrichment ever reported in a single pass chromatographic separation study. We concluded that $^{10}$B isotope enrichment ratio can be further increased with P-CAC apparatus either operating in recycle mode or with the employment of P-CAC apparatus having longer bed height or both. Furthermore, since P-CAC is a continuous process, very large volumes of feed solution can be processed for $^{10}$B isotope enrichment that cannot be matched by conventional chromatography.

Acknowledgements

This work was supported by National Boron Research Institute – BOREN, under project number2011.B0341.
References


Microwave-assisted direct synthesis of boronated alkanolamine succinic anhydride esters as potential surfactants for various application

Arun K. Chattopadhyay1*, Troy Gaona1, Beth Bosley2

1Etimine USA Inc., One Penn Center West, Suite 400, PA 15276, Pittsburgh, USA
2Boron Speciality, 2301 Duss Avenue, Bldg 9, PA 15003, Ambridge, USA

ARTICLE INFO

Article history:
Received 5 March 2016
Received in revised form 14 March 2016
Accepted 14 March 2016
Available online 24 March 2016

Keywords:
Boron, esters, microwave, surface area, surfactant

ABSTRACT

A method of microwave assisted synthesis of a new surfactant family whose hydrophilic head is derived from the ethanolamine adduct of boric acid containing polar –NR-B(OH)2, -O-B(OH)2, and (OH)3B→NR-. These compounds were synthesized in two steps. First the boric acid adduct was prepared by reacting ethylene diamine with boric acid and then the adduct was reacted with alkenyl succinic anhydride. The product with boronated alkanol amine showed good yields (>90%). Both reaction steps were carried out by microwave. Boron NMR suggests that probably Boron is mostly in –O-B(OH)2 form (~80%), about 13% as (OH)3B→NR-(CH2)2-O-B(OH)2, and approximately 7% in the form of (OH)2B-NR-(CH2)2-OH. The product apparently exhibited good detergency. Parameters characterizing their surface activity (critical micelle concentration, surface tension, and molecular area at the water−air interface) was studied with the dodecenyl succinic anhydride derivative of the Boronated diethanolamine adduct. The compounds show promise for use in organized molecular systems. By altering the hydrocarbon chain length of alkenyl succinic anhydride, the derivatives can be either water or solvent soluble. Hexadecenyl succinic anhydride derivatives are highly oil-soluble, whereas the dodecenyl succinic acid anhydride derivative is primarily water soluble. Total B2O3 content in the product is approximately 12.4%. Besides their surface activity, this series of products have a great potential for treating wood for antifungal and anti-termite properties.

1. Introduction

Microwave technique has gone far from its original use of typical industrial drying, and food processing to more chemical applications from synthetic chemistry to analytical processes, including digestion, extraction of samples etc. As microwave irradiation expands its horizons and proves its utility as both a timesaving tool and a novel means to perform challenging transformations, it is becoming an increasingly important method of chemical synthesis in the industrial community. Microwave acceleration has proven to be a valuable tool for any synthetic chemist and will only continue to become more prevalent in the future [1].

In this paper the microwave assisted technique, a green methodology, for the direct esterification of alkenyl succinic anhydride with boronated alkanol amine adducts under solvent free conditions has been discussed. The scope of this method is already expanded for the use of several complex reactions involving aliphatic, aromatic, unsaturated and fatty acid derivatives. The reaction can also be applied to different primary and secondary amines.

This novel experimental method of synthesis was employed for the first time to synthesize borated surfactants for both aqueous and non-aqueous dispersions. This methodology can also be carried out with several other functionalized acids and amines, preferably primary amines.

The conventional condensation method for the esterification or amidation of alkenyl succinic anhydride (ASA) with secondary alkanol amines, di-ethanolamine

*Corresponding author: Arun@etimineusa.com
(DEA) for example, generally takes several hours to complete. Moreover, using conventional means of synthesis it is very difficult to get diester or ester-amide forms of the product.

There has been a growing interest in new surfactants over the last few decades not only from a fundamental point of view but also for applications in chemical synthesis and elsewhere. These amphiphilic molecules decrease interactions at interfaces via their surface active properties, and they are classified as ionic, zwitterionic, or nonionic. For that matter the ASA based surfactants are well known in the industry for formulating of lubricants, dispersants for dyes, paper sizing, detergents, dispersion chemicals etc. The ASA based surfactants offer a great versatility to design surfactants for a wide range of solvent systems of varied Hydrophobic Lipophilic Balance (HLB). The two carboxyl groups in ASA allow an unusual amount of flexibility in designing anionic, non-ionic and zwitterionic surfactants. The versatility of such surfactants stems from ASA’s ability to react with adducts of either lipophilic or hydrophilic nature, or both [2-7].

In the course of our studies on forming boronated alkanolamine and ASA condensation products, we envisaged a new family of surfactants with hydrophilic heads containing boron atoms. The boronated polar heads of these amphiphilic molecules were derived from the affinity of boron for amine and hydroxyl groups, which were then linked through the acid-anhydride group of ASA comprising a long-chain alkenyl group to form an amphiphilic compound by condensation reaction.

The benefit of using microwave technique over the conventional method for the synthesis of such surfactants is to quicken the reaction rate under milder reaction conditions with expected higher yields. Those very specific effects that microwave offers cannot be easily matched using conventional methods [2,3].

We describe here the synthesis, characterization and surface active properties of the condensation reaction product of dodecenyl succinic anhydride and the adduct prepared from the reaction between DEA and Boric Acid (BA).

Boron NMR was used for identifying the most probable nature of Boron linkages in the surfactant molecules.

2. Materials and method

2.1. Reagents

Dodecenyl Succinic Anhydride (DDSA), Aldrich Chemicals, USA; Hexadecenyl Succinic Anhydride (HDSA), Dixie Chemicals, USA; Octadecenyl Succinic Anhydride (ODSA), Milliken Chemicals, USA, and Diethanol Amine (DEA) Sigma-Aldrich, USA used for the experiment were of at least 90% active technical grade quality. Boric Acid powder (BA) of Etimine USA Inc. used for the preparation of adducts was of 99.9% purity. High purity Ethylenediamine (EDA) of Sigma Aldrich, USA was used NMR study.

2.2. Apparatus

For the present study a standard 0.9 kW microwave oven was equipped in-house to be able to handle a reaction volume of 500ml. 11B NMR spectroscopy was performed at 21°C (room temperature) using a 300 MHz (300 DPX Bruker) spectrometer. A DuNouy tensiometer was used for the determination of surface tension at 25 °C.

2.3. Procedure

The experimental goal was to develop a microwave-assisted synthesis of a new series of boron containing surfactants of the present study that could be performed in a domestic microwave oven that was a faster, greener alternative to the traditional synthesis. The microwave oven used was suited for the esterification and amidation chemistry containing boron at a mini-scale rather than microscale level under solventless conditions that allowed the synthesis to take place involving green chemistry as well.

The reaction scheme used for the synthesis of the surfactants of the present series, the boronated alkanol amine esters of ASA, primarily involved two steps.

The first step of reaction was to form Boric Acid (BA) and diethanolamine (DEA) adduct by allowing them to react at 2:1 molar ratio. The reaction between BA and DEA offers many possibilities for the way BA can react with DEA.

$$2\text{B(OH)}_3 + \text{HN}-(\text{CH}_2\text{OH})_2 \rightarrow (\text{OH})_2\text{B-N}[(\text{CH}_2\text{OH})_2 + \text{HN}-(\text{CH}_2\text{OH})_2 \rightarrow (\text{OH})_2\text{B-}NH-(\text{CH}_2\text{OH})_2 + (\text{OH})_2\text{B-(CH}_2\text{OH)}_2\text{NH-(CH}_2\text{OH)}}$$

The second step was to allow BA-DEA adduct thus formed to react with 0.5 molar quantity of ASA following a condensation reaction. Such reaction can also offer multiple possibilities the way BA-DEA adducts can combine with ASA under intimate microwave heating conditions. The most probable condensation reaction products that could possibly be formed under microwave assisted synthesis, are shown below:  

![Diagram of condensation reaction products](image)
The same condition of synthesis was applied for the synthesis of DDSA, HDSA and ODSA derivatives of the DEA-BA adducts. The DDSA derivative appeared water dispersible whereas the HDSA and ODSA derivatives are more solvent soluble. In this communication all discussions are on the DDSA-DEA-BA product only as full characterization of HDSA and ODSA are still in progress.

In view of its Lewis acid nature, boric acid associates readily with the atom of oxygen and nitrogen of –(OH) and –(NR₂) groups where R being alkyl, alkanol, etc. The addition of BA into DEA is exothermic in nature. Using the Microwave setup the reaction between BA and DEA (at a 2:1 molar ratio) to prepare BA-DEA adduct under a solventless condition, was followed in a stepwise addition mode. For each addition of BA into DEA, the mixture was exposed to microwaves for approximately thirty seconds. It is to be noted, for microwave assisted reactions exposure of reactants under controlled heating conditions is always beneficial [8,9]. Upon completion of addition of BA, the mixture was further heated for another few minutes until the bubbling was visibly slowed down. The solventless preparation method is very tricky and difficult to handle. However, it is worth mentioning that a small addition of xylene or toluene is always helpful for the ease of transfer and handling, which can be distilled off at the end of the process. The BA-DEA adduct thus formed was allowed further to react with DDSA by mixing DDSA slowly into BA-DEA. The final molar composition between BA, DEA and DDSA was maintained at 4:2:1. The mixture was exposed to microwave heating for approximately 10 minutes to obtain mostly diester forms of DDSA as shown in equation (1). Due to the very sticky nature of the product, a small addition of xylene or toluene can always be useful as mentioned above. The average molecular weight of the final product was approximated as 350.

