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Nano-Metal Borides of Cobalt, Nickel and Copper

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Abstract

The magnesiothermic reaction of CoO, NiO with B_2O_3 and Mg yielded only Co_3O_4, NiO. Similarly, direct reaction of CoO, NiO with elemental boron yielded CoB_2O_4 and NiO respectively. The reaction of $CoCl_2$, $NiCl_2$ with elemental boron yielded Co_2B, NiO 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 $Cu(BO_2)_2$. So, Solid phase with metal oxides and chlorides ended with metal oxides except with cobalt oxide and elemental Boron where CoB_2O_4 was produced. Reacting pure metals and elemental boron produced nano-metal borides for Co, Ni and Cu. The liquid phase reaction of $CoCl_2$, $NiCl_2$ and $CuCl_2$ with sodium borohydride, $NaBH_4$, produced black nanocrystals and nanorods of CoB_2O_4, Ni_4B_3, CuB_{24} and CuO.

Keywords: Nanoparticles; Nano nickel; Nano-rod

Introduction

Cobalt borides are inorganic borides with general formula Co_mB_n. The most common cobalt borides are CoB and Co_2B. 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 super paramagnetic regime at room temperature, whereas the largest particles show ferromagnetic behavior [2].

Nano nickel boride Ni_7B_3, is an example of metal-rich boride. Wodnieka 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 Ni_3B were synthesized by chemical vapor deposition method [4] or during the crystallization of Nickel–Boron metallic glasses [5]. Machizaud et al. studied an amorphous alloy, $Ni_{66}B_{34}$, and postulated that Ni_7B_3 decomposes above 500°C to form Ni_3B and Ni_2B [6]. Lattice parameters are known from electron diffraction [3]. Katherine et al. described that Ni_7B_3 is the first binary boride of a 3d metal and proposed that a single-phase bulk synthesis of Ni_7B_3 that crystallized with unknown disordered structure [7].

Zahida et al. have demonstrated that the metal-rich Ni_7B_3 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 (B_2O_3, Alfa Aesar), Magnesium Powder (BDH), Cobalt (II) Chloride ($CoCl_2$, Fluka AG), Nickel (II) Chloride Hexahydrate Puriss ($NiCl_2.6H_2O$, Riedel _de Haen), Cupper Chloride Dihydrate ($CuCl_2.2H_2O$, Alfa Aesar). Cobalt Powder (Co, Alfa Aesar), Copper Powder (Cu, Alfa Aesar), Sodium Borohydride ($NaBH_4$, 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

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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 Co_3O_4.

$$3\ CoO + B_2O_3 + 2\ Mg \xrightarrow{\Delta} Co_3O_4 + 2\ B + 2\ MgO$$

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.

$$NiO + B_2O_3 + 3\ Mg \xrightarrow{\Delta} NiO + 2\ B + 3\ MgO$$

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 CoB_2O_4.

$$CoO + 2\ B \xrightarrow[400\text{-}500^{\circ}C]{x\ [O_2]} CoB_2O_4$$

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 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 and washed with distilled water three times and then dried in the vacuum oven at 150°C for 3 hours. Yield was NiO.

$$NiO + 2\ B \xrightarrow[500\text{-}600^{\circ}C]{x\ [O_2]} NiO + B_2O_3$$

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 for three 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. The yield is 54.89%.

$$3\ CoCl_2 + 4\ B \xrightarrow[400\text{-}700^{\circ}C]{\Delta} Co_2B + CoB + 2\ BCl_3$$

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.

$$3\ NiCl_2 + 2\ B \xrightarrow[200\text{-}400^{\circ}C]{x\ [O_2]} 3\ NiO + 2\ BCl_3$$

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 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 h. Yield was CoB_2O_4.

$$CoCl_2 + 2\ B + 2\ Na \xrightarrow[300\text{-}1000^{\circ}C]{x\ [O_2]} CoB_2O_4 + 2\ NaCl$$

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%.

$$Co + B \xrightarrow[700\text{-}900^{\circ}C]{\Delta} CoB \quad 1{:}1$$

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, 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%.

$$Co + 2B \xrightarrow[700\text{-}900^{\circ}C]{\Delta} CoB_2 \quad 1{:}2$$

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%.

$$Co + B \xrightarrow[700\text{-}900^{\circ}C]{\Delta} CoB \quad 1{:}3$$

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%.

