Nano-Metal Borides of Cobalt, Nickel and Copper

Al-Zain Omar Ali*, Al-Masoudi and Reem Soliyman
Department of Chemistry, Faculty of Science, King Abdulaziz University, Jiddah, Saudi Arabia

Abstract

The magnesiothermic reaction of CoO, NiO with B₂O₃ and Mg yielded only Co₃O₄, NiO. Similarly, direct reaction of CoO, NiO with elemental boron yielded CoB₂O₄ and NiO respectively. The reaction of CoCl₂, NiCl₂ with elemental boron yielded CoB, NiB respectively. On the other hand direct reaction of pure Co, Cu metal with elemental boron in 1:1, 1:2 and 1:3 ratios produced metal oxides except 1:3 ratio produced was CoB and Cu(BO₃). So, Solid phase with metal oxides and chlorides ended with metal oxides except with cobalt oxide and elemental Boron where CoB₂O₄ was produced. Reacting pure metals and elemental boron produced nano-metal borides for Co, Ni and Cu. The liquid phase reaction of CoCl₂, NiCl₂ and CuCl₂ with sodium borohydride, NaBH₄ produced black nanocrystals and nanorods of CoB₄, NiB₄, CuB₄ and CuO.

Keywords: Nanoparticles; Nano nickel; Nano-rod

Introduction

Cobalt borides are inorganic borides with general formula Co₅B₃. The most common cobalt borides are CoB and Co₅B₃. Cobalt boride nanoparticles in the size range of 18 to 22 nm have been produced. The physical properties of cobalt borides are refractory materials, highly resistant to oxidation. It increases the lifespan of metal parts when used as coating. It imparts surface corrosion and wear resistant. It is used as catalyst for reduction [1] and fuel cell technologies, and they are applied in biomedical sciences for the design of drug delivery system. The cobalt borides exhibit superparamagnetic regime at room temperature, whereas the largest particles show ferromagnetic behavior [2].

Nano nickel boride NiB₂ is an example of metal-rich boride. Wodniak et al. crystallized amorphous Nickel-boride alloys and observed a side product in the final yield [3]. A similar behavior was seen when thin films of NiB were synthesized by chemical vapor deposition method [4] or during the crystallization of Nickel–Boron metallic glasses [5]. Machiavelli et al. studied an amorphous alloy, Ni₅B₃ and postulated that NiB decomposes above 500°C to form NiB and NiB [6]. Lattice parameters are known from electron diffraction [3]. Katherine et al. described that NiB, is the first binary boride of a 3d metal and proposed that a single-phase bulk synthesis of NiB₄ that crystallized with unknown disordered structure [7].

Zahida et al. have demonstrated that the metal-rich NiB₄ is paramagnetic. They also exhibit small ferromagnetic impurity. A very weak temperature independent paramagnetism was found for nickel boride [8].

Due to special characters of transition metal borides including high hardness, high melting points, high-temperature strength, corrosion resistance, chemical stability, wear resistance and electrical properties, transition metal borides have a wide applications in different fields like medicine, high resistant furnaces and others [9-14].

Several synthetic procedures were applied to produce borides almost none of these studies proved the formation of single phase borides, rather a mixture of boride phases was formed [15,16]. In this paper two different procedures have been carried out in the synthetic process of Cobalt, Nickel and Copper borides, namely, solid states and wet reaction.

One of the elements which did not react with boron was copper. It was found to cause some wetting problems which made the addition of this metal rather useless. One of the elements which did not react with boron was copper. It was found to cause some wetting problems which made the addition of this metal rather useless. One of the elements which did not react with boron was copper. It was found to cause some wetting problems which made the addition of this metal rather useless.

