Physicochem. Probl. Miner. Process. 52(1), 2015, 136−146

www.minproc.pwr.wroc.pl/journal/

Physicochemical Problems of Mineral Processing

ISSN 1643-1049 (print)
ISSN 2084-4735 (online)

Received December 14, 2014; reviewed; accepted May 18, 2015

ELECTRO-DEPOSITION PARAMETERS OF BORON CARBONITRIDE (BCN) FROM BORAX PENTAHYDRATE ($NA_2B_4O_7 \cdot 5H_2O$)

Baran TUFAN*, Turan BATAR**

* Dokuz Eylul University, Department of Mining Engineering, 35390, Buca, Izmir, baran.tufan@deu.edu.tr
** Gediz University, Department of Mechanical Engineering, Seyrek, Izmir

Abstract: The primary objective of this research is the fabrication of boron end products from boron derivatives by electro-deposition as powder or coating. The production of boron carbonitride is achieved by electro-deposition at low temperatures without carbon dioxide emission, regardless of sintering and thermal treatment. The extensive usage of boron is aimed and should be accomplished by application of electro-deposition method for boron carbonitride fabrication.

Keywords: *electro-deposition, boron carbonitride, borax pentahydrate, low temperature*

Introduction

Turkey has the most abundant boron reserves in the world, however the boron end products to be used in advanced technology are not available since the existing production plants in Turkey do not fit the requirements and technology to produce high-end and sophisticated boron products. The production of boron end products such as boron carbide (B_4C, BC_5 and $B_{13}C_2$), boron nitride (BN) and boron carbonitride (BCN) are possible in industrial scale (Tufan and Batar, 2014). However such procedures require great energy consumption and also result in environmental problems such as CO_2 emission.

A technology for obtaining material based boron nitride and boron carbide powders, called boron carbonitride (BCN), was developed more than three decades ago. Since then, boron carbonitride has been used in various areas of high temperature technology. However, its structure has not been conclusively studied so far. It has been hypothesized that in addition to the starting components (BN, B_4C), a third phase of the B-N-C compound type was present in the material (Ulrich et al, 2005). Evidence for this finding arises from the properties of boron carbonitride, which differ

http://dx.doi.org/10.5277/ppmp160112

from the properties of a mechanical mixture of the starting components, and specifically, from the substantial increase in the crystal lattice parameter c of BN and a decrease in the B_4C content during reactive sintering. The sinterability of the material was also explained by the formation of a ternary B-N-C compound, since the components BN and B_4C themselves were not sintered under the synthesis conditions (Grigorev et al, 2005).

BCN can be synthesized through different routes, including thermolysis of organic, inorganic and polymeric precursors. Arc-methods and laser ablation may additionally be used for direct synthesis of BCN, utilizing solid state sources of B, C and a N compound. The BCN synthesis method, utilizing a substitution reaction where the high temperature reaction (2000 K) of carbon nanotubes performed, can be managed within a stream of gaseous nitrogen or NH_3 or in the presence of B_2O_3 powder, CuO and Au_2O_3 (Blank et al, 2009; Zhi et al, 2002; Zhuge and Yamanaka, 2008).

There has been much effort to synthesize the new BCN phase by various techniques such as nitriding of solid phase precursors at relatively high temperatures, gas phase reactions using CVD techniques and solid phase's pyrolysis (Watanabe et al, 1996). However, few reports consider solvothermal synthesis of boron carbonitride phase. Recently, the solvothermal technique has attracted much attention and has been used to synthesis some important semiconductors (Mannan et al, 2008). In a study by Huang et al. (2004), a solvothermal reaction of $CH_3CN{\cdot}BCl_3$ and lithium nitride (Li_3N) using benzene as the solvent has been successfully applied to prepare boron carbonitride at 300 ^oC and less than about 7 MPa. X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy were used to confirm their chemical composition and atomic-level hybrid. X-ray diffraction and transmission electron diffraction analysis indicated that the powders had hexagonal network structures.