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

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 47%.

$$Cu + 2B \xrightarrow[700\text{-}900^{\circ}C]{\Delta} CuB_2 \quad 1:2$$

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 $Cu(BO_2)_2$.

$$Cu + 2B \xrightarrow[700\text{-}900^{\circ}C]{x\,[O_2]} Cu(BO_2)_2 \quad 1:3$$

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_2O_4 Precipitate was dried in the oven (open air) at 400°C for five hours. Yield was CoB_2O_4.

$$CoCl_2 + 2\,NaBH_4 + 4\,H_2O \longrightarrow CoB_2O_4 + 2\,NaCl + 4\,H_2$$

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_4B_3 Precipitate was dried in the oven (open air) at 400°C for five hours. Yield was 75%.

$$8\,NiCl_2 + 16\,NaBH_4 + 30\,H_2O \longrightarrow 2\,Ni_4B_3 + 16\,NaCl + 47\,H_2 + 10\,B(OH)_3$$

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_{24} Precipitate was dried in the oven (open air) at 400°C for five hours. Yield was 58%.

$$12\,CuCl_2 + 24\,NaBH_4 + 11\,H_2O \longrightarrow CuB_{24} + 11\,CuO + 24\,NaCl + 59\,H_2$$

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_2O_3 and Mg, either in open air or under a blanket of argon, yielded Co_3O_4. 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_2O_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_2B (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_2O_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_2O_3 and Mg, either in

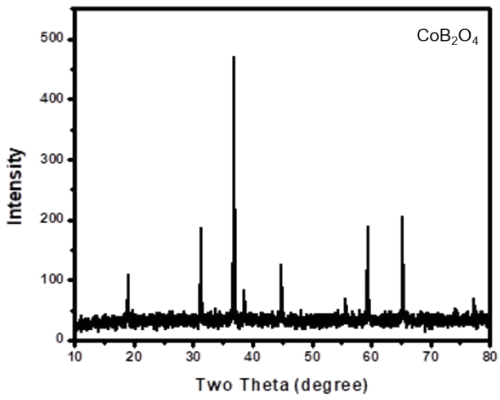

Figure 1a: XRD spectra of CoB_2O_4 produced by direct reaction of CoO and B.

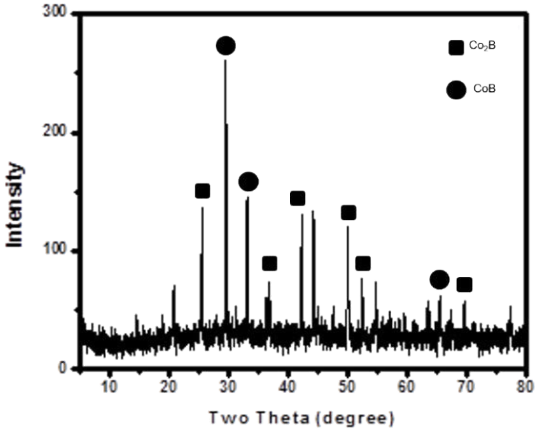

Figure 1b: XRD spectra of CoB and Co_2B produced by direct reaction of $CoCl_2$ and B.