All solutions for the NMR studies were kept at pH 8.5.

3. Results and discussions

By conventional means, formation of diesters or amide-ester of alkenyl succinic anhydride does not happen easily with alkenyl succinic anhydride and DEA. Depending on the reaction conditions, they generally form mono esters, mono-amides or their mixtures. Under a solventless condition, the microwave assisted synthesis of ester derivatives of DDSA, HDSA or ODSA using DEA-BA adducts was found very beneficial. Besides a faster rate, it was able to form mostly diesters. All reactions of the present study are primarily characterized by the formation of nonpolar ester linkages with intramolecular –NR-B(OH)₂, -O-B(OH)₂, and (OH)₃B→NR B−N bonds. Furthermore the DEA-BA adduct is comprised of all possible boron linkages either via –O-, or –NR-, which constitutes the common reaction precursor for the surfactants of the present series. In this communication we’ll discuss mainly the product DDSA-DEA-BA.

For ¹¹B NMR studies all samples were kept at pH 8.5. Chemical shifts from ¹¹B NMR spectra of DDSA-DEA-BA, BA and Ethylenediamine (EDA) complex of BA (BA-EDA) at pH 8.5 (Figure 1) suggested that the intramolecular linkages thus formed between B, O and N in the compound of DDSA-DEA-BA could be a mixture of all possible forms as shown above (Eqn. 1-4), of which –O-B(OH)₂ type was most prevalent. In Figure 2 the integrated areas of each individual fractions indicated that the linkages viz. –O-B(OH)₂ was found to be about 80% or more with a small fraction of (OH)₃B→NR- and (OH)₂B→NH- type. The ratio of the individual linkage types thus formed in DDSA-DEA-BA appeared to be 80% of type (1), 13% of type (2) and 7% of type (3) and (4).

It was indeed a lucky coincidence that the chemical shift, δ, of Boric Acid does not change very abruptly between pH 4-9 (between 19-17 ppm) [10]. The δ drops very sharply only between pH 9.5-10. Therefore the observed δ values at lower ppm for DDSA-DEA-BA product were indicative of the true changes in the Boron environment and they were indeed different from BA under similar pH conditions. A comparison of chemical shifts of BA, BA-EDA and DDSA-DEA-BA are presented in Table 1.

Figure 1. ¹¹B NMR of (A) boric acid alone; (B) boric acid complexed with ethylenediamine (EDA) and the product DDSA-DEA-BA at pH 8.5
It is to be noted that the sequential addition of 2 molar equivalent of boric acid gave better results than the addition of whole amount at a time. The chemical shift data also suggested the derivative of DDSA (1) was largely formed due to the identical nature of both –O-\(\text{B(OH)}_2\)- linkages and a small fraction might have undergone to form amide as shown in (2). A small peak at \(\delta = 0.89\)ppm suggests that the DDSA-DEA-BA derivative may also contain a small fraction of the structures (3) and (4).

The shape of the curve shown in Figure 3 is characteristic of a surfactant, and the values of the parameters of surface activity are obtained using the above equations (See Table 2). It was observed that the DDSA-DEA-BA surfactant have reduced surface pressures equivalent to those for liquid alkanes [14] of similar hydrocarbon chain (~0.6 nm\(^2\)).

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>cmc (mM) at 25°C</th>
<th>Surface tension ((\sigma)) at cmc (mN/m)</th>
<th>Surface excess (m(^2))</th>
<th>Molecular area (nm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDSA-DEA-BA</td>
<td>1.65</td>
<td>26.3</td>
<td>3.1x10(^{-6})</td>
<td>0.533</td>
</tr>
</tbody>
</table>

4. Concluding remarks

In conclusion from the very basic evaluation of the DDSA-DEA-BA surfactant containing non-polar head groups containing Boron, we have demonstrated the method of synthesis of a new series of surfactants employing microwave technique. Their structures contain intramolecular \(--\text{O-}\text{B(OH)}_2\) and \(\text{OH}_2\) - B-NR-bonds, giving rise to a stable amphiphilic molecule with very good surfactant properties. The results of surface properties offer an excellent possibility for such compounds in the areas of detergents and dispersion formulations for various anti-fungal and insecticide applications, and also for formulating both water and oil dispersible wood-treatment chemicals.

Acknowledgements

We thank Dr. Gokhan Yazici of Etimine USA Inc. for the opportunity. We are also thankful to Mr. Philip Ford for taking trouble to go through the manuscript.
References


Bor bileşiklerinin alev geciktirici ve yüksek sıcaklığa dayanıklı pigment olarak uygulanabilirliği

Duygu Yılmaz Aydın1, Metin Gürü1, Barış Ayar2, Çetin Çakanyıldırım2

1Gazi Üniversitesi, Kimya Mühendisliği Bölümü, 06570, Ankara, Türkiye
2Hitit Üniversitesi, Kimya Mühendisliği Bölümü, 19030 Çorum, Türkiye

ÖZET

MAKALE BİLGİSİ
Makale Geçmişi
ilk gönderi 12 Şubat 2016
Revize gönderi 14 Mart 2016
Kabul 14 Mart 2016
Online yayınlanması 24 Mart 2016

Anahtar kelimeler:
Bor bileşikleri,
alev geciktirici,
yüksek sıcaklığa dayanıklı pigment,
boratlar,
floroboratlar

ARTICLE INFO
Artice history:
Received 12 February 2016
Received in revised form 14 March 2016
Accepted 14 March 2016
Available online 24 March 2016

Keywords:
Boron compounds,
flame retardant,
high temperature resistant pigment,
borates,
fluoroborates

ABSTRACT
The search for functional materials which have specialities such as broad applicability, eco-friendly, being non-toxic, durable at high temperature and flame resistance is increasing with industrialization and technological development. Boron is one of the indispensable mineral resources which can respond the all of these needs, having strategic importance and one of the main input materials of the growing industrial and technological progress. Except of crude and refined products, special boron compounds which are commercially produced by using especially refined boron products with methods which require high technology are available in the world. Each of these special boron compounds is used for specific purposes in different sectors. One of the purpose of use of special boron compounds is that they can use as flame retardant. Flame retardant additives inhibit the initiation and progress of the combustion so that they help to protect in some cases, environment, in some cases, life and property safety. To provide ignition of flammable materials later and to reduce significantly the progress of combustion can be realized by addition of flame retardant additives. Boron compounds have wide usage area as flame retardant. Boron compounds participate in wood, cellulose insulation, PVC and textile materials and they bring flame retarding property to these materials. An overall review have been conducted on the flame retardants in this study and flame retardant effect of boron compounds have been shown through other studies.

*Sorumlu yazar: d.yilmaz@gazi.edu.tr
1. Giriş

Bor; rezervlerinin %73,5'i Türkiye'de bulunan; cam, ta- rim, savunma, saflık, nükleer, seramik sanayileri gibi birçok alanda kullanılan oldukça değerli bir elementtir. Tutmusa sıcaklığının yüksek olması, yanıma sonucunda kolaylıkla aktarılabilen bir tür, çevreyi kirletmek emisyonu açısından çıkarması gibi özellikleri sahip olan bor, yakıt hücrelerinde de kullanılmaktadır.

Boron alev genteçirme etkisi birçok çalışmaya konu olmuştur. Özel bor bileşiklerinden olan çinko borat ve floroboratlar gibi alev genteçirici özelliği sahip borlu bir bileşik artik günümüzde en çok kullanılabilecek alev genteçirici olma potansiyelini taşımaktadır [1].


Alev genteçiricilerin, özellikle alev genteçirme etkisine sahip olması ve içine katısal olduğu ana malzemelerin işlenme özelliklerine zarar vermemesi beklenir. Belli oranlarda ise bu alev genteçirici katkı maddeleri, hem alevleme hızını azaltar, seramik bazlı tabakaların mekanik ve yüksek sıcaklığa dayanıklı pigment özellikleri taşıma eğilimindedir. Metal hidroksitler antimon trihidroksitin yanında diğer bileşik katı madde içerikli alev genteçirici malzemenin etkinliği ve ürünün yaklaşık 10.mp4

Şekil 1. Polimerlerde kömürleşme mekanizması

Bu çalışmada borlu bileşiklerin alev genteçirici etkisinden ve yüksek sıcaklığı dayanıklı pigment olarak uygulanabilirliğinden bahsedilmiştir.

2. Geleneksel alev genteçiriciler


Bu çalışma sonucunda borlu bileşiklerin alev genteçirici etkisinden ve yüksek sıcaklığı dayanıklı pigment olarak uygulanabilirliğinden bahsedilmiştir.

3. Borlu alev geçictirciler


Borlu bileşiklerin alev geçictirciliği ve duman oluşumunu konusunda çalışmalar gün geçikçe artmaktadır. Sadowski ve diğerleri; çalışmalarda boru, polüüretan ve poliposiyanürat köpüklerin hazırlanmasında kullanılarak, borun bu köpükler üzerinde alev geçictircisi etkisini olduğu görülmuştur [6]. Akarslan borik asitli pamuklu kumaşta alev geçictirciliği en iyi gelmiştir ve borik asitin pamuklu kumaşta gerilme mukavemetini azaltabileceği ve alev geçictirciliği artırıldığı gözlemlemiştir [7].

Yapılan çalışmalar borlu bileşiklerin etkili alev geçictirci özellikle sahip olduktularını göstermektedir.