BCN films were deposited by plasma-assisted chemical vapor deposition (PACVD) at 390°C by Aoki et al. (2008). A Si wafer, used as a substrate, was placed in a quartz reactor and source gases were introduced into the reactor. Boron trichloride (BCl_3), methane (CH_4), and nitrogen (N_2) were used as source gases. A radio frequency (RF) power of 80W was supplied to produce N_2 remote plasma by induction coupling. BCl_3 was transported with hydrogen (H_2) gas near the substrate. The substrate temperature was maintained at 390 °C using an infrared lamp. The deposition time was 30 min. BCN films with thicknesses of 150–250 nm were prepared in this experiment.

Transparent and hard BCN films were deposited on polycarbonate and silicon wafer by means of different radio frequency plasma-assisted chemical vapor deposition conditions with two liquid organic compounds as precursors by Ahn et al. (2003). The mechanical and optical properties of BCN films deposited were characterized by nano-indentation. The chemical composition of BCN films was determined by Rutherford backscattering spectroscopy and elastic recoil detection analysis. The influence of the plasma parameters on the mechanical and optical

properties of films was described. Hard and transparent BCN films with low refractive index were deposited through low-energy and high-density ion.

Wohle et al. (1999) have given an overview of the plasma-assisted techniques for coating ceramics on polymer substrates at low temperature. Deposition of boron carbon nitride was carried out on polycarbonate substrates by a radio-frequency plasma-assisted chemical vapor deposition process using different metallo-organics as precursors. The films deposited were found to be stable and adherent under ambient conditions. The chemical composition of the layers varied in a wide range. Nearly stoichiometric BCN layers, as well as films with high carbon content, were obtained. The chemical bonding of boron, carbon and nitrogen was analyzed by X-ray photoelectron spectroscopy.

In a study by Torres et al. (2007), ternary boron-carbon-nitrogen (BCN) compounds have been prepared as nano-metric powders by low-energy ball milling, using as precursors h-BN, graphite and polypropylene micrometric powders. Different proportions of the reactants were used aiming at the synthesis of BCN, BC_2N, BC_4N and $BCNH_2$ compositions. Ball milling induced chemical reaction between the precursors resulting in ternary BCN materials in the form of nanoparticles with an average diameter of 60 nm, as revealed by Scanning Electron Microscopy. Infrared spectroscopy confirmed the dominant hexagonal bonding structure, although with new spectral features.

The primary objective of this study was to reveal the possibility of production of a boron end product by a low cost and low energy consuming method, namely electro-deposition. Faraday's first law of electrolysis and Faraday's second law of electrolysis state that the amount of a material deposited on an electrode is proportional to the amount of electricity used. The amount of different substances liberated by a given quantity of electricity is proportional to their electrochemical equivalent (Lou and Huang, 2006). An electrolytic cell essentially consists of two or more electrodes dipping into an electrolyte. These electrodes are connected to an external electric power source (Gupta, 2003). When a direct electric current passes through an electrolyte, chemical reactions take place at the contacts between the circuit and the solution. By this the electrolysis or electroplating takes place.

During electrolysis the cations or the positively charged ions move towards the cathode and the anions or the negatively charged ions migrate towards the anode. Various reactions take place at the electrodes during electrolysis. In general, reduction takes place at the cathode, and oxidation takes place at the anode (Bosso and Gaseca, 1971; Lou and Huang, 2006). Many different studies have been conducted by using electro-deposition method such as Chen et al. (2011); Ebrahimi et al. (1999) and Naik et al. (2002). Boron was electro-extracted from boron carbide and deposited on a mild steel cathode as boron related electro-deposition study by Jain et al. (2013). Boron nitride was successfully deposited on copper electrodes by Tufan and Batar (2014).

There exist many different studies in the literature on the application of many different methods. However, electro-deposition, a classical method to be utilized mainly

in electro-plating, has not been employed for the production of BCN. The production of boron carbonitride (BCN) was achieved at low temperatures, regardless of sintering and thermal treatment. Unlike the conventional production methods relying on high energy consumption and high temperatures reported in literature, electro-deposition method is anticipated to provide an opportunity for environmentally justifiable boron carbonitride production at relatively lower energy consumption levels.