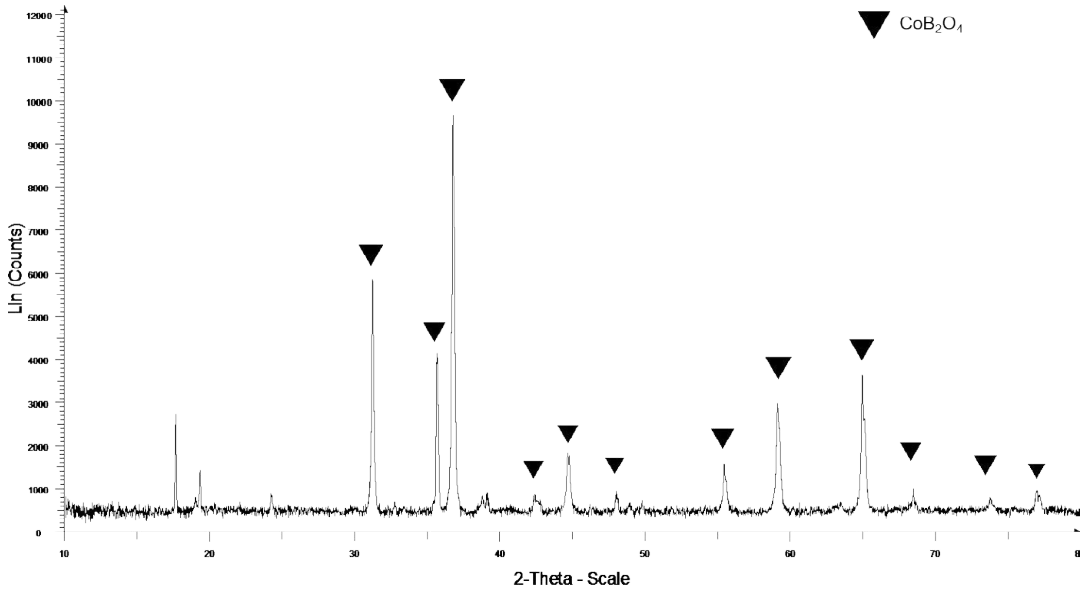

Figure 1c: XRD spectra of CoB_2O_4 produced by direct reaction of $CoCl_2$, B and Na.

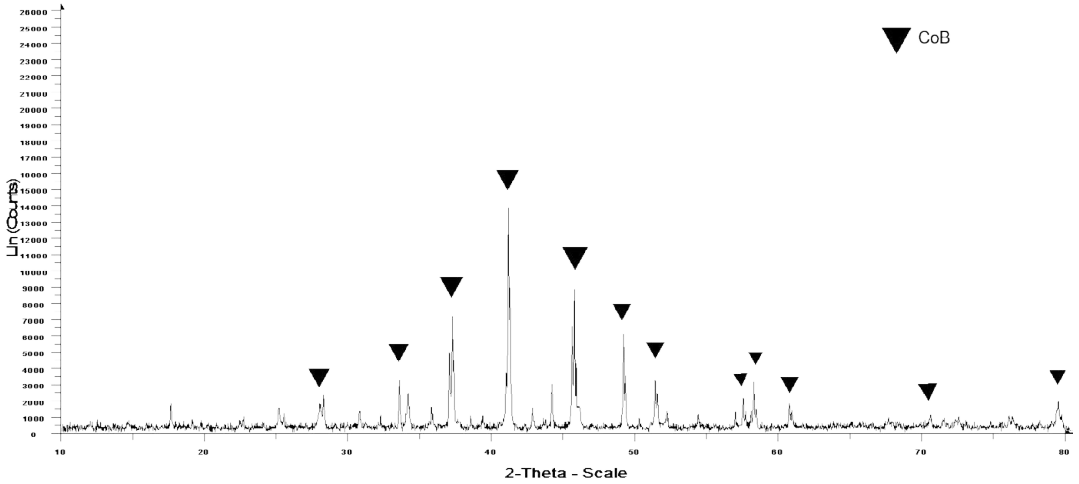

Figure 1d: XRD spectra of black crystals of CoB produced by direct reaction of Co and B.