3.1. Borat bileşikleri

Borat bileşikleri; alev geçictirci, duman bastırıcı, korozyon geçictircisi olarak polimerlerde ve kaplamalarda, halojenli polyester ve naylonlarda, kablolarla, yanna ya dayanıklı boyalarda, kumaşlarda, elektrik/elektronik parçalarda, manya dayanıklı hari kaplamalarda, otomobil/uçak iç aksamaldarda, tekstil ve kağıt endüstrisinde kullanılır. Yüksek dehidrasyon sıcaklığı sahip olduğu için yüksek sıcaklıklarda dayanıklık plastik malzemelerin imalatında yaygın olarak kullanılır. Diğer alev geçictircilerle karşılaştırıldığında çok daha etkili bir duman bastırıcı olması ve diğer alev geçictircilerde göre daha ucuz olması sebebiyle kullanımı gün geçtikçe artmaktadır. Çünkü boratın halogen içeren ve içermeyen sistemlerde alüminyum hidroksit ve magnezyum hidroksit ile birlikte kullanılma özelliğine sahip olduğu alev geçictircilerle farklı uygulamalarda kombineler kullanılıncaya kadar borat talebini daha fazla artırmaktadır.

Çinko borat, alev geçictirci olarak kullanılmasını dişında, manzar ve böcek öldürücü olarak ahşap aksamların korunmasında, bor silikat cam hammaddesi ve seramik sanayiinde ergime noktasonu düşürürülük olarak da kullanılabilmektedir. Çinko boratın diğer alev geçictirci özelliklerini sahip, antimon monoksit gazsalınımına altına monte etmek ve körülmüşümsüz tabakaları meydana getirir. Çok çeşitli sayida plastikte, etkili alev geçictirci olarak kullanılabilir, boron varlığı için borat etkin bir alev bastırıcı yapar, anti mon ile birlikte kullanılındığında yüksek dereceler bir alev geçictirci özelliğine sahiptir, antimon trioksit ile birlikte kullanılarak duman bastırma özelliği kuvvetlendirilir. Boyama (renk verme) kuvvetini zayıflaştırarak, elektriksel özelliklerini iyileştirmek, deliklerde plastikler arasında yapışma özelliğini artırır. Zehirli olma sahip olduktan sonra, reçinele ilave edildiğinde esnashın özelleştirilmesine intihap yoktur. Nem absorpsiyonu ve suda çözünmez [8].


Isı etkisi altında çinko borat camı faz a dönüşerek yalıtık bir bariyer oluşturmakta ve yanmayı engellemektedir. Çinko borat ve alüminyum trihidroksit birlikte kullanıldığında, daha yüksek sıcaklıklarda bile malzemenin mekanik ve elektrik özellikleri korunmasını sağladığından, özellikle kablo üretiminde sıkça tercih edilen bir yöntemdir [5].

Mekanokimyasal yöntemle sentezlenen susuz çinko boratın DSC-TGA grafikleri Şekil 2 ve Şekil 3'te verilmiştir.

Şekil 2. Susuz çinko boratın DSC grafiği [5]


Şekil 2'de verilen DSC grafiği incelemekte endotermik olarak kristal suyu 400 °C'da bıraktığı düşünülkte, bunun dışında oldukça kararlı bir yapı olduğu tespit edilmiştir. Yine aynı grafik incelemesinde 700 °C'de ekzotermik bir reaksiyon meydana geldiği tespit edilmiştir ve buradan hareketle sinterleme sıcaklığı, 700 °C olarak belirlenmiştir. Bu reaksiyon neticesinde Şekil 3'teki TGA grafikinde yapılan ölçümlerde yaklaşık % 2,6'lık bir kütle kaybının olduğu tespit edilmiştir. Şekil 2 ve Şekil 3'te verilen DSC – TGA grafiklerinden de görüldüğü gibi 900 °C'a kadar çinko borat pigmentinde önemli bir ayrışma meydana gelmediği görülmektedir.

Yaş yöntemi sentezlenen çinko boratın DSC-TGA grafikleri Şekil 4 ve Şekil 5'te verilmiştir.


Şekil 5. Sulu çinko borat pigmenti TGA grafiği [5]

TGA – DSC grafikleri incelendiğinde 100 – 175 °C sıcaklıklar aralığında endotermik bir reaksiyon gerçekleştiği ve bu noktada % 2,3'lik bir kütle kaybının olduğu tespit edilmiştir. Bu kayıp pigmentin bileşikinde bulunan bağlı kristal suyun uzaklaşması olarak tanımlanabilir. Şekil 4'te verilen DSC analizi incelemesinde herhangi bir biçimde çinko borat pigmenti yönünden parçalanma söz konusu değildir.

LOI (Limiting Oxygen Index) test metodu malzemenin alevlenebilirliğini ve yanma karakteristiklerini görmeye açısından en iyi test metotlarından birisidir. LOI değeri, bir materyalin havada yanmaya devam etmesi için gereklenin duyduğu % oksijen miktarını anlamına gelmektedir. Yüksek LOI değeri standart atmosfer ortamında o malzemenin daha zor yanma karakteristiğine sahip olduğunu göstermektedir.

Yapılan bir çalışmada ise bir malzemenin alev geciktirici olarak nitelendirilebileceği için, deneysel limit % 28 LOI oranıdır ve sonuçta bütün numunelerin bu sınırlandıığını ve ayrıca yine bu çalışmada, alev geciktirici pigmentlerin LOI değerleri üzerinde belirgin bir etkisi olduğunu göstermiştir [16].
Yapılan bir diğer çalışmada mekanokimyasal yöntemle magnezyum borat sentezlenmiş ve.phenol tapınmış. Boron polimerize edilen silikönsel bir bağlayıcısı ile hazırlanan yüksek sıcaklık boyası numunelerine uygulandı. ISO 4589-2 standartı ile hazırlanan numunelerin % 35 oksijen konsantrasyonunda yanmadığı tespit edilmiştir. İşlem görmemiş haldeki tahta parçasının alev testinde %22 oksijen konsantrasyonu tespit edilmiştir. Hazırlanan yüksek sıcaklık boyası ile Kaplanılan tahta parçasında ise LOI değeri % 39 oksijen konsantrasyonunda olduğu belirlenmiştir [14].

Resim 1. LOI Test Cihazı

Yapılan çalışmada çinko borat katlı silikon esaslı bağlayıcı ile Kaplanılan tahta numunelerine uygulanmış ve LOI testine tabi tutulmuş. İşlem görmemiş haldeki parçasının alev testinde %23,7 oksijen konsantrasyonu tespit edilmiştir. Hazırlanan çinko borat katlı yüksek sıcaklık boyası ile Kaplanılan tahta parçasında ise LOI değeri % 55 oksijen konsantrasyonun üzerinde çıktığı belirlenmiştir.

Resim 2. %45, %50, %55 oksijen konsantrasyonu ile Kaplanılan numuneler

Yapılan çalışmada çinko borat katlı silikon başlayıcı ile yüksek sıcaklık boyası ile boyanan pamuklu kumaş parçasında LOI değeri belirlenmiştir. Pamuklu kumaş için % oksijen konsantrasyonu %19,39 olarak bulunmuştur. Silikon esaslı bağlayıcı ile Kaplanılan tahta parçasında ise %42,43 değerinde LOI değeri belirlenmiştir. Böylece kolay yanan pamuklu kumaşın yüksek oksijen konsantrasyonunda yanmazlık özelliği kazandığı saptanmıştır [17].

3.2. Floroborat bileşikleri

celikli kullanımı elektro kaplamalarıdır. Floroborat an-
yonu elektrokimyasal olarak inertert ve floroboratlarla-
巴西 çözelti̇lerinın kaplanan metaller arasında Cd, Cu, Fe, Pb, Ni, Ag, zn ve Sn vardır [18].

Floroborat bileşikleri genel olarak; kaplama çözelti-
lerinde, birçok polimer reaksiyonda ve organik sentez-
de katalizör olarak, tekstil sanayinde alev geciktirici olarak, buruşmazlık apresi reçinelerinde kır kımyasalı olarak ve optik camlarda kullanılmaktadır [18].

Ceyhan; amonyum floroborat üretimi şarلتılan belirle-
yerek, amonyum floroboratın yangına dayanıklı malze-
me üretiminde kullanılabilirliğini incelemiştir. Analizler-
sonucunda amonyum floroboratın katıldığı malzeme
üzende oldukça güçlü bir alev geciktirici etkiye sahih
olduğunu görmüştür [19].

Yapılan çalışmalarda LOI testleri için farklı derişimlerde
çinko floroborat çözelti̇leri (%30, %50, %60 ) hazırlan-
muş, temin edilen çadir kumaşlarına emdirilmişdir. Kullanılan kumaşlar Türk Kızılayından temin edilmişdir.