Materials and methods

The commercially available borax pentahydrate samples used were obtained from the borax pentahydrate (BPH) production plant of Eskisehir, Kirka Boron Works. Borax pentahydrate is the refined form of natural sodium borate and has the chemical formula $Na_2B_4O_7 \cdot 5H_2O$. Composed of boron oxide (B_2O_3), sodium oxide, and water, it is a mild, white and crystalline alkaline salt, with excellent buffering and fluxing properties. It is available in crystalline (granular) form and is an important multifunctional source of B_2O_3, particularly for processes for which the simultaneous presence of sodium is beneficial. Borax pentahydrate used at the correct equivalent rate gives solution or melts identical in composition with those of borax decahydrate. It may, therefore, be substituted in all applications where borax is used. Among the applications of borax pentahydrate are the production of wire drawing baths, corrosion inhibitor solutions, starches, adhesives and the manufacture of other boron compounds (Eti Mine, 2003). The physical and chemical characterization and particle size distribution of commercially available BPH is listed in Table 1. The solubility of borax pentahydrate in distilled water with respect to electro-deposition bath temperature was also determined (Fig. 1).

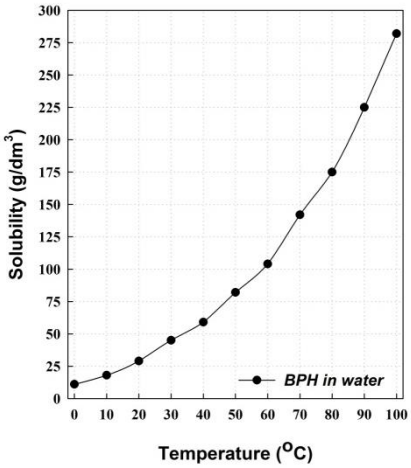

Fig. 1. Solubility of borax pentahydrate (BPH) in distilled water

Table 1. Features of borax pentahydrate (BPH) (Eti Mine, 2012)

Physical and chemical properties	
Physical State	White crystals
Melting Point	741 ^{o}C
Boiling Point	1575 ^{o}C
Specific Gravity	1.81 g/cm^3 at 20 ^{o}C
Molecular Weight	291.35 g/mole
pH	9.3 (3% solution)
Physical State	White crystals
Melting Point	741 ^{o}C
Boiling Point	1575 ^{o}C
Chemical specifications	
B_2O_3	47.76 % (min.)
Purity	99.90% (min.)
Na_2O	21.25% (min.)
SO_4	135 ppm (max.)
Cl	70 ppm (max.)
Fe	5 ppm (max.)
Insolubles in Water	150 ppm (max.)
Particle size distribution	
+1.000 μm	6% (max.)
-1.000 +0.063 μm	90% (min.)
-0.063 μm	4% (max.)

Electro-deposition tests

Electro-deposition tests were performed to determine the optimum parameters for production of boron carbonitride from borax pentahydrate. Copper, iron and graphite electrodes with dimensions of 100×20×0.2 mm were used during electro-deposition tests. The dissolved B2O3 amounts were investigated for borax pentahydrate with respect to bath temperature to achieve the most stable and saturated solution. The bath temperature was set at 80 ^{o}C and the initial concentrations of solutes were determined with respect to their solubilities at this temperature. The laboratory experimental setup involved a polypropylene bath, a thermo-couple, a magnetic stirrer with a heating feature and an Alpha-Tech brand redressor which can operate at 0–200 amperes and 0–600 volts (Fig. 2).

The design of electro-deposition tests using $Na_2B_4O_7{\cdot}5H_2O$ as the solute is listed in Table 2. The table lists the experimental conditions for the tests conducted. Several different electrode types were used for the electro-deposition tests. The combinations of copper, graphite and iron were determinant in the formation of BCN with several additives. The chemical, surface and phase characterizations of electrolytes and deposited electrode bars were performed using Thermo Scientific, Cu-Kα type X-ray diffractometer (XRD); Coxem, EM-30 type scanning electron microscope (SEM) and Varian, 710-ES type inductively coupled plasma optical emission spectroscopy (ICP-OES).

