SYNTHESIS OF COBALT-NICKEL-BORON BASED COMPOSITE POWDERS USING METAL CHLORIDE POWDER BLENDS

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Abstract

This study reports an alternative route for obtaining crystalline metal boride composite powders at low temperatures using various chemical reactions. The ternary system of Co-Ni-B was studied by using anhydrous metal chlorides and sodium borohydride powder mixtures. The reactions were carried out in a sealed reactor under autogenic pressure, placed in a chamber furnace. The unwanted chloride phases were removed by hot water leaching after reaction. Some of the purified powders were annealed at 1100 °C to improve the crystallinity. Effects of different reaction conditions on the formation and microstructure of the final powders were investigated. Phase, chemical and microstructural characterizations and particle size measurements of the synthesized and annealed powders were conducted using X-ray diffractometer (XRD), X-ray fluorescence spectrometer (XRF), scanning electron microscope (SEM/EDX) and dynamic light scattering technique. The results revealed the positive effect of inorganic molten salt mixture (LiCl/KCl eutectic mixture) on the formed phases during the reaction between $CoCl_2$, $NiCl_2$ and $NaBH_4$ powder blends. After their reaction at 750°C in a sealed reactor under autogenic pressure, crystalline cobalt-nickel-boron based composite powders were achieved with an average particle size of 60 nm.

Keywords: Cobalt, nickel, boride, low temperature synthesis, microstructural characterization

1. INTRODUCTION

Cobalt-nickel-boron based metal borides are technologically highly valuable boron-based materials with a high application potential in wide range of multi-functional areas due to their magnetic and catalytic properties. Cobalt boride (CoB, Co_2B) has been in the center of attention recently due to its high melting point, good chemical stability, hardness and corrosion resistance. Cobalt boride synthesized via different methods, has been investigated in literature and its electrochemical, anti-corrosion, biocompatibility, catalytic and magnetic properties have shown promising results [1,2]. In comparison to their binary phases, cobalt-based borides synthesized by adding of the elements such as Ni, Fe and Ti have presented better and improved properties [3-6]. Some of the most important and investigated areas for Co-Ni-B applications include its role as catalyzer in hydrogen storage and fuel cell technology, as an additive for grain reducing material, as improving agent for abrasion resisting coatings and as magnets [3,7]. The catalytic effect of Co-B compounds was discovered during investigations of effective catalyst for the hydrolysis reaction of $NaBH_4$ solutions. In these studies, it was observed that cobalt borides (CoB, $Co_{2.0\text{-}3.3}B$, Co_3B) and Co-B alloys in different stoichiometry significantly improved the hydrogenation rate of the $NaBH_4$ hydrolysis reaction [8, 9]. It has been reported that the catalytic effect of Co_3B is quite high compared to Ni_3B in the studies reported the hydrolysis kinetics of $NaBH_4$ [9]. In a later study, it has been observed that the metal deposition process on metal boride compounds or alloys has significantly increased its catalytic performance [10]. Furthermore, magnetic Co-Ni-B nanoparticles obtained via various methods, having large surface areas and low particle size, appear to be suitable candidates for use as electromagnetic wave absorbing material [3]. The new stable compounds obtained by the incorporation

of Co-Ni-B nanoparticles into MgB_2 had a significant effect on superconducting properties of MgB_2 [11]. Furthermore, studies on significant improvements in the mechanical properties (elastic modulus, fracture toughness, etc.) of some cobalt boron coated or doped alloys are available [7,12]. Various production techniques have been employed to synthesize crystalline cobalt boride-nickel boride based powders: This studies mostly included the high-temperature reactions between the elemental powders of Co, Ni and B. On the other hand, low-temperature routes have come into prominence due to the importance of preparing these powders at submicron or Nano-sized scales. Some studies reported the wet or solution techniques at low temperatures; however, the powders were obtained as amorphous phase [13,14]. Thus, this study will contribute to the literature by means of preparation of nanocrystalline cobalt-nickel-boron based composite powders with the utilized inorganic molten salt reaction technique at low temperatures.