<table>
<thead>
<tr>
<th>%100 Pamuk Ring İpliği</th>
<th>%100 Pamuk Ring İpliği</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lif Cinsi</td>
<td>%100 Pamuk Ring İpliği</td>
</tr>
<tr>
<td>Dokuma Biçimi</td>
<td>%100 Pamuk Ring İpliği</td>
</tr>
<tr>
<td>Alan Yoğunluğu</td>
<td>%100 Pamuk Ring İpliği</td>
</tr>
<tr>
<td>İp Sıklığı</td>
<td>%100 Pamuk Ring İpliği</td>
</tr>
<tr>
<td>2x2</td>
<td>2x2</td>
</tr>
<tr>
<td>35 g/m²</td>
<td>35 g/m²</td>
</tr>
<tr>
<td>Alk Yüzünde 15 adet/cm</td>
<td>Alk Yüzünde 23 adet/cm</td>
</tr>
</tbody>
</table>

Resim 4. LOI test için kullanılan kumaş örnekleri

Dynisco marka cihazda %30, %50, %60 konsantrasy-
yonu sahip çinko floroborat çözelti̇ emdirilmiş kuma-
şunununun test edilmiştir. Rotametre değerleri O₂ ve
N₂ için ayarlanıp yama işlemi yapılmıştır. Konsantrasy-
yon değerleri %50 olan çözelti, emdirilmiş kumaş numu-
nununununun maksimum oksijen konsantrasyo-
nunun %55 değerinin büyük olduğu, tahta parçası
boyanmasında hem de pigment yüksek sıcaklıkta boya
boya kolay yanan tahta parçasına yüksek yanmaz-
lık özelliği kazandırılmış. Çinko katılı boya için kesenlediği her
yerde, aleve temas etiği ve alevin tutuşma kumaşının
boya ile boyanmasına yüksek yanmazlık kazanması
sağlanabildir. Diğer bir boya katılı olarak maznegyum boya,
silikos esası geciktirici olarak kullanılan boya katılı maddesii olarak kullanılmıştır. LOI değeri %22
olan tahta parçasının, bu boya ile boyanlığında LOI
değeri %39'a çıktığı görülmuştur. Bu değer muame-
le edilende tahta parçasına kullanılan maznegyum borat
katılı boyanın yüksek yanmazlık özellikine kıyasla-
görÜme gösterilmektedir. Yaptılan çalışmalarla çinko floroborat çözelti̇ emdiril-
müş kumaş numunununun LOI testi uygulanmış, çinko floroboratin alev geciktirici özellikini incelemiştir. Çinko floroborat katılı, diğer pamuklu kumaşlar göre yüksek yanmazlık özellikine sahip çadir kumaşının LOI
değerleri, LOI test cihazının çalıştığı en yüksek de-
geğerden %55'ten daha yüksek olduğu görülür. Bu değer çinko floroboratinın yüksek etkili bir alev geciktirici olduğu göstermektedir.

4. Sonuçların değerlendirilmesi ve öneriler

Bor bileşikleri, geniş uygulama alanı sahip, çevre
duğü görülmüştür. Kritik oksijen indeksi, malzemenin
de LOI değerinin, beklenildiği gibi %55' in üzerinde
olduğu görülmüştür. %60 konsantrasyona sahip numunenin
LOI değerinin %55 değerinin oldukça üstünde olduğu
durumda kumaşta ilerleyen bir yanma görülmemiştir. Bu değer çinko floroboratinın oldukça etkili bir alev geciktirici olduğu göstermektedir.

Kaplama ve polimerlerde alev geciktirici katki
maddesi olarak genellikle antimon oksit veya alümin-

Kartal Kızılayından temin edilmiş, temin edilen çadır kumaşlarına emdirilmiş, çinko floroborat çözelti̇leri (%30, %50, %60 ) hazırlanması, temin edilen çadır kumaşlarına emdirilmişdir. Analizler sonucunda amonyum floroboratın katıldığı malzeme üzerinde oldukça güçlü bir alev geciktirici etkiye sahih oldu…

Kaynaklar

Resin type and resin diameter effect on the adsorption of boron isotopes

Gonca Sağlam\textsuperscript{1*}, Zeynep Aktosun\textsuperscript{1}, Gülşah Özçelik\textsuperscript{1}, Ahmet R. Özdural\textsuperscript{2}

\textsuperscript{1}National Boron Research Institute, 06520 Ankara Turkey
\textsuperscript{2}Hacettepe University, Department of Chemical Engineering, 06800 Ankara, Turkey

ARTICLE INFO

Article history:
Received 29 January 2016
Received in revised form 14 March 2016
Accepted 14 March 2016
Available online 24 March 2016

Keywords:
Chromatography, stationary phase, boron isotopes, Langmuir adsorption isotherm parameters

ABSTRACT

Chromatography is a technique for molecular partition in which a fluid (mobile phase) carries the material containing the mixture to be separated (sample) past or through a solid or gel (stationary phase) contained in a vessel. The stationary phase has characteristics that delay the passage of some molecular components of the sample more than the passage of others causing them to separate in the mobile phase emerging from the column. The selection of stationary phase is one of the key factors for reaching an optimum separation in chromatographic applications. The scope of this work is to investigate the effect of resin type and diameter from the point of Langmuir adsorption isotherm parameters of \textsuperscript{10}B and \textsuperscript{11}B isotopes for chelating resin and weak base anion exchange resin.

1. Introduction

Chromatography is a widely used and highly selective process of separation, employed in the separation of complex mixtures of which the overall product yield of sugars, proteins, pharmaceuticals, fine chemicals, flavorings, foods, enantiomers and isomers…etc. is governed by the individual yields of discrete operations. It is admitted by several researchers that no other separation method is as powerful and generally applicable as is chromatography [1-4].

The successful design and the operation of chromatographic separations require the optimization of a large number of parameters which affect the separation in interacting fashion. Resin which is used as stationary phase in chromatographic separations plays a key role in order to increase resolution as well as productivity of the chromatographic system. Adsorption isotherm expressions give the relationship between the stationary phase and liquid phase concentrations of components. In other words, adsorption isotherms relates the stationary phase concentration that is in equilibrium with the liquid phase concentration. Thus the easiest and accurate way to select stationary phase is to determine the suitable adsorption isotherm expression as well as the adsorption isotherm constants that belongs to that expression. Several types of adsorption isotherm models have been introduced to describe the adsorption behavior of chromatography columns such as competitive Langmuir isotherm, bi-Langmuir isotherm, Freundlich isotherm and linear adsorption isotherm [5-11]. Among these isotherms, competitive Langmuir adsorption isotherm is the commonly used one that express the equilibrium stationary phase and liquid phase concentrations for most enantiomer, protein and concentrated sugar mixtures [11-14].

The competitive Langmuir isotherm model assumes monolayer coverage of the adsorbate molecules over a homogeneous adsorbent surface [15-16] and the rate of adsorption and desorption are equal for each component in the case of equilibrium. The Competitive Langmuir adsorption isotherm equations for \textsuperscript{10}B and \textsuperscript{11}B isotopes are given in Eq. (1).

\begin{align}
q_{10B} &= \frac{q_{m_{10B}} c_{10B}}{1 + K_{10B} c_{10B} + K_{11B} c_{11B}} \quad (1a) \\
q_{11B} &= \frac{q_{m_{11B}} c_{11B}}{1 + K_{10B} c_{10B} + K_{11B} c_{11B}} \quad (1b)
\end{align}

\*corresponding author: gonca@boren.gov.tr
In Eq. (1) $q_{m10B}$ (mg$_{10B}$/cm$^3$ resin) and $q_{m11B}$(mg$_{11B}$/cm$^3$ resin) are the maximum $^{10}$B and $^{11}$B isotope adsorption capacities of the resin respectively, whereas $K_{10B}$ (mg$_{eq}$/cm$^3$) and $K_{11B}$ (mg$_{eq}$/cm$^3$) are the adsorption isotherm constants, that states the affinity of $^{10}$B and $^{11}$B isotopes to the resin phase.

There are several types of resins for boron isotope enrichment with ion exchange principle such as weak base anion exchange resin, strong base anion exchange resin and chelating resins. Weak or strong base anion exchange mechanism is depends on anion exchange between the anions in the liquid phase and the functional groups in the resin phase whereas chelating mechanism is much more complicated such that functional groups in the resin phase is specialized only specific anion in the liquid phase. Thus resin selection is one of the most important parameter for optimum separation of components. Not only the resin type but also resin particle diameter affects the resolution of components to be separated. It is well known that as the resin particle diameter decreases, the surface area of resin increases so that H.E.T.P. of chromatographic column increases. Briefly, decrease in particle diameter, increases the resolution of chromatographic application [16-19] but while decreasing particle diameter, the pressure drop along the column should be considered.

In this study, chelating and weak base ion exchange resin types are compared for the adsorption of $^{10}$B and $^{11}$B isotopes. In addition to that the effect of resin particle diameter is investigated in terms of competitive Langmuir adsorption isotherm parameters of boron isotopes.

2. Materials and methods

In the experimental part of this study, batch uptake experiment are performed for 100, 500, 1000, 2000, 3000, 4000, 5000, 6000, 7000 and 8000 mg/L boric acid (Eti Mine Works General Directorate) initial concentrations. Equilibrium time is 3 hours and 400 rpm rotational speed is applied for ten different, 50 mL boric acid solution at room temperature.

Relite CRB03 (Mitsubishi Chemical, Japan) chelating resin and Diaion WA21 (Mitsubishi Chemical, Japan) weak base anion exchange resin is investigated for boron isotope adsorption mechanism. In addition to that particle diameter effect of chelating resin, Relite CRB03 is studied. The average particle diameter of Relite CRB03 resin is 580 µm and 270 µm and average particle diameter of Diaion WA21 is 580 µm. The particle size distribution of resins are given is Fig. (1).

In batch uptake experiments, 1 g resin that is regenerated with 0.025 M HCl (Merck, U.S.A.) solution and distillate water, is used for each boric acid solution. Initial and equilibrium boron isotope concentrations are analyzed with ICP-MS (Perkin Elmer ELAN 9000, U.S.A.). The analysis results of bulk liquid boron isotope concentration show that after 4 hours the equilibrium is reached between the stationary and liquid phase as the boron isotope concentrations in liquid phase remain constant after 20 hours.