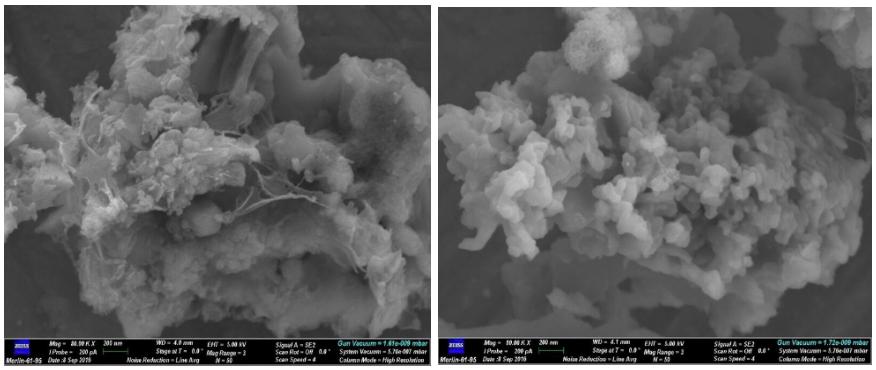

Figure 1e: SEM image of black crystals of CoB.

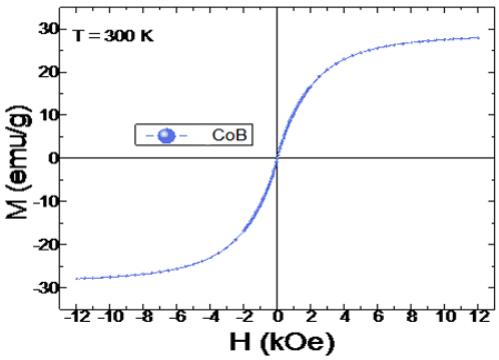

Figure 1f: Magnetic hysteresis of CoB

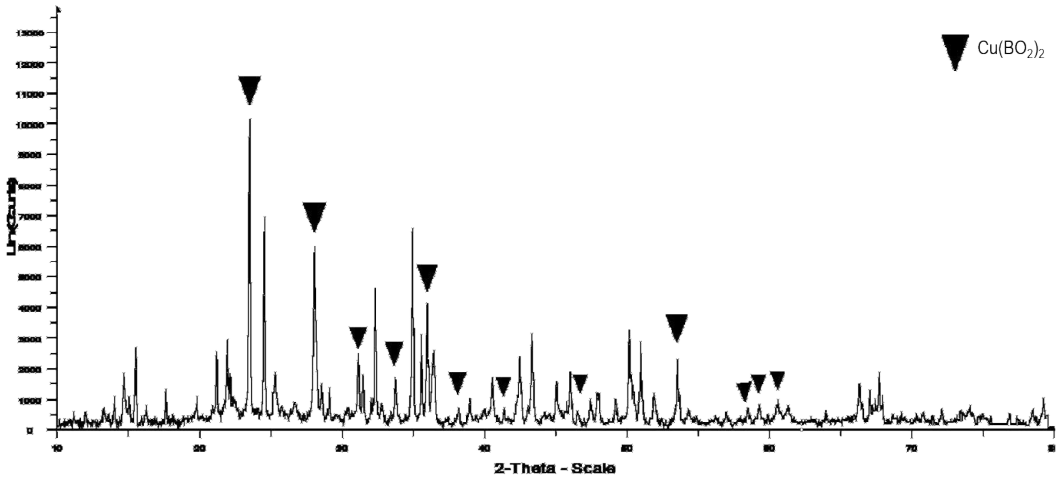

Figure 2a: XRD spectra of $Cu(BO_2)_2$ produced by direct reaction of Cu and B.