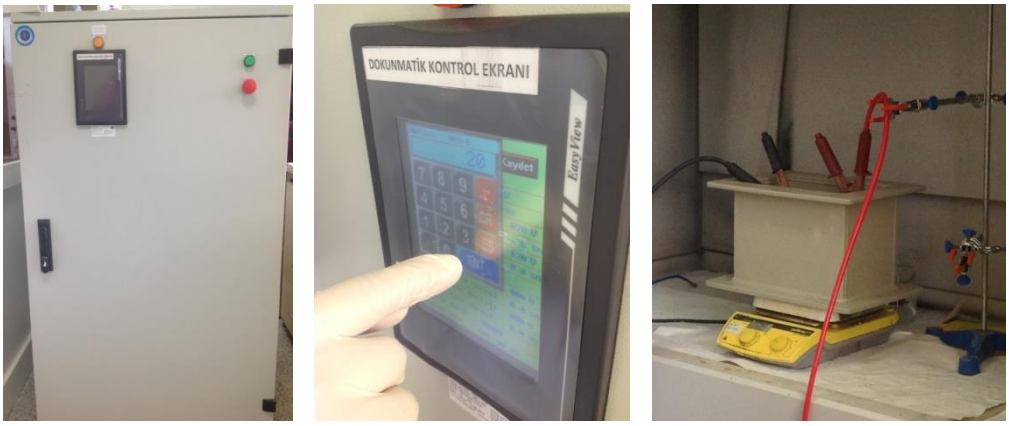

Fig. 2. Setup for electro-deposition tests: From left to right: the redressor, touch screen control panel and electro-deposition bath

Table 2. Experimental conditions for electro-deposition tests

Code	Anode	Cathode	pH	Addition	V	A	Duration (min.)
BPH01	Cu	Cu	9–10	–	6	3	10
BPH02	Cu	Cu	9–10	–	8	3	10
BPH03	Cu	Cu	9–10	–	10	3	10
BPH04	Cu	Cu	9–10	–	12	3	10
BPH05	Cu	Cu	9–10	–	14	3	10
BPH06	Cu	Cu	9–10	–	16	4	10
BPH07	Cu	Cu	9–10	–	18	5	10
BPH08	Cu	Cu	9–10	–	20	5	10
BPH09	Cu	Cu	9–10	–	22	5	10
BPH10	Cu	Cu	9–10	–	24	7	10
BPH11	Cu	Cu	9–10	–	26	7	10
BPH12	Cu	Cu	9–10	–	28	8	10
BPH13	Cu	Cu	9–10	–	30	7	10
BPH14	Cu	Cu	9–10	–	14	3	10
BPH15	Cu	Cu	9–10	–	14	5	10
BPH16	Cu	Cu	9–10	–	14	7	10
BPH17	Cu	Cu	9–10	–	14	9	10
BPH18	Cu	Cu	9–10	–	14	11	10
BPH19	Cu	Cu	9–10	–	18	13	10
BPH20	Cu	Cu	9–10	–	20	15	10
BPH21	Graphite	Fe	9–10	–	4	1	10
BPH22	Graphite	Fe	9–10	–	6	1	10
BPH23	Graphite	Fe	9–10	–	8	1	10
BPH24	Graphite	Fe	9–10	–	18	4	10
BPH25	Graphite	Fe	9–10	–	20	5	10
BPH26	Graphite	Cu	9–10	–	12	3	10
BPH27	Graphite	Cu	4.5	$C_6H_8O_7$	24	9	10
BPH28	Cu	Cu	9–10	Active C	24	7	10
BPH29	Cu	Cu	9–10	NaSCN	24	7	10
BPH30	Graphite	Cu	4	CH_3COOH	24	10	10

For the tests listed in Table 2 initial concentration of borax pentahydrate was set at 175 g/dm^3 which corresponds to its maximum solubility value for its saturated solution at 80^{o}C. The bath temperature was varied between 60 and 100^{o}C to achieve rapid crystallization and precipitation of borax pentahydrate at low temperatures and to avoid possible safety issues at high temperatures. The bath volume, and thus, the electrode surface area changed with tests, resulting in variations in the current densities.

Results and discussion

In several experiments conducted, formation of BCN was observed. The objective was determining the optimum parameters for such formations. For instance, in the test BPH21 with parameters listed in Table 3, a small amount of deposition on Fe cathode was observed and the coated substrate was analyzed by XRD to determine the phases formed (Fig. 3). This impurity detected in XRD analysis was due to a non-uniform coating, causing the substrate (Fe) identification in XRD.