3. Results and discussions

The equilibrium resin phase concentration is calculated from the difference between the initial and equilibrium concentrations of $^{10}$B and $^{11}$B isotopes, given in Eq. (2a) and (2b) respectively.

\[
q_{eq10B} = \frac{(C_{eq10B} - C_{010B}) \cdot V_{solution}}{m_{resin} / \rho_{resin}} \quad (2a)
\]

\[
q_{eq11B} = \frac{(C_{eq11B} - C_{011B}) \cdot V_{solution}}{m_{resin} / \rho_{resin}} \quad (2b)
\]
In equation $q_{10B}$ (mg/cm$^3$/resin) and $q_{11B}$ (mg/cm$^3$/resin) are the equilibrium stationary phase concentrations of $^{10}$B and $^{11}$B isotopes respectively, $C_{10B}$ (mg/cm$^3$/liquid) and $C_{11B}$ (mg/cm$^3$/liquid) are the initial concentrations of $^{10}$B and $^{11}$B isotopes respectively, $C_{q10B}$ (mg/cm$^3$/liquid) and $C_{q11B}$ (mg/cm$^3$/liquid) are the equilibrium concentrations of $^{10}$B and $^{11}$B isotopes in the liquid phase respectively, $V_{solution}$ (mL) is the solution volume, $m_{resin}$ (mg) is the weight of resin and $p_{resin}$ (mg/mL) is the density of the resin.

The competitive Langmuir adsorption isotherm of chelating resins 580 µm average particle diameter Relite CRB03, 270 µm average particle diameter Relite CRB03 and weak base anion exchange resin 580 µm average particle diameter Relite CRB03 and 270 µm average particle diameter Diaion WA21 for $^{10}$B and $^{11}$B isotopes are given in Fig.(2), (3) and (4).

Figure 2. Competitive Langmuir adsorption isotherm of Relite CRB03 chelating resin of 580 µm average particle diameter for (a) $^{10}$B isotope and (b) $^{11}$B isotope.

Figure 3. Competitive Langmuir adsorption isotherm of Relite CRB03 chelating resin of 270 µm average particle diameter for (a) $^{10}$B isotope and (b) $^{11}$B isotope.

Figure 4. Competitive Langmuir adsorption isotherm of Diaion WA21 weak base anion exchange resin of 580 µm average particle diameter for (a) $^{10}$B isotope and (b) $^{11}$B isotope.

The competitive Langmuir adsorption constants are calculated from the linearization of competitive Langmuir adsorption isotherm expression. The y-intercept of the linearized $^{10}$B isotherm curve corresponds to $K_{10B}$/qm$^{10B}$ and the slope of the linearized curve equal to 1/qm$^{10B}$ value of $^{10}$B isotope whereas the y-intercept of the linearized $^{11}$B isotherm curve corresponds to $K_{11B}$/qm$^{11B}$ and the slope of the linearized curve equal to 1/qm$^{11B}$ value of $^{11}$B isotope for the selected resin. In Tables 1 and 2 the adsorption isotherm parameters are given for chelating and weak base anion exchange resins.
From Table 1 and 2 it is clearly realized that three of all of the resins are higher affinity to $^{10}$B isotope as the three of the resins have higher $^{10}$B maximum adsorption capacity values ($q_m$) than the that of $^{11}$B whereas the constant isotherm parameter, $K$ that is inversely proportional with particle affinity is higher for $^{11}$B isotope at Relite CRB03 with small particle diameter and Diaion WA21. On the other hand, this value is higher for $^{11}$B isotope at large particle diameter Relite CRB03. In addition to that as the particle diameter decreases, the adsorption capacity of the resin increases because of increasing resin surface area.

Researchers suggest that the difference between the tetrahedral coordinational geometry of boron complex of $^{11}$B isotope in the resin and the planar trigonal coordinational geometry of boron complex in solution phase result in fractionation of boron isotopes. With N-methyl glucamine type resins, it is observed that when pH < 7, adsorption of $^{10}$B isotope to the resin phase is greater than that of $^{11}$B and for the case of pH values greater than 11, no enrichment in boron isotopes occur [20, 21]. After regeneration with dilute HCL solution, the pH of N-methyl glucamine type resin, Relite CRB03 is 3.03 whereas the pH of weak base anion exchange resin, Diaion WA21 is 5.25. When chelating and weak base anion exchange resins are compared from the viewpoint of boron adsorption capacity Diaion WA21 is superior than Relite CRB03 since the maximum adsorption capacity, $q_m$ of Diaion WA21 is the highest among that of other resins, for both $^{10}$B and $^{11}$B isotopes. On the other hand, as the medium pH of Relite CRB03 is more acidic the enrichment of boron isotopes in other words resolution parameter for this resin is greater than the that of Diaion WA21. Thereby, $^{10}$B isotope enrichment in stationary phase meanwhile $^{11}$B isotope enrichment in liquid phase is greater for Relite CRB03. Sonoda et. al [22, 23] revealed the effectiveness of N-methyl glucamine type resins in the scope of boron isotope enrichment with column chromatography whereas weak base anion exchange resins are preferred by several researchers for boron isotope enrichment [21, 24].

4. Concluding remarks

In this study the effect of resin type and resin particle diameter is investigated for $^{10}$B and $^{11}$B isotopes in terms of competitive Langmuir adsorption isotherm constants. It is concluded that the best resin from the point of isotope productivity is weak base anion exchange resin as it has the highest maximum adsorption capacity. But with regard to boron isotope selectivity it is logical to choose chelating resin, Relite CRB03 with small particle diameter since it has the lowest constant isotherm parameter, $K$ and pH value in the adsorption medium.

References


Characterization of $W_2B$ nanocrystals synthesized by mechanochemical method

Mustafa Barış¹, Tuncay Şimşek², Hakan Gökmeşe³, Adnan Akkurt⁴

¹Eti Mine Works General Management, 06105 Ankara, Turkey
²Hacettepe University, Department of Physics Engineering, 06800 Ankara, Turkey
³Necmettin Erbakan University, Department of Metallurgical and Materials Engineering, 42090 Konya, Turkey
⁴Gazi University, Department of Industrial Design Engineering, 06500 Ankara, Turkey

ARTICLE INFO

Article history:
Received 6 February 2016
Received in revised form 21 March 2016
Accepted 21 March 2016
Available online 24 March 2016

Keywords:
Ball milling,
mechanochemical synthesis,
nanocrystals,
$W_2B$.

ABSTRACT

In this study; $W_2B$ nanocrystals were synthesized with $B_2O_3/Mg/WO_3$ starting materials via mechanochemical method. Starting materials were mixed according to the reaction stoichiometry and reduction processes were performed in a planetary ball mill under Argon gas atmosphere. Phase and morphology structure of particles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy with energy-dispersive X-ray spectroscopy (TEM/EDX) and the specific surface area was measured by Brunauer-Emmet-Teller (BET) theory. The effect of milling period and molar ratios of starting powders were investigated in detail. Results showed that $W_2B$ nanocrystals were obtained successfully without different tungsten compounds after 30 h milling and purification in 2 M HCl solution. Coaxial/spherical shaped and agglomerated $W_2B$ nanocrystals were observed by microstructural examinations. Crystallite size and specific surface area of the $W_2B$ nanocrystals were determined as 13.61 nm and 18 m²/g respectively.

1. Introduction

Tungsten boride compounds ($W_B$, $WB$, $W_B_5$, $WB_3$ and $WB_{12}$) have remarkable properties like high hardness, melting point and electrical resistivity [1]. There are many methods for production of tungsten borides such as chemical vapour deposition, solid state reaction, ionic melts, self-propagating high temperature synthesis, arc plasma melting and mechanochemical method. Syntheses of these compounds are started in 1960’s by Woods et al. and by Peshev et al. [2-3]. In the following years, some properties like mechanical and electrical properties were investigated by some researchers [4-6]. Itoh et al. synthesized $W_B$, $WB$, $W_B_5$ and $WB_3$ compounds via thermal method with elemental tungsten and amorphous boron powders in 1987 [7]. The contribution of $W_B_5$ to oxidation resistance of composite materials was investigated by Radev et al. in 1993 [8]. In 1995, Otani et al. produced a $WB_3$ single crystal via melting process and studied the effects of the boron on the crystal structure [9]. In the same year by melting method Okada et al. produced $W_B$, $δ-WB$ and $WB_3$ crystals and determined the hardness, electrical conductivity and oxidation resistance properties of crystals [10]. Gostishchev et al. have produced $W-WB$ and $W-WB_2$ powders via the reduction of metal oxides and boron mixtures with magnesium in molten salts and demonstrated the effect of NaF-NaCl systems on phases of final product [11]. Mohammadi et al. have produced $W-WB_2$ via elements in arc furnace melting method in 2011 [12]. Yeh et al. [13] and Yazıcı et al. [14-15] have produced and characterized a tungsten boride compound via self-propagating high-temperature synthesis (SHS) using oxides form of tungsten. Besides studies for synthesizing and characterization of tungsten boride compounds, coating [16-17] and composite material development studies [18-19] have also been carried out in the literature. Studies for determining the physical and chemical properties of the synthesized compounds of tungsten boride are expected to lead to an increase in practical work in the future [20-24].
A number of studies have been reported for transition metal boride via mechanochemical method in the literature [25-41], but there are only a few studies for production of tungsten boride [42-44]. In one of these studies, Coskun et al. have reduced tungsten oxide and boron oxide with Mg and leached the obtained powder mixture with HCl and produced W$_2$B$_5$ [42]. Tabrizi and et al. investigated the effect of boron amount on the tungsten boride phases which were synthesized by mechanochemical method [43]. Bahrami-Karkevandi et al. investigated the phase changes of WO$_3$-B$_2$O$_3$-Mg ternary system according to milling period. It is reported that the formation of W$_2$B-W nanocomposite powders after 60 min of milling was achieved [44].

To the best of our knowledge, it is noticed that W$_2$B phases were not obtained alone via mechanochemical method. In the most of studies, it was seen that synthesized W$_2$B powders were composed of different W$_2$B$_x$ phases [42-44]. In this study, W$_2$B nanocrystals were synthesized without any other phases of tungsten or tungsten boride via mechanochemical method by changing reaction stoichiometry. The W$_2$B nanocrystals synthesizing route, morphology and characterization were discussed in detail.