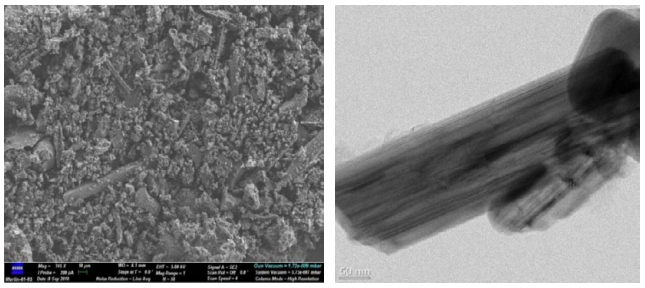

Figure 2b: SEM image of $Cu(BO_2)_2$.

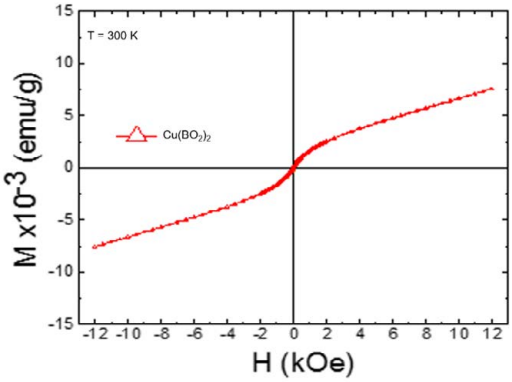

Figure 2c: Magnetic hysteresis of $Cu(BO_2)_2$.

open air or under a blanket of argon, yielded only NiO. Also a direction reaction of nickel oxide, NiO, and chloride, $NiCl_2$, 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 $Cu(BO_2)_2$ 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, $NaBH_4$ to cobalt (II) Chloride, $CoCl_2$, solution (1:2 ratio) produced CoB_2O_4 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, $NiCl_2$, with sodium borohydride, $NaBH_4$, in solution (1:2 ratio) produced Ni_4B_3 as XRD

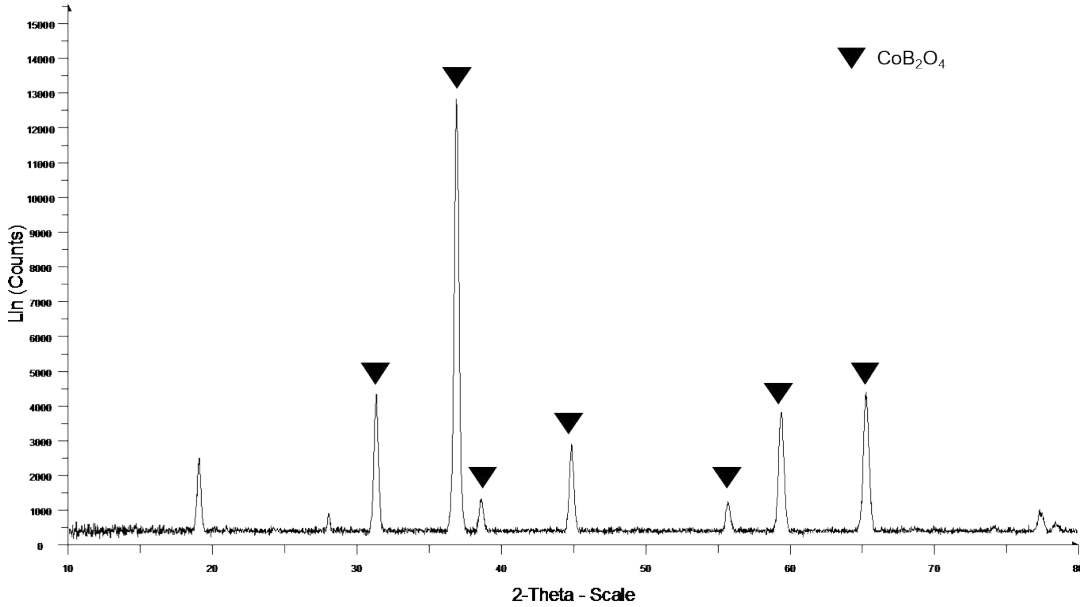

Figure 3a: XRD pattern of CoB_2O_4 yielded by reaction of $CoCl_2$ with $NaBH_4$.