Table 3. Experimental conditions of BPH21 test

Anode	Cathode	pH	Addition	V	A	Duration (min)
Graphite	Fe	9–10	–	4	1	30

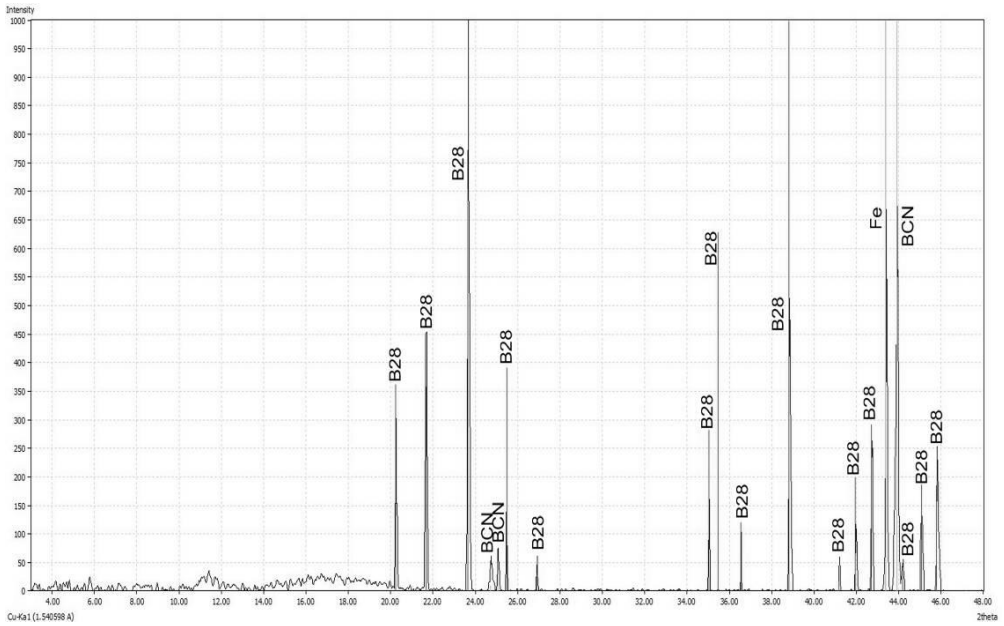

Fig. 3. XRD spectrum of deposited Fe cathode of BPH21

The formation of BCN, B_{28} and Fe phases were determined as a result of XRD analysis. The formation of B_{28} and BCN peaks were proven, however the B_2O_3 removal from the electrolyte during the experiment remained low. It was found that a sufficient amount of B_2O_3 should be bound and removed from solution to form boron carbide. Otherwise, elemental boron or other boron products could be deposited.

As a result of the BPH29 test (Table 4), a successful deposition on Cu cathode was achieved and the coated substrate was analyzed by XRD (Fig. 4). The XRD spectrum showed that addition of NaSCN not only enhanced the formation of nitrogen and carbon based boron products, such as BC_5 and BCN, but also caused some impurities such as oxides of copper and free carbon peaks due to the undesired reactions amongst the substrate (Cu) and remaining dissolved carbon. NaSCN, as a source of nitrogen and carbon dissolved in distilled water (solvent) provided sufficient amounts liable to react with boron, showing the highest electron affinities with N and C.

Table 4. Experimental conditions of BPH29 test

Code	Anode	Cathode	pH	Addition	V	A	Duration (min.)
BPH29	Cu	Cu	9-10	NaSCN	24	7	10