2. Materials and method

2.1. Materials

As starting materials, B$_2$O$_3$ (Eti Maden, 545.74 µm, 98.00 %), Mg (Aldrich, 138.86 µm, 99.00 %) and WO$_3$ (Merck, 3.03 µm, 99.50 %) were used. All experiments were performed under Argon gas atmosphere in a hardened steel vial and 3x15 mm hardened steel balls. 2 M HCl (aq) solution was used for purification of powder mixtures.

2.2. Mechanochemical synthesis method and characterization

The milling processes were carried out by planetary high energy ball mill (Fritsch P6). The synthesis studies were performed with different reaction stoichiometry. In the all experiments, Mg was used 20% wt excess for the reduction reactions and possible oxygen remained in the vial. In the first stoichiometry, B$_2$O$_3$’s molar ratio was not changed while its molar ratio increased twice in the second stoichiometry. Mixtures of starting materials were prepared according to Equation 1 and placed with balls into vial and sealed tightly in the glove box. At the first stage of milling, WO$_3$ and B$_2$O$_3$ were reduced by Mg (Eq. 1.1 & 1.2 and so on ). During the milling, MgO phase was occurred while W and B were released in the vial. Then, W and B reacted by the effect of mechanical energy and formed a W$_2$B ceramic phase (1.3).

$$4WO_3 + 12Mg \rightarrow 4W + 12MgO$$ (1.1)

$$B_2O_3 + 3 Mg \rightarrow 2B + 3MgO$$ (1.2)

$$4W + 2B \rightarrow 2W_2B$$ (1.3)

Starting powders prepared at 4:1:18 and 4:2:18 molar ratios were milled according the parameters given in Table 1. Then mixtures were milled up to 30 h and analyzed by XRD in every 5 h periods. The powders obtained after milling were purified via aqueous HCl solution prepared with distilled water. Leaching process was performed by using 2 M HCl solution at 400 rpm for 30 minutes at room temperature and 1 g/250 ml were used as a solid to liquid ratio. After leaching, particles were firstly washed with distilled water-ethanol and dried in a vacuum oven at 70 °C for 12 h.

Phase structure was determined by X-Ray Diffraction Pattern (XRD, Rigaku, D/MAX-2200, Cu–Kα radiation, 4°/min, 28.2-90°, 40 kV, 30 mA). Particle morphologies and microstructures were examined by Scanning Electron Microscope (SEM, FEI, Quanta 200F) and high-definition Transmission Electron Microscope (HRTEM, FEI, Tecnai G2 F30). The specific surface area was measured by Brunauer-Emmet-Teller (BET) apparatus (Quantachrome, Nova 2200E, UK) through nitrogen adsorption/desorption.

Crystallite sizes of the powders were calculated by using the Scherrer formula in Eq. 2.

$$\tau = \frac{K \cdot \lambda}{\beta \cdot \cos \theta}$$ (2)

In the formula; τ is the crystallite size, K is the constant taken according to the crystal shape (0.89), λ is the X-ray wavelength (0.154 nm), β is the full width at half maximum (FWHM) and θ is the Bragg angle. Crystallite size calculations were performed according to (100) peak of WB, and the FWHM values used were specified in the graphical analysis made in XRD analysis software JADE 7.0.

3. Results and discussion

Figure 1 shows the SEM image and XRD pattern of the unmilled powders. From the SEM image, it was observed that WO$_3$ and B$_2$O$_3$ were in irregular powder shape and morphology while Mg was in flat/flaky morphology. Crystalline WO$_3$ (PDF-032-1395) and Mg (PDF-01-089-4244) were observed in the XRD pattern, but B$_2$O$_3$ was not observed because of its amorphous structure.
Figure 1. SEM image and XRD pattern of initial powders

Starting powders were prepared at 4:1:18 and 4:2:18 molar ratios. Firstly, powder mixture with 4:1:18 molar ratio was ball milled up to 30 h. XRD pattern of the milled powder is presented in Figure 2. As can be seen from this figure, milled powder mixture was composed of W (peaks at about 2θ ~ 40.267°, 58.260°, 73.196°), W₂B (22.565°, 32.125°, 37.900°, 40.898°, 46.070°, 51.886°, 67.197°, 72.749°, 85.424°) and MgO (36.889°, 42.856°, 62.216°, 74.577°) phases and some Fe (44.673°, 65.022°, 82.334°) contamination was seen in the synthesized powders because of worn of vial and balls. Similar situation was also reported in the Bahrami-Karkevandi’s et al. studies. It was reported that powder mixture was composed of W, WB, W₂B and MgO phases via milling [44]. Existing of W phase and transition between phases in the final mixture was probably because of absence of B amount in the reaction environment. Therefore, the molar ratio of B was increased twice in the second stoichiometry for this study.

Figure 2. XRD pattern of milling up to 30 h with powder mixture prepared at 4:1:18 molar ratio

Figure 3 shows the XRD pattern of milled powder mixtures prepared at 4:2:18 molar ratio at selected times (1, 10, 20 and 30 h). It was observed from the figure that the diffraction peaks were shortened and the areas under peaks were expanded over the milling. This phenomena explained by the grain size and crystallite size of starting powders decreasing via plastic deformation inflicted by compressive force of ball-powder collisions [41]. As seen from the XRD pattern, the grain sizes of initial powders were decreased at the end of the first hour of milling. After 10 h milling, W (peaks at about 2θ ~ 40.267°, 58.260°, 73.196°), WB (29.961°, 36.191°, 42.194°, 52.715°), W₂B (22.565°, 32.125°, 37.900°, 40.898°, 46.070°, 51.886°, 67.197°, 72.749°, 85.424°), MgO (36.889°, 42.856°, 62.216°, 74.577°) phases were observed in the powder mixtures. But there was also Fe (44.673°, 65.022°, 82.334°) contamination caused by worn of hardened steel vial and balls. With milling up to 20 h, the height of peaks of W and WB were decreased and the peaks of impurities were nearly disappeared. Prolonging the milling time to 30 h, the only phase of W₂B and MgO were observed.

Figure 3. XRD pattern of milling up to 30 h powder mixture prepared at 4:2:18 molar ratio

In the mechanochemical method, mechanism such as flattening, cold welding, fraction, and re-flattening of starting powders occurs by mechanical energy released during the milling. This repeated mechanism causes the decrease in the grain size while it increases the surface area of the particles. Therefore, increased surface area improves the chemical reactivity of the powders. Figure 4 shows the 5 h milled particles images taken by SEM. Fracturing, flattening and cold welding mechanism occurred by the mechanochemical method can be seen clearly in these images. Particles are firstly fractured and cold welded, then agglomerated and formed a coarse particle.

Figure 4. SEM images of the powders milled up to 5 h

In addition, Figure 5 also shows the SEM images of the powder mixtures milled at 1, 10 and 30 h. When the SEM images are examined, due to the formation...
of agglomeration, it was observed that similar microstructures were seen in terms of the time variables. It can be considered from the figure that powders at the beginning of synthesis, transformed from ductile-ductile structure to ductile-brittle structure. Powder particles were flattened over time so that after repeated of this mechanism particle sizes were decreased significantly. It was determined that shapes of the particles were mostly in nearly coaxial/spherical shape and morphology towards to end of milling. After 1 h grinding, aggregate size of about 50 µm (a) were observed from the SEM images given in Figure 5. With the progress of grinding to 10 h (b) and 30 h (c), aggregate size ranges were decreased to approximately under ~5 µm and ~2 µm, respectively. It was also seen from the SEM images that wide ranges of initial particle size distribution at the beginning of grinding were decreased sharply with prolonged grinding period.

XRD patterns of final powder mixtures before and after purifying processes were given in Figure 6. The figure indicates that the powder mixtures were composed of W$_2$B, MgO and Fe phases after mechano-chemical synthesis. By purification, MgO and Fe were eliminated and final compound was composed of W$_2$B phase without other tungsten boride phases. Furthermore, because of excess usage of Mg and B$_2$O$_3$, a low amount MgB$_2$ was observed in the final product. Additionally, the specific surface area and mean crystallite size of W$_2$B nanocrystals were measured as 18 m$^2$/g by N$_2$ absorption using Brunauer-Emmett-Teller (BET) method and about 13.61 nm via Scherrer formula respectively. The crystal structure of W$_2$B nanocrystals were found tetragonal and the lattice parameters a and c were found 5.568 Å and 4.744 Å respectively from the ICDD PDF Card of XRD graph at Figure 6. These results also match up with Coşkun et al. study [42].

Figure 7 shows the SEM images of purified W$_2$B nanocrystals. As it can also be seen from this figure, particles were agglomerated again and mostly were in coaxial and spherical shape and morphology. The basic reason of the agglomeration was the because of cold welding of reactants due to mechanic energy released during the milling. The drying of purified particles under vacuum also contributed the agglomeration. It was determined from the SEM images that the agglomerates had a wide particle size distribution range under -2 µm.
The TEM images of the W$_2$B nanocrystals after purification are shown in Figure 8. As seen clearly in this figure, intensive agglomeration was also observed with in various sizes due to the high energy ball milling. The single particle sizes were varied between about 40 and 80 nm. The EDS analysis of purified powders showed that W was the main phase, however low Cu and C peaks were observed due to used carbon coated copper TEM grid. In addition, B peaks were not observed in the EDS analysis because of its light atomic absorption characteristic.