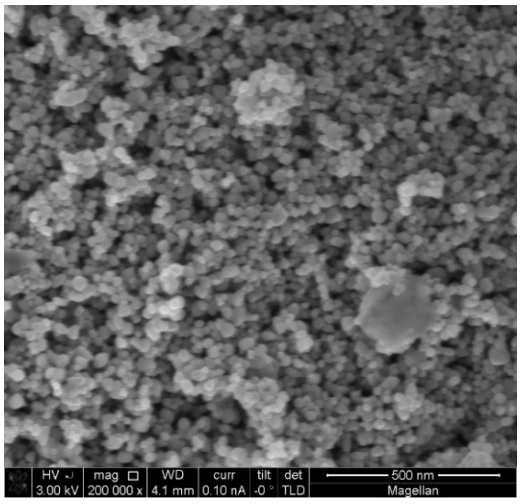

Figure 3b: SEM image of CoB_2O_4.

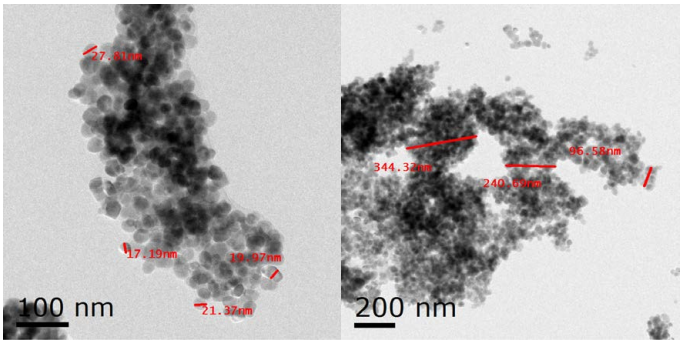

Figure 3c: TEM image of CoB_2O_4.

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, $CuCl_2$, reacted with sodium borohydride, $NaBH_4$, in solution (1:2 ratio) to produce a mixture of CuB_{24} 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.x

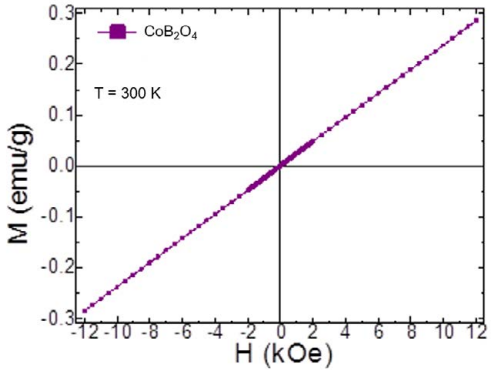

Figure 3d: Magnetic hysteresis of CoB_2O_4.