Experimentation/Empirical Analysis

Reagents

Unless otherwise specified, reagent grade chemicals were employed. The precursor materials were Cobalt Oxide Black (CoO, BDH), and Nickel Oxide (NiO, BDH), Boron Powder (Amorphous) (B, Loba Chemie), Boron (III) Oxide (B₂O₃, Alfa Aesar), Magnesium Powder (BDH), Cobalt (II) Chloride (CoCl₂, Fluka AG), Nickel (II) Chloride Hexahydrate Puriss (NiCl₂.6H₂O, Riedel _de Haen), Cupper Chloride Dihydrate (CuCl₂.2H₂O, Alfa Aesar), Cobalt Powder (Co, Alfa Aesar), Copper Powder (Cu, Alfa Aesar), Sodium Borohydride (NaBH₄, Sigma-Aldrich), Hydrochloric acid (HCl, Sigma-Aldrich, fuming >37%). The Powder X-ray diffraction (XRD) measurement was carried out with a Bruker D8 Advance diffractometer (CuKα λ=1.54 Å; Ni filter; 40 KV, 40 mA; Divergence slit: 1 mm, LynxEye one-dimensional detector, Detector slit: 8 mm). Scanning Electron Microscope and Transmission Electron Microscope (SEM and TEM) were performed by employing a microscope of model Titan 80-300 CT from FEI Company (Hillsboro, OR), which was equipped with a field emission gun (FEG) and a charged-Couple Devices (CCD) camera of 4k × 4k pixels. Furthermore, the analyses of all samples were performed by operating the microscope at 300 kV accelerating voltage in order to take full advantage of the highest spatial resolution possible from this microscope. An aperture of 100 microns was also inserted into the back-focal plane (BPF) of
the objective lens, to improve the image contrast. The Magnetization measurement was carried out in an ever-cool Squid-Vibrating Sample Magnetometer (SVSM), from the manufacturer Quantum Design, USA.

Synthesis

Solid phase

Preparation of metal borides using boron oxide and magnesium

Cobalt boride: 2.2479 g of Cobalt Oxide (10 mmol), 0.6962 g Boron (III) Oxide (10 mmol) and 0.4861 g Magnesium (10 mmol), were mixed in a porcelain crucible. Mixture was placed in a muffle furnace. Heating was started at 600°C and temperature elevated subsequently up to 900°C. XRD shows that the reaction product was CoO.3

3 CoO + B2O3 + 2 Mg \rightarrow Co3O4 + 2 B + 2 MgO

Nickel boride: 1.4939 g of Nickel Oxide (20 mmol), 1.3924 g Boron (III) Oxide (20 mmol) and 1.4583 g Magnesium (10 mmol), were mixed in a porcelain crucible and placed in a muffle furnace. Since the melting point of Mg is 650°C, reaction was started at 600°C and temperature was elevated subsequently up to 900°C. XRD shows that the reaction product is a nickel oxide.

NiO + B2O3 + 3 Mg \rightarrow NiO + 2 B + 3 MgO

Preparation of metal borides using metal oxide and boron powder

Cobalt boride: 7.4933 g of Cobalt Oxide (100 mmol) and 2.1622 g of Boron Powder (100 mmol), were mixed in a porcelain crucible and placed in a muffle furnace. Temperature was set up at 400 and elevated to 500°C for six hours. After cooling to the room temperature the black precipitate was leached with concentrated hydrochloric acid (conc. HCl) for one hour under magnetic stirring. Product was filtered and washed with distilled water three times and then dried in the vacuum oven at 150°C for 3 hours. Yield was CoB1.3

CoO + 2 B \xrightarrow{\Delta} \text{CoB}_2O_4

Nickel boride: 7.4693 g of Nickel Oxide (10 mmol) and 0.3243 g Amorphous Boron Powder (10 mmol), were mixed in a porcelain crucible and placed in a muffle furnace. Temperature was set at 500 and elevated to 700°C for four hours. After cooling to the room temperature in a muffle furnace, the black precipitate was leached in concentrated hydrochloric acid (conc. HCl) for one hour under magnetic stirring. Product was filtered and washed with distilled water three times and then dried in the vacuum oven at 150°C for 3 hours. Yield was NiO.

NiO + B2O3 + 3 Mg \rightarrow NiO + 2 B + 3 MgO

Preparation of metal borides using metal chlorides and boron

Cobalt boride: 3.8952 g of Cobalt Chloride Anhydrous (10 mmol) and 0.4324 g Boron Powder (10 mmol), were mixed in a porcelain crucible and placed in a muffle furnace. Temperature was ranged between 400 and 700°C for six hours. After cooling to room temperature in a muffle furnace, the black precipitate was leached in 1 N HCl at 100°C for three hour under magnetic stirring. Solution was filtered and washed with distilled water, 1 N NaOH and absolute ethanol and dried in a vacuum oven at 150°C for 3 hours. Yield was CoB2O4.