4. Concluding remarks

Results of the experimental studies are summarized as follows:

- While W, W$_2$B, MgO, and Fe phases were observed with milling at 4:1:18 molar ratio, no W was observed at the end of 30 h milling performed at 4:2:18 molar ratio.
- W$_2$B nanocrystals were successfully obtained after the leaching with 2 M aqueous HCl solution at room temperature.
- The mean crystallite size of the nanocrystals was calculated as 13.61 nm.
- The specific surface area of nanocrystals was measured about 18 m$^2$/g by BET method.
- Intense agglomeration formations and nearly coaxial/spherical powder shape and morphology of W$_2$B nanocrystals were observed with SEM/TEM examinations.

Acknowledgment

The authors are very grateful to Eti Mine Works General Management for financial support and laboratory facilities usage.

References


[39] Jafari M., Tajizadegan H., Golabgir M. H., Chami A., Torabi O., Investigation on mechanochemical be-


YAZAR KILAVUZU

1. Genel Bilgi


Dergi, bor ile ilgili ulusal ve uluslararası alanlarda yapılan bilimsel çalışmaları, güncel teknolojileri, özgün teknikleri ve yaklaşımları yayılmaktadır. Fen, tıp, enerji, mühendislik, eczacılık, tarım, savunma sanayi, madencilik, kimya ve uzay sanayi gibi alanılarda bor ile ilgili makaleleri bekliyoruz.

BOR Dergisi’ne gönderilen tüm bilimsel makaleler önce Baş Editör tarafından değerlendirilir. Gereklilik öncelik derecesini sağlayaman, Yazar Kilavuzuna uymayan ya da dergi kapsamında olmayan makaleler daha ileri değerlendirmeye alınmaz ve ayrıntılı yorum yapılmadan yazarlara geri gönderilir. Öncelik ve/veya kapsam yönünden yapılan bir değerlendirmeye göreceli olduğunu, sadece bu yönden değerlendirilmeye bağlı ret kararlarının hatalı olduğunu kanıtlamak ve deneysel ve teoretik çalışmalarından ziyade makalelerin kapsamlı bir eleştirel analizini ve seçimi önceliklidir. Bu yüzden genellikle 45000 karakteri (boşluklar dahil) geçmemeli ve en fazla 15 şekil içermelidir.


2. Bilimsel Yazıların Kategorileri

Bilimsel yazılar üç kategoride yaşama kabul edilmektedir:

a.) Öğzün Araştırma Makalesi: Tamamlanmış çalışmaları açıklayan, en çok 30000 karakterden (boşluklar dahil) oluşan ve yeni sonuçları içeren deneySEL ve teori çalışmalarından oluşmaktadır. Araştırma makalesinde de ayrıca en çok 8 şekil ve en çok 6 çizelge yer alabilir.

b.) Kısa Araştırma Makalesi: Hızlı bir şekilde yayımılanan istenen kısa ve önemli sonuçları açıklayan yazıdır. Bu yazı 18000 karakter (boşluklar dahil) ve 6’ya kadar şekil içerenlerdir.

c.) Derleme Makalesi: Belirli bir konu hakkında yayımılanmış bilgileri özetleyen ve araştırmacıların kendi sonuçlarıyla sınırlı olmayan yazıdır. Sadece literatür taramalarıyla readonly bilgi topluluğundan ziyade makalelerin kapsamlı bir eleştirel analizini ve seçimi önceliklidir. Bu yüzden genellikle 45000 karakteri (boşluklar dahil) geçmemeli ve en fazla 15 şekil içermelidir.

3. Yazıların Dergiye Gönderilmesi

3.1. Genel


3.2. Makale nasıl gönderilir

Yazarlar, web tabanlı Makale Sunum Sistemi kullanarak elektronik ortamda BOR Dergisine (journal of BORON) gönderilimleridir. Hizmet yazarların hızlı, güvenli gönderilmesini ve hızlı değerlendirmesini sağlar. Yazarların gönderisi için aşağıdaki basamaklardan oluşur:


C.) Derginin web sitesinde verilen “Açıklamalar” dikkatlice okunmalıdır. Bu sistem makale gönderme süreçinde rüberlerdir eder. Online yardım, süreç boyunca her zaman kullanılabilir. Yazarlar makale...
göndermeyi sonlandırmadan önce, herhangi bir aşamada çıkar/tetak giriş işlemleri yapabilirler. Tüm başvurular kesinlikle gizli tutular. Online başvuru programı ile ilgili tüm sorunlarınızı için fkuru@boren.gov.tr ve ormanabdullah@gmail.com editörel destek adresleri ile temas kurabilirsiniz.

Yazar, yazının başka bir yerde ya da dergide kısmen, tamamen ya da başta bir forma yayınlanmış olduğunu doğrulamalıdır. Makaleyi gönderen yazar (“Sorumlu yazar”) diğer tüm yazarların sorumluluğunu kabul eder. Makaleyi gönderen yazar, tüm ortak yazarların makaleyi gördüklerini ve bu dergide göndermeyi kabul ettiğini onaylar.

Tüm bilimsel yazılara, hakem değerlendirmesine tabi tutulacak ve özgün, yenilik ve kalite açısından değerlendirilecek. Yazarlar, Sunuş Mektubunda kursal e-posta adresleri ve website linkleri ile birlikte değerlendirme sürecinin dışında tutmak istedikleri 5 hakem de öne çıkarabilirler.

Düzeltme istenen makaleler yalnızca iki ay içinde düzeltip tekrar gönderilirler.

Eğer Bor Dergisine başka bir yerde yayımlanan bilgileri (örneğin şekiller) gönderiyorsanız, bu bilgilerin BOR Dergisinde tekrar basılması için izin almanız gerektiğine dikkat ediniz.

4. Yazıların Organizasyonu

4.1. Birinci Sayfa İçeriği

1.) Yazının Başlığı: Ana bulguları kapsayan kısımların özetini ve akış şekilleri ile 15 kelimeden oluşmalıdır.

2.) Yazarların tam adları (ilk adları dahil) ve kurumları: Eğer yayın farklı kurumlarda çalışan yazarların ortak çalışması ise, çalıştıkları kurumlar her yazarın adı 1, 2 gibi üst rakam ile numaralandırılır.

3.) Sorumlu yazarın adı (ve unvanı), posta adresi ve e-posta adresi vb. gerekli iletişim bilgileri gönderilmelidir.

4.) Makalede geçen standart kısaltmaların listesi.

5.) Konu ile ilgili en çok 5 anahtar kelime alfabetik olarak yazılımalıdır.

4.2. Bölümler

Yazilar aşağıdaki gibi bölümlere ayrılmıştır:

1.) “Özet”: Ana metne atıf yapılmadan konuyla anaşılı bir şekilde özetlemelidir. Özet, araştırma ve derleme makaleleri için 220 kelimeli geçmemelidir. Kısa araştırma makaleleri için 80 kelimeli geçmemelidir.

Standart olmayan kısaltmalar ilk kullanıldığında tam olarak yazılımalıdır. Alıntı yapılan her kaynak tam olarak verilmelidir. Türkçe yazılar için özgün İngilizcesi de yazılımalıdır.

ii.) “1 Giriş”: Araştırma konusunu, sorunun açıklanmasını ve bu konu ile ilgili var olan literatürün kısa bir araştırmasını içerir.

iii.) “2 Malzemeler ve Yöntemler”: Araştırma kapsamında kullanılan özel malzeme, donanım ve cihazlar bu bölümde üreticisinin adı ve mümkünse yer (şehir adı) ile birlikte verilmelidir.

iv.) “3 Sonuçlar”

v.) “4 Tartışma”

vi.) “Kaynaklar”

Bölüm 3 ve 4 “Sonuçlar ve Tartışma” adı altında birleştirilebilir. Bölümlerin alt başlıkları numaralandırarak verilmelidir.

4.3. Kaynaklar


http://woodward.library.ubc.ca/research-help/journal-abbreviations/.

Kaynaklar için örnekler aşağıdaki verilmiştir:

Dergi


Kitap


Kitapın bir bölüm ise:

Tez


Kongre veya Sempozyum


- Birden fazla yazari makalelerde ilk yedi yazar ile sınırlıdır, daha fazla varsa vd. şeklinde devam edilir.
- Baskıdaki makalelerin DOI numarası belirtilmelidir.
- Tüm seri Yayınlara dergilerle aynı şekilde atıflapılmalıdır.
- Web sitesi adresleri (URL) kaynak olarak verilmelidir. Ancak metin içerisinde verinin geçtiği yerden sonra belirtilmelidir.

4.4. Teşekkür
Maddi destek kaynaklarına ilişkin teşekkür yazısı metnin sonunda kaynaklardan önce ayrı bir sayfada verilmelidir.

4.5. Çıkar Çatışması
Tüm yazarlar mali ve ticari çıkar çatışmalarını bildirmelidir. Çıkar çatışması yoksa ancak metin içerisinde geçtiği yerde verilen sonra belirtilmelidir.

4.6. Çizelgeler
Çizelgeler, uygun başlıklar ve normal rakamlarla numaralandırılmış bir şekilde metnin sonunda kullanılarak formlanmalıdır. Sütun başlıklarını mümkün olduğuna kısa tutulmalı ve birimleri içermelidir. Çizelge dipnotları çizelge ile aynı sayfada; a), b), c) gibi gösterilmelidir.

4.7. Şekiller, Şemalar ve Başlıklar
Şekiller 80 mm genişliğine küçültüldüğünde basılabilircek kalitede olmalıdır. Sayılar, yazılar ve simgeler yerli büyükükte okunaklı olmalıdır. Tüm şekiller metin-
6. Makale Taslak Metni ve Baskı

AUTHOR GUIDELINES

1. Instructions to Authors

Journal of BORON is the first and only journal in the Science World, in which original and basic scientific research and application studies related to boron are published. Journal of BORON covers all aspects of boron science, boron technology, boron usage, boron chemicals and fields which used boron. The journal focuses on innovative element boron giving interdisciplinary insights on a broad range of fields including science, medicine, energy, engineering, agriculture, pharmacy, defense industry, mine industry, chemical industry and aerospace industry.