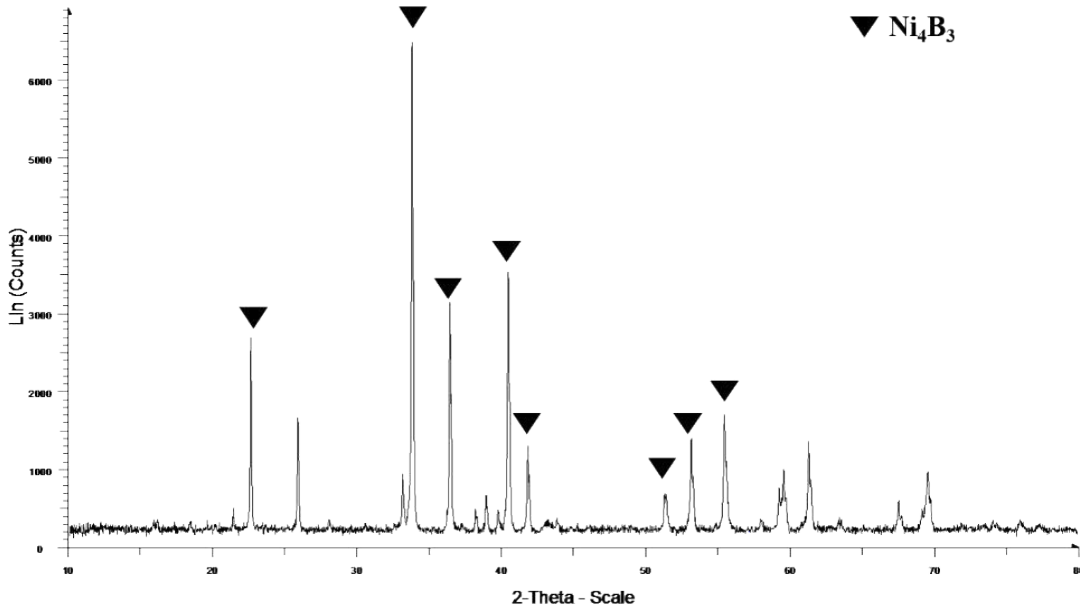

Figure 4a: XRD spectra of Ni_4B_3 produced by direct reaction of $NiCl_2$ with $NaBH_4$.

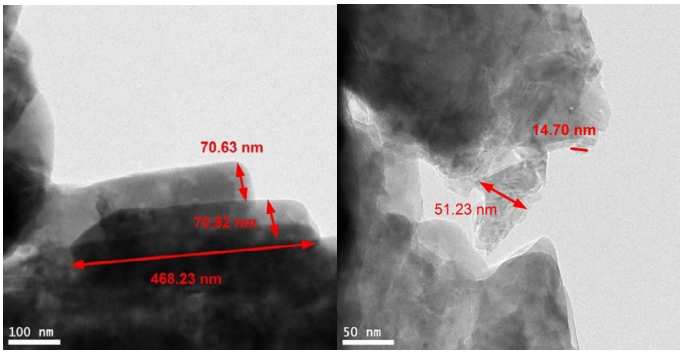

Figure 4b: TEM image of nanocrystals and nanorods of Ni_4B_3.

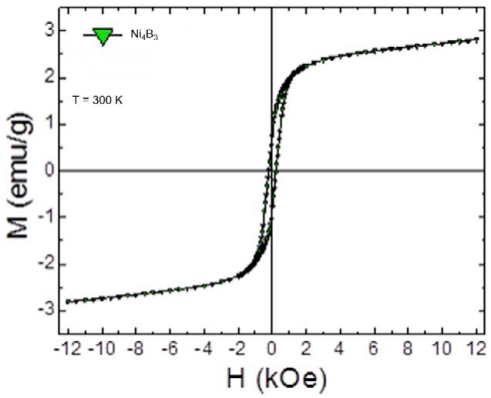

Figure 4c: Magnetic hysteresis superparamagnetism of Ni_4B_3.