2. EXPERIMENTAL PROCEDURE

The anhydrous $CoCl_2$ (Alfa Aesar, 99.7 % purity) and $NiCl_2$ (Alfa Aesar, 99 % purity) powders as the metal chlorides and sodium borohydride ($NaBH_4$, Alfa Aesar, 98 % purity) as the boron source were used in the experiments. The amounts were weighed in regard of the theoretical reaction between the precursors by using 50 wt.% excess amount of $NaBH_4$ resulting in $CoNiB_{x(s)}$, $NaCl_{(s)}$ and $H_{2(g)}$ reaction products. The reaction was carried out in an inorganic molten salt medium. To carry out the reaction in liquid phase, the LiCl/KCl eutectic mixture (45:55 wt.%) was used as an inexpensive, water-soluble and low-melting-point inorganic salt solvent. The powder mixtures were prepared under Ar atmosphere in a MBraun glove box. To obtain a homogenous mixture they were introduced to a short-time ball mill process, which was carried out for 3 min using a Retch PM100 planetary ball mill with a rate of 600 rpm and a ball to powder ratio of 1:4. For a comparison, a powder mixture without the eutectic phase was also prepared to observe the formed phases between the precursor materials. The mixtures were then introduced into a 316-L stainless steel tube and sealed via Ar welding. All the reactions were carried out in a sealed tube under autogenic pressure, placed in a Protherm chamber furnace. The powders were heated to 550 °C, which followed a hold period of 2 h and then heated up to 750 and 850 °C and kept at that temperature for duration of 2 h. The as-synthesized powders were leached with hot distilled water using an ultrasonic bath for 15 min, for the elimination of NaCl by-product. The leached solution was then introduced to a Sigma centrifuge device for precipitation of the powders at 3500 rpm for a duration of 15 min. The obtained solution was dumped, and precipitated powder was extracted and dried overnight under vacuum at 70 °C. Purified powders were annealed at 1100 °C for 2 h under Ar gas to observe the microstructural change. Phase analysis was conducted using a Rigaku Miniflex600 Series X-ray diffractometer (XRD) with CuK_α radiation with a scan rate of 10°/min and a step size 0.02°. The International Center for Diffraction Data (ICDD) powder diffraction files were used to determine the crystalline phases. Thermal behavior of the powder mixture was investigated using a NETSZCH DSC 204 differential scanning calorimeter (DSC) in alumina crucible up to 600 °C at a rate of 10 °C/min under Ar atmosphere. The microstructures were investigated using a Zeiss Ultra Plus Field Emission Scanning Electron Microscope (FE-SEM) coupled with an energy dispersive X-Ray spectrometer (EDX). Particle size of the final powder was determined using a Malvern Zetasizer dynamic light scattering (DLS). Chemical analyses of the powders were conducted using a Bruker S8 TIGER X-ray fluorescence spectrometer (XRF).

3. RESULTS AND DISCUSSION

DSC and XRD diagrams of the $CoCl_2$-$NiCl_2$-$NaBH_4$ powder mixtures (mentioned as powder mixtures hereafter) are illustrated in **Figures 1a** and **1b**, respectively. DSC scan of the powder mixtures (**Figure 1a**) was obtained after heating it up to 600 °C in presence of LiCl/KCl eutectic phase. The exothermic peak at 354 °C is corresponding to the melting temperature of the eutectic mixture (T_m = ~350 °C) and proves that the molten salt ratio is correct. Decomposition of the $NaBH_4$ was observed in the endothermic peak at an approximate temperature of 503 °C which is in agreement with the values in literature [15]. For complete decomposition of

$NaBH_4$ to happen, the reaction was put on hold at the temperature of 550°C for 2h. **Figure 1(b)** illustrates the XRD pattern of the products before leach obtained from the reaction at 750°C. As shown in the diagram, NaCl, KCl and LiCl phases were detected. Presence of NaCl in the products indicates that the reaction had occurred; however, intense chloride peaks, occurring as a result of their highly crystalline structure, has suppressed peaks belonging to other phases present in the obtained products.