3 CoCl2 + 4 B \xrightarrow{\Delta} \text{Co}_2B + \text{CoB} + 2 \text{BCl}_3

Nickel boride: 3.8879 g of Nickel Oxide (10 mmol) and 0.21622 g Amorphous Boron Powder (50 mmol), were mixed in a porcelain crucible and placed in a muffle furnace at 500-600°C for four hours. After cooling to the room temperature in a muffle furnace, the black precipitate was leached in concentrated hydrochloric acid (conc. HCl) for one hour under magnetic stirring. Product was filtered, washed with distilled water three times and then dried in the vacuum oven at 150°C for 3 hours. Yield was NiO.

3 NiCl2 + 2 B \xrightarrow{200-400 \degreeC} 3 NiO + 2 \text{BCl}_3

Preparation of metal borides using metal chlorides with boron, sodium and aluminum chloride

Cobalt boride: 1.2984 g of Cobalt Chloride Anhydrous (10 mmol), 0.2162 g Boron Powder (10 mmol), 0.4598 g Sodium (10 mmol) and 5 g of Anhydrous Aluminum (III) Chloride were mixed in a porcelain crucible and placed in a muffle furnace. Temperature gradually raised starting 300°C for two hours then 600°C for four hours and finally 1000°C for 12 hours. After cooling to room temperature the mixture was leached with 1 N HCl at 100°C for three hours under magnetic stirring. Solution was filtered and washed with distilled water, 1 N NaOH and absolute ethanol and dried in a vacuum oven at 150°C for 3 hours. Yield was CoB2O4.

CoCl2 + 2 B + 2 Na \xrightarrow{300-1000 \degreeC} \text{CoB}_2O_4 + 2 \text{NaCl}

Preparation of metal borides using metal powder and boron

Cobalt boride: 5.8933 g of Cobalt (100 mmol) and 1.0811 g Amorphous Boron Powder (100 mmol), were mixed in a porcelain crucible and placed in a muffle furnace at 700-900°C for five hours under inert atmosphere. After cooling to the room temperature in a muffle furnace, the black precipitate was leached in concentrated hydrochloric acid (conc. HCl) for 24 hours under magnetic stirring. Product was filtered and washed with distilled water three times and then dried in the vacuum oven at 150°C for 3 hours. Yield was 46%.

Co + B \xrightarrow{700-900 \degreeC} \text{CoB} : 1:1

5.8933 g of Cobalt (100 mmol) and 2.1622 g Boron Powder (200 mmol), were mixed in a porcelain crucible and placed in a muffle furnace. Temperature was ranged between 700 and 900°C for five hours under inert atmosphere (argon atmosphere). After cooling to the room temperature in a muffle furnace, the black precipitate was leached in concentrated hydrochloric acid (conc. HCl) for 24 hours under magnetic stirring. Product was filtered and washed with distilled water three times and then dried in the vacuum oven at 150°C for 3 hours. Yield was 53%.

Co + 2B \xrightarrow{700-900 \degreeC} \text{CoB}_2 : 1:2

5.8933 g of Cobalt (100 mmol) and 3.2433 g Amorphous Boron Powder (300 mmol), were mixed in a porcelain crucible and placed in a muffle furnace at 700-900°C for five hours under inert atmosphere. After cooling to the room temperature in a muffle furnace, the black precipitate was leached in concentrated hydrochloric acid (conc. HCl) for 24 hours under magnetic stirring. Product was filtered and washed with distilled water three times and then dried in the vacuum oven at 150°C for 3 hours. Yield was 61%.

Co + B \xrightarrow{700-900 \degreeC} \text{CoB} : 1:3

Copper boride: 6.3546 g of Copper (100 mmol) and 1.0811 g Amorphous Boron Powder (200 mmol), were mixed in a porcelain crucible and placed in a muffle furnace at 700-900°C for five under inert atmosphere. After cooling to the room temperature in a muffle furnace, the precipitate was leached in concentrated hydrochloric acid (conc. HCl) for 24 hours under magnetic stirring. Product was filtered and
washed with distilled water three times and then dried in the vacuum oven at 150°C for 3 hours. Yield was 30%.

\[
\text{Cu + B} \xrightarrow{\Delta\text{700-900°C}} \text{CuB} \quad 1:1
\]

6.3546 g of Copper (100 mmol) and 2.1622 g Amorphous Boron Powder (200 mmol), were mixed in a porcelain crucible and placed in a muffle furnace at 700-900°C for five hours under inert atmosphere. After cooling to the room temperature in a muffle furnace, the precipitate was leached in concentrated hydrochloric acid (conc. HCl) for 24 hours under magnetic stirring. Product was filtered and washed with distilled water three times and then dried in the vacuum oven at 150°C for 3 hours. Yield was 75%.