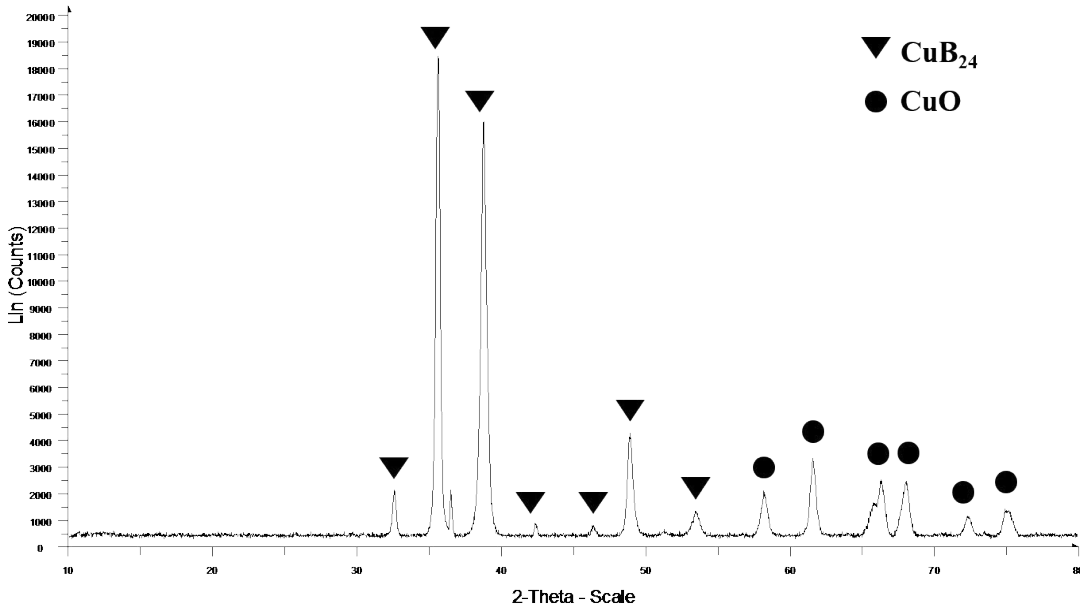

Figure 5a: XRD spectra of CuB_{24} and CuO by direct reaction of $CuCl_2$ with $NaBH_4$.

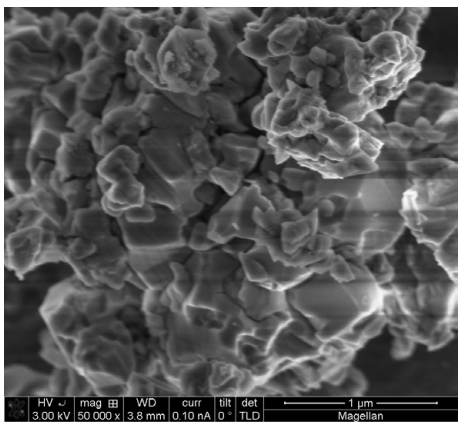

Figure 5b: SEM image of nanocrystals and nanorods of CuB_{24} and CuO.

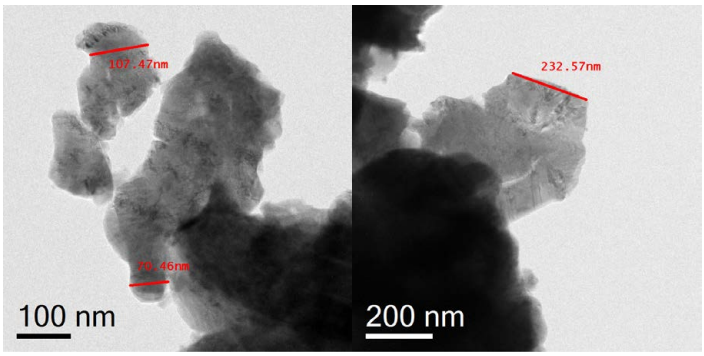

Figure 5c: TEM image of nanocrystals and nanorods of CuB_{24} and CuO.

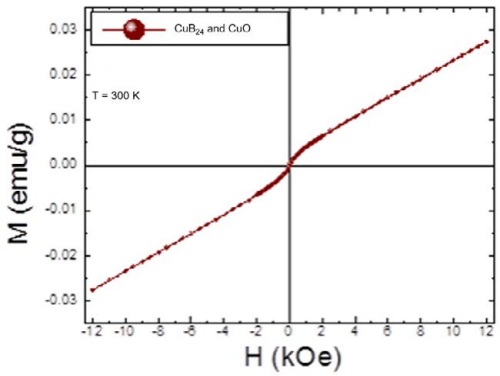

Figure 5d: Magnetic hysteresis of CuB_{24} and CuO.

Conclusion

Both solid and liquid phases produced metal borides with different levels between Cobalt, Nickel and Copper. Cobalt and Cupper successfully produced metal borides while Nickel produced only metal oxides. On the other hand Nickel and Copper produced nano-metal boride but Cobalt produced CoB_2O_4. 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].

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