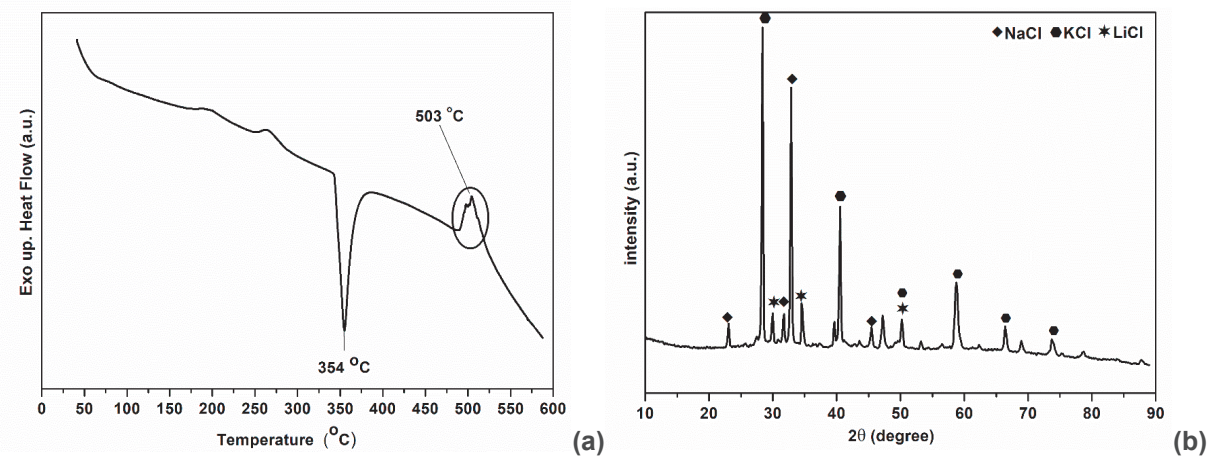

Figure 1 (a) DSC scan of the $CoCl_2$-$NiCl_2$-$NaBH_4$ powder mixtures in presence of LiCl/KCl eutectic phase after heating up to 600 °C and **(b)** XRD pattern of the powder mixtures after a reaction at 750 °C

XRD patterns of the powder mixtures in presence of LiCl/KCl eutectic phase after reactions at 750 and 850°C are illustrated in **Figures 2 (a)** and **(b)**, respectively. Co_2B, CoB, $Ni_4B_{2.81}$, Ni_2B, CoB_x and CoNi phases were detected in the powder mixtures after the reactions at 750 and 850 °C. It is anticipated that anhydrous metal chlorides of $CoCl_2$ and $NiCl_2$ react in the inorganic solvent having low melting point. Using this method, the reaction was triggered in the liquid phase. One of the advantages of this method is that the final product can be obtained in the form of Nano-crystals as a result of reaction occurring at low temperatures [16]. It was observed that the intensity of the XRD peaks increased with an increase in the reaction temperature from 750 to 850 °C. There are few studies in the literature reporting the synthesis of binary metal boron compounds such as HfB_2, NbB_2, and FeB as nanocrystalline particles by reacting anhydrous chloride and $NaBH_4$ powder mixtures in the appropriate inorganic solvent medium [16 - 18]. **Figure 3** shows the XRD pattern of the powder mixtures without a eutectic phase after a reaction at 850 °C. In the absence of the eutectic mixture, and as a result of corrosive nature of the chloride powders, stainless steel reaction tubes were severely corroded and Fe impurities were introduced to the reaction environment: Various intermetallic phases formed as a result of the reactions between Fe-Ni, Fe-Co, Fe-Ni-B etc. (**Figure 3**). Chemical analysis of the powder mixtures with and without eutectic mixture illustrates an increase in the number of elements present in the final powder as impurity. In case of having eutectic salt composition in the mixture, Ni, Co, Fe and Si was observed with the amounts of 44.11, 40.35, 2.45 and 0.61 wt.%, respectively. While not having the eutectic salt composition in the powder mixture yields Ni, Co, Fe, Na, Cr, Si, Al, Ca and Mn with 41.59, 37.41, 4.06, 3, 2.06, 0.43, 0.21, 0.15 and 0.11 wt.%, respectively. This obviously illustrates the higher number of impurity elements and higher percentage of Fe present as impurity.

In order to get rid of the unreacted and/or unstable phases, the powder mixtures were subjected to an annealing process after the reaction. **Figure 4** illustrates the XRD patterns of the powder mixtures in presence of LiCl/KCl eutectic phase after reaction at 750 °C and annealing at 1100 °C for 2 h. It was observed that the unstable $Ni_4B_{2.81}$ phase is completely eliminated, yielding composite powders including Co_2B, CoB and Ni_2B phases.