\[
\text{Cu + 2B} \xrightarrow{\Delta\text{700-900°C}} \text{CuB}_2 \quad 1:2
\]

6.3546 g of Copper (100 mmol) and 3.2433 g Amorphous Boron Powder (300 mmol), were mixed in a porcelain crucible and placed in a muffle furnace at 700-900°C for five hours under inert atmosphere. After cooling to the room temperature in a muffle furnace, the precipitate was leached in concentrated hydrochloric acid (conc. HCl) for 24 hours under magnetic stirring. Product was filtered and washed with distilled water three times and then dried in the vacuum oven at 150°C for 3 hours. Yield was Cu(BO$_2$)$_2$.

\[
\text{Cu + 2NaBH}_4 + 4\text{H}_2\text{O} \rightarrow \text{CuB}_2\text{O}_4 + 2\text{NaCl} + 4\text{H}_2
\]

**Liquid phase**

**Preparation of metal borides using metal chlorides and sodium borohydride**

*Cobalt boride*: 1.2984 g of Anhydrous Cobalt Chloride (10 mmol) was dissolved in 100 ml distilled water, stirred on a magnetic stirrer. 0.7566 g (10 mmol) of sodium borohydride was dissolved in 50 ml distilled water and dropwise added from separator funnel. Mixture was left stirring for 30 minutes at room temperature. The precipitate was filtered and carefully washed with dilute hydrochloric acid then with distilled water. CoB$_2$O$_4$ Precipitate was dried in the oven (open air) at 150°C for five hours. Yield was CoB$_2$O$_4$.

\[
\text{CoCl}_2 + 2\text{NaBH}_4 + 4\text{H}_2\text{O} \rightarrow \text{CuB}_2\text{O}_4 + 2\text{NaCl} + 4\text{H}_2
\]

*Nickel boride*: 3.8032 g of Nickel Chloride Hexahydrate (2 mmol) was dissolved in 100 ml distilled water, stirred on a magnetic stirrer. 1.2106 g (2 mmol) of sodium borohydride was dissolved in 50 ml distilled water and dropwise added from separator funnel and left stirring for 30 minutes at room temperature. The precipitate was filtered and carefully washed with dilute hydrochloric acid then with distilled water. Ni$_2$B$_2$ Precipitate was dried in the oven (open air) at 400°C for five hours. Yield was 75%.

\[
8\text{NiCl}_2 + 16\text{NaBH}_4 + 30\text{H}_2\text{O} \rightarrow 2\text{Ni}_2\text{B}_2 + 16\text{NaCl} + 47\text{H}_2 + 10\text{B(OH)}_3
\]

*Copper boride*: 2.0458 g of Copper Chloride Dihydrate (1 mmol) was dissolved in 100 ml distilled water, stirred on a magnetic stirrer and 1.8158 g (2 mmol) of sodium borohydride dissolved in 50 ml distilled water and dropwise added from separator funnel and left stirring for 30 minutes. The precipitate was filtered and carefully washed with dilute hydrochloric acid then with distilled water. CuB$_2$ Precipitate was dried in the oven (open air) at 400°C for five hours. Yield was 58%.

\[
12\text{CuCl}_2 + 24\text{NaBH}_4 + 11\text{H}_2\text{O} \rightarrow \text{CuB}_2\text{O}_4 + 11\text{CuO} + 24\text{NaCl} + 59\text{H}_2
\]

**Results and Discussion**

Two different preparation methods, solid phase (five different ways) and liquid phase (one way), were attempted to reach the most proper way to produce Co, Ni and Cu metal-borides.

**Solid phase**

Mixing stoichiometric amounts of CoO, B$_2$O$_3$ and Mg, either in open air or under a blanket of argon, yielded CoO$_2$. Direct reaction of cobalt metal oxide, CoO, with elemental boron mixed in a porcelain crucible and placed in a muffle furnace for several hours under argon atmosphere yielded CoB$_2$O$_4$ (Figure 1a).

Reaction of cobalt chloride, CoCl$_2$, with elemental boron mixed in a porcelain crucible and placed in a muffle furnace for six hours under argon atmosphere yielded a mixture of CoB and Co$_2$B (Figure 1b).