The journal publishes current technologies, original methods, applications and all approaches about boron. Papers dealing with boron issues from such fields as science, medicine, energy, engineering, agriculture, pharmacy, defense industry, mine industry, chemical industry and aerospace industry, etc., are welcome.

All scientific contributions are assessed initially by the Editor-in-Chief. Those manuscripts failing to reach the required priority rating, failing to comply with the Instructions to Authors or not fitting within the scope of the journal are not considered further and are returned to authors without detailed comments. It should be noted that rebuttals that challenge rejections based on priority and/or scope alone will rarely be successful, since such a decision is necessarily a matter of opinion.

Manuscripts meeting the requirements will be peer-reviewed on the criteria of originality and quality. Authors may suggest up to five potential referees in the Cover Letter. Please provide their institutional e-mail addresses and a link to the website as well as individuals whom they wish to exclude from the review process. If the decision following review is “reject subject to major revision”, a revised version may be submitted, but if major issues with the revised version are still identified by the reviewers, it will then be rejected outright. On acceptance, papers may be subjected to editorial changes. Responsibility for the factual accuracy of a paper rests entirely with the author.

All instances of publishing misconduct, including, but not limited to, plagiarism, data fabrication, image/data manipulation to falsify/enhance results, manipulation of the reviewing process, etc., will result in rejection/retraction of the manuscript.

This journal endorses the Higher Education Scientific Research and Publication Ethics Guidelines rules and will pursue cases of suspected research and publication misconduct. For more information about Higher Education Scientific Research and Publication Ethics visit the Higher Education website at http://www.yok.gov.tr/web/guest/icerik/journal_content/56_INSTANCE_rEHF8BIsfYRx/10279/18187

2. Categories of Scientific Contributions

Three categories of scientific contributions are accepted for publication:

a.) Original Research Article: It consists of experimental and theoretical work with new results describing completed studies and should comprise about 30 000 characters (including spaces). In addition, up to 8 figures or schemes, and 6 tables may be included.

b.) Short Communication: It describes results that are brief, timely and/or of such importance that rapid release is warranted. This manuscript should be in the range of 18 000 characters (including spaces) and 6 figures.

c.) Review Article: It summarizes information published on a certain topic and is not limited to own results. Rather than an assemblage of information with a complete literature survey, a comprehensive critical description and selection of the material is indispensable. This contribution should typically not exceed 45 000 characters (including spaces); up to 15 figures may be included.

3. Submission of Manuscripts

3.1. General

This journal will be published in an online-only format and printed edition will be published. There will be no cost to authors for the publication of manuscripts. All copyright of the accepted manuscripts belong to BOREN.

3.2. How to submit

Manuscripts to Journal of BORON have to be submitted via a web-based manuscript submission and peer-review system. This service guarantees fast and safe submission of manuscripts and rapid assessment. Submission of manuscripts consists of the following steps:

A.) Preparation of the manuscript and illustrations in the appropriate format, according to the instructions given below (see Sections 4.1 to 4.9). The paper has to conform to the scientific and style instructions of the Journal of BORON as given herein. A link to these instructions can be found at the submission site at www.journal.boren.gov.tr/about/submission or directly at the homepage of the journal at www.journal.boren.gov.tr under the link “For Authors”.

B.) For the first submission an author’s account in the system at the submission site, www.journal.boren.gov.tr/user/register has to be created by clicking on the “Registration” button.
C.) The “Author Guidelines” given on the Journal website have to be read carefully. The system guides through the submission process. Online help is available at all times during the process. Authors are also able to exit/re-enter at any stage before finally “submitting” the work. All submissions are kept strictly confidential. For any questions concerning the online submission program, Editorial Support at fkuru@boren.gov.tr andormanabdullah@gmail.com can be contacted.

The author vouches that the work has not been published elsewhere, completely, in part, or in any other form, and that the manuscript has not been submitted to another journal. The submitting author (listed under “Correspondence”) accepts the responsibility of having included as coauthors all appropriate persons. The submitting author certifies that all coauthors have seen the manuscript and agreed with its submission.

All scientific contributions will be peer-reviewed and judged on the criteria of originality, quality, and novelty. Authors may suggest up to five potential referees in the Cover Letter, including their institutional e-mail addresses and a link to the website as well as individuals whom they wish to exclude from the review process.

A revised paper will retain its original date of receipt only if it is resubmitted within two months after revision.

Please note that if you are submitting material (e.g., figures) which has already been published elsewhere, you must also provide permission in writing that this material may be reprinted in the Journal of BORON.

4. Organization of Manuscripts

4.1. Contents of First Page of Manuscript

1.) Title of the paper, concise (15 words maximum), providing the main finding of the paper and, only if necessary, with standard abbreviations.

2.) Full names (including first name) of the authors and their affiliation(s). If the publication originates from several institutes, the affiliation of each author should be clearly stated by using superscript Arabic numbers after the name and before the institute.

3.) Name (and title) and full postal address, e-mail address of the author to whom all correspondence (including galley proofs) is to be sent.

4.) A list of the nonstandard abbreviations used in the paper.

5.) Up to 5 keywords in alphabetical order which will be used for compiling the subject index.

4.2. Sections

Manuscripts should be divided into the following sections:

i.) “Abstract” It must be self-explanatory and intelligible without reference to the text. It should not exceed 220 words for research and review articles. Abstracts for Short Communications should not exceed 80 words. Abbreviations, but not standard abbreviations, must be written in full when first used. Any references cited must be given in full.

ii.) “1 Introduction” containing a description of the problem under investigation and a brief survey of the existing literature on the subject.

iii.) “2 Materials and Methods” for special materials and equipment, the manufacturer’s name and, if possible, the location should be provided.

iv.) “3 Results”

v.) “4 Discussion”

vi.) “References”

Sections 3 and 4 may be combined and should then be followed by a short section entitled “Concluding Remarks”. Subdivisions of sections should be indicated by numbered subheadings.

4.3. References

References should be numbered sequentially in the order of citation. The reference numbers within the text should be set in brackets, thus [3, 14]. They are to be collected in numerical order at the end of the manuscript under the heading “References”. Titles of journals should be abbreviated according to e.g. http://woodward.library.ubc.ca/research-help/journal-abbreviations/.

Please note the following examples:

Journals

Books


Chapter in a book:


Thesis


Conference and Symposium


Please note that:

- Papers with multiple authors should be limited to listing the first seven authors, followed by et al.
- Papers which accepted for publication should be cited with their DOI.
- Other serial publications should be cited in the same manner as journals.
- Website addresses (URL) must not be included as a reference, but should be inserted in the text directly after the data to which they refer.

4.4. Acknowledgements

Acknowledgements as well as information regarding funding sources should be provided on a separate page and will appear at the end of the text (before References).

4.5. Conflict of Interest

All authors must declare financial/commercial conflicts of interest. Even if there are none, this should be stated in a separate paragraph following on from the acknowledgements section as follows: The authors have declared no conflict of interest. This is a mandatory requirement for all articles.

4.6. Tables

Tables with suitable captions at the top and numbered with Arabic numerals should be collected at the end of the text, each table on a separate sheet. Column headings should be kept as brief as possible and indicate units. Footnotes to tables should be indicated with a), b), c), etc. and typed on the same page as the table.

4.7. Figures, Diagrams, and Legends

The quality of the figures must be such that they can be reproduced directly after reduction to 80 mm width and the numbers, letters, and symbols must be large enough to still be legible. All figures must be referred to in the text and numbered with Arabic numerals in the sequence in which they are cited. Each figure must be accompanied by a legend explaining the contents of the figure.

4.8. Structural Diagrams and Mathematical Equations

Structures of molecules as well as mathematical equations should be drawn or written in the manuscript in the position where they belong. They should always stand alone, i.e., occupy extra lines. If reference to them is made repeatedly, structures and equations may be marked with Arabic numerals in parentheses in the right-hand margin.

Use the equation editor of the current MS Word for equations. Do not import special symbols and characters as graphics/formula in the running text. Please use in Word Insert/Symbol.

4.9. Units and Symbols

The use of SI units is mandatory. Generally accepted nomenclature and symbols as recommended by ASTM or IUPAC are preferred. In the interest of clarity, symbols should be defined in the text. If numerous symbols are involved, they should be listed and defined at the end of the text (before “References”).
4.10. Abbreviations

Abbreviations should be restricted to a minimum and be introduced only when repeated use is forthcoming. Abbreviations used only in a table or a figure may be defined in the legend. Standard abbreviations may be used in the title and keywords. If nonstandard abbreviations are used in the Abstract they should be defined there, in the list of abbreviations of the manuscript, as well as when first used in the body of the paper.

5. Electronic Manuscripts

All submissions will be converted to PDF format during the upload process. The system automatically generates a single PDF file which contains all parts of the manuscript. File management requires the following:

Main text (incl. front material) as well as figure legends and tables (in this order) should be given in one file, preferably saved in doc, docx or rtf format.

Figures should preferably be in JPG, EPS, TIFF or in the original format; no ppt(x) or pdf.

In revised manuscripts the areas containing the major required changes should be marked and the color of the text changed. The file(s) with the changes visible on screen should be re-submitted online. Upon acceptance of the manuscript the final uploaded version will be taken as the basis for copy editing and the subsequent production process.

6. Proofs and Reprints

Before publication authors will receive page proofs via e-mail in PDF low resolution file format, together with a sheet including instructions and a reprint order form, also as PDF files. The proofs should be carefully corrected following the instructions. In particular, authors should answer any editing queries. The author(s) will receive 5 free reprints and two hard copies of the related issues.