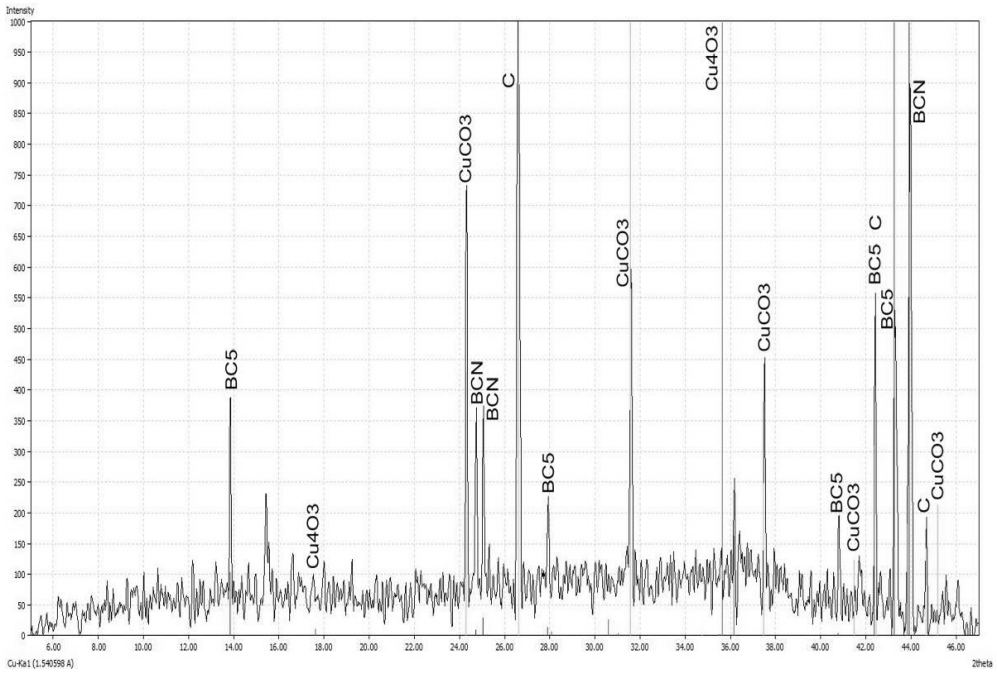

Fig. 4. XRD analysis of deposited Fe cathode of BPH29

The experimental studies conducted with borax pentahydrate as solute were finalized by the determination of optimum intervals for production of boron

carbonitride. The maximum optimum deposition time was determined as 8 to 10 minutes as a result of observations and B_2O_3 removal amount from the electrolyte. Addition of sodium cyanide in equal molar ratios as solute enhanced the formation of boron carbonitride. The optimum experimental conditions as intervals and the resultant phases detected by XRD analysis are listed in Table 5.

Table 5. Optimum experimental conditions and resultant products

Borax pentahydrate as solute (saturated, 175 g/dm^3)					
Fixed Parameters					
Solvent		pH		Temperature	Duration
Distilled Water		9.0–10.0 (natural)		75–85^{o}C	8–10 min.
Variables					
Anode	Cathode	Potential (volt)	Current (amper)	Additive	Deposited Products
Cu	Cu	18–30	5–7	NaSCN	BC_5, BCN
Gr	Fe	4–20	1–5	–	BCN, B_{28}

Conclusions

This study shows the possibility of boron carbonitride production using an environmental friendly, low energy consuming alternative methodology at significantly lower temperature levels (80 ^{o}C) as compared to the conventional procedures. Among many different variables, emphasis were given on the intervals of pH, bath temperature, solute concentration, voltage set, current acquired and duration of the tests. Different phase formations with different anode and cathode electrodes and different chemical compound additions were achieved. Successful depositions of BCN were obtained after a deep parameter screening process. The addition of sodium cyanide had positive affects in formation of carbon and nitrogen based phases. BCN, BC_5 and elemental boron formations were achieved in low voltage (max. 30 V) and current (max. 7 A) levels.

The optimum parameter intervals to form BCN were determined and the opportunity of purifying the product was revealed. The necessity in purification of final coatings was revealed, in addition to further characterization of purified coatings by different methods. For future work, studies to produce BCN in pilot or industrial scale should be performed. In addition, the mechanical properties of the product should be compared to the commercially available alternatives and market value of the laboratory scale product should be determined prior to further studies.

References

AHN H., KLIMEK K.S., RIE K.T., 2003, *BCN coatings by RF PACVD at low temperature*, Surface and Coatings Technology, 174-175, 1225-1228.