Reaction of a mixture of cobalt chloride, CoCl$_2$, elemental boron and sodium metal in a muffle furnace at variant temperature and time (300, 600 and 1000°C for 12 hours) under argon atmosphere yielded CoB$_2$O$_4$ (Figure 1c). Direct reaction of cobalt metal and elemental boron tried in three different proportions (1:1, 1:2 and 1:3). Mixture was placed in a porcelain crucible in muffle furnace at 900°C for five hours under argon atmosphere. 1.3 Proportions was the best among all where produced CoB according to XRD graph (Figure 1d). SEM image shows an irregular texture of mixed crystals sizes (Figure 1e). Magnetic hysteresis (Figure 1f) shows that CoB possess superparamagnetism [17,18]. Magnesiothermic Reduction of NiO, B$_2$O$_3$ and Mg, either in
Figure 1c: XRD spectra of CoB₂O₄ produced by direct reaction of CoCl₂, B and Na.

Figure 1d: XRD spectra of black crystals of CoB produced by direct reaction of Co and B.

Figure 1e: SEM image of black crystals of CoB.
open air or under a blanket of argon, yielded only NiO. Also a direction 
reaction of nickel oxide, NiO, and chloride, NiCl₂, with elemental 
boron mixed in a porcelain crucible and placed in a muffle furnace 
for several hours under argon atmosphere yielded Nickel oxides. 
Direction reaction of cupper metal with elemental boron tried in three 
proportions 1:1, 1:2 and 1:3. Proportion of 1:3 was the best among 
all where produced Cu(BO₂)₂ according to XRD graph (Figure 2a). 
SEM image (Figure 2b) shows an irregular texture of mixed crystals 
which is in agreement with of the XRD. Figure 2c shows a low profile 
superparamagnetic curve which might indicates a nanocrystals and 
nanorods.

**Liquid phase**

Addition of sodium borohydride, NaBH₄ to cobalt (II) Chloride, 
CoCl₂ solution (1:2 ratio) produced CoB₂O₄ as it could be seen in the 
XRD pattern (Figure 3a). SEM image (Figure 3b) shows a texture of 
crystals. TEM image (Figure 3c) clearly indicates nanocrystals and 
nanorods. Figure 3d reflects regular paramagnetic properties of cobalt 
compound. Reaction of nickel (II) Chloride, NiCl₂ with sodium 
borohydride, NaBH₄ in solution (1:2 ratio) produced Ni₃B₂ as XRD
Figure 3a: XRD pattern of CoB$_2$O$_4$ yielded by reaction of CoCl$_2$ with NaBH$_4$.

Figure 3b: SEM image of CoB$_2$O$_4$.

Figure 3c: TEM image of CoB$_2$O$_4$.
pattern indicated (Figure 4a). TEM image (Figure 4b) clearly indicates nanocrystals and nanorods. Figure 4c shows superparamagnetic curve which in support of nanocrystals and nanorods. Copper (II) Chloride, CuCl₂, reacted with sodium borohydride, NaBH₄, in solution (1:2 ratio) to produce a mixture of CuB₂ and CuO as the XRD pattern shows (Figure 5a). SEM image (Figure 5b) shows the crystal texture of the product. TEM image (Figure 5c) clearly indicates nanocrystals and nanorods which is reflected on the magnetism of the product. Figure 5d shows a low profile superparamagnetic curve which might indicates a nanocrystals and nanorods.
Figure 4c: Magnetic hysteresis superparamagnetism of Ni$_2$B.

Figure 5a: XRD spectra of CuB$_{24}$ and CuO by direct reaction of CuCl$_2$ with NaBH$_4$.

Figure 5b: SEM image of nanocrystals and nanorods of CuB$_{24}$ and CuO.
Conclusion

Both solid and liquid phases produced metal borides with different levels between Cobalt, Nickel and Copper. Cobalt and Copper successfully produced metal borides while Nickel produced only metal oxides. On the other hand Nickel and Copper produced nano-metal boride but Cobalt produced CoB2O4. All Cobalt, Nickel and Copper are 3d metal (first raw transition metal series), but definitely the electronic configuration of the d orbital plays its role (please see previous publications) [18,19].

Acknowledgement

Authors would like to express gratitude and appreciation to King Abdulaziz City for Science and Technology for providing the research Grant AT-34-255. Authors would also like to express thanks to King Abdulaziz University and in particular, the chemistry department for their continuous support.

References