AOKI H., TOKUYAMA S., SASADA T., WATANABE D., MAZUMDER M.K., KIMURA C., 2008, *Dry etching properties of boron carbon nitride (BCN) films using carbon fluoride gas*, Diamond & Related Materials, 17, 1800-1804.

BLANK V.D., SEEPUJAK A., POLYAKOV E.V., BATOV D.V., KULNITSKIY B.A., PARKHOMENKO, 2009, *Growth and characterization of BNC nanostructures*, Carbon, 47, 3167-3174.

BOSSO J.F., GASECA G.R., 1971, *Electro-deposition process*, US Patent 3,619,398.

CHEN C.S., SHIH Y.J., HUANG Y.H., HUANG G.H., 2011, *Recovery of nickel with the addition of boric acid using an electro-deposition reactor*, Desalination and Water Treatment, 32 (1-3), 345-350.

EBRAHIMI F., BOURNE G.R., KELLY M.S., MATTHEWS T.E., 1999, *Mechanical properties of nanocrystalline nickel produced by electro-deposition*, NanoStructured Materials, 11 (3), 343-350.

ETI MINE, 2003, Pre-feasibility report summaries, Boron nitride planning and data processing department, Ankara.

ETI MINE, 2012, *Activity report*, Retrieved December 12, 2013, from http://www.etimaden.gov.tr

GRIGOREV O.N., BEGA N.D., LYASHENKO V.I., DUBOVIK T.V., PANASHENKO V.M., SHCHERBINA O.D., 2005, *Dependence of the structure of sintered boron carbonitride on the defect level in the starting BN powder*, Powder Metallurgy and Metal Ceramics, 44, 5-6.

GUPTA C.K., 2003, *Chemical Metallurgy: Principles and Practice*, Weinheim: Wiley-Vch, 670-710.

HUANG F.L., CAO C.B., XIANG X., LV R.T., ZHU H.S., 2004, *Synthesis of hexagonal boron carbonitride phase by solvothermal method*, Diamond & Related Materials, 13, 1757-1760.

JAIN A., ANTHONYSAMY S., ANANTHASIVANA K., RANGANATHANA R., MITTAL V., NARASIMHAN S.V., 2008, *Characterization of electrodeposited elemental boron*, Materials Characterization, 59, 890-900.

LOU H.H., HUANG Y., 2006, *Electroplating*, Encyclopedia of Chemical Processing, Taylor & Francis, 1-10.

MANNAN M.A., NAGANO M., HIRAO N., BABA Y., 2008, *Hexagonal BCN Films Prepared by RF Plasma-Enhanced CVD*, Chemistry Letter, 37 (1), 96-97.

NAIK Y.A., VENKATESHA T.V., NAYAK P.V., 2002, *Electro-deposition of zinc from chloride solution*, Turkish Journal of Chemistry, 26, 725-733.

TORRES R., CARETTI I., GAGO R., MARTIN Z., JIMENEZ I., 2007, *Bonding structure of BCN nanopowders prepared by ball milling*, Diamond & Related Materials, 16, 1450-1454.

TUFAN B., BATAR T., 2014, *Production parameters of boron nitride from boric acid by low temperature electro-deposition*, Ciencia e Tecnica (ISSN:0254-0223), 29 (10), 24-36.

ULRICH S., HOLLECK H., LEISTE H., NIEDERBERGER L., NOLD E., SELL K., 2005, *Nano scale, multi-functional coatings in the material system B-C-N-H*, Surface & Coatings Technology, 200, 7-13.

WATANABE M.O., ITOH S., MIZUSHIMA K., SASAKI T., 1996, *Bonding characterization of BC_2N thin films*, Applied Physics Letter, 68, 2962-2964.

WOHLE J., AHN H., RIE K.T., 1999, *BCN coatings on polymer substrates by plasma CVD at low temperature*, Surface and Coatings Technology, 116-119, 1166-1171.

ZHI C.Y., BAI X.D., WANG E.G., 2002, *Raman characterization of boron carbonitride nano-tubes*, Applied Physics Letter, 80, 3590-3592.

ZHUGE F., YAMANAKA S., 2008, *Ternary compound B_4CN_4 prepared by direct nitridation of B_4C*, Journal of Alloys and Compounds, 466, 299-303.