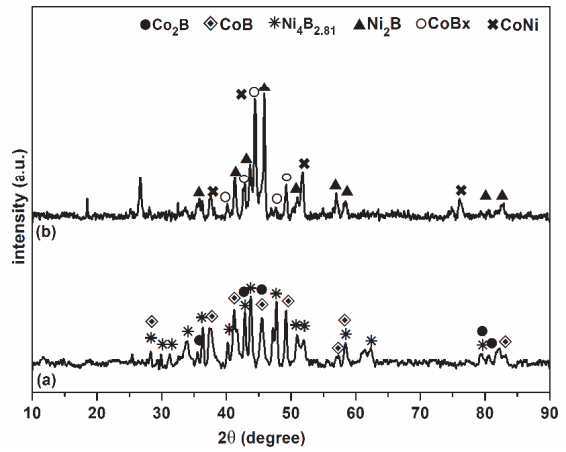

Figure 2 XRD patterns of the powder mixtures in presence of eutectic phase after a reaction at (a) 750 and (b) 850 °C and leaching

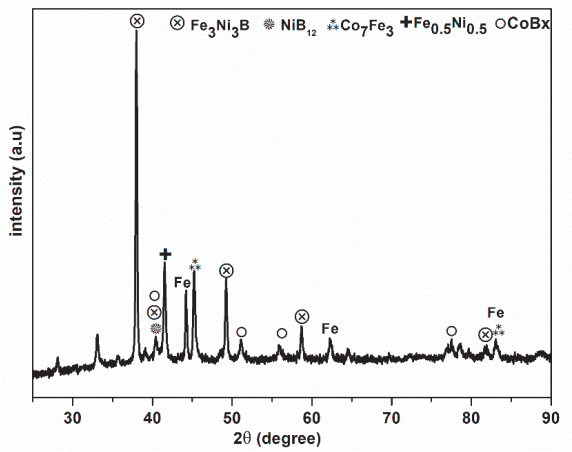

Figure 3 XRD pattern of the powder mixtures without a eutectic phase after a reaction at 850 °C and leaching

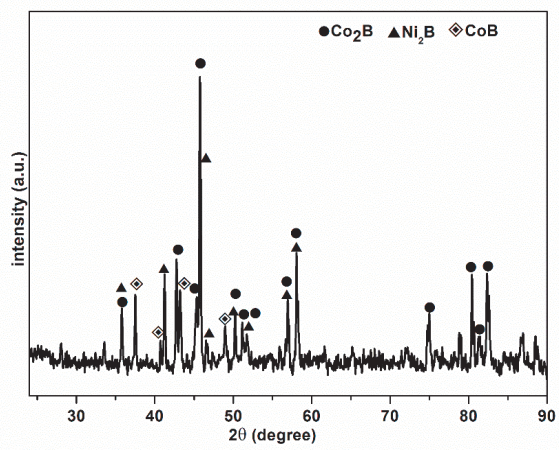

Figure 4 XRD pattern of the powder mixtures in presence of eutectic phase after a reaction at 750 °C, leaching and annealing at 1100 °C for 2 h

SEM images of the powder mixtures after the reaction are illustrated in **Figure 5a**. Agglomerated particles have an average size distribution of almost 6-8 μm with an interwoven structure. EDX analysis was performed on the samples proving presence of Co and Ni at the same position in the sample which is in agreement with XRD pattern from **Figure 2a**. Very small peaks observed at low KeV values belong to B phase that possesses a less intense peak because of its low atomic number. Presence of trace amounts of O is related to the surface oxidation of the samples which occurs as a result of their Nano-sized structure which exposes a huge amount of surface area to the atmosphere. **Figure 5b** presents the DLS measurement which inhibited the agglomeration of the powder particles and yielded an average particle size of 60 nm. Furthermore, **Figure 5c** shows the grain growth and agglomeration in the annealed sample. The SEM images of the powder mixtures reacted at 850°C are illustrated in **Figures 6a** and **b**. It was observed that the agglomerates still exist; however, when compared with **Figure 5c,** a change in the morphology was observed in that agglomerate particles with spherical structure were observed in **Figure 6b**. The 100 °C change in the reaction temperature had resulted in particles with more spherical structures after annealing at 1100 °C for 2h. Thus, by changing the reaction temperature, products with different morphologies can be synthesized [16] as observed in the SEM images of **Figures 5 and 6**. Previous studies had reported very amorphous and uncertain XRD results on the final powders obtained while in this study, with the help of the eutectic mixture melting at around 350 °C, it is claimed

that the reaction was carried out in a molten environment at low temperatures and the final powders obtained had nanocrystalline structure [13, 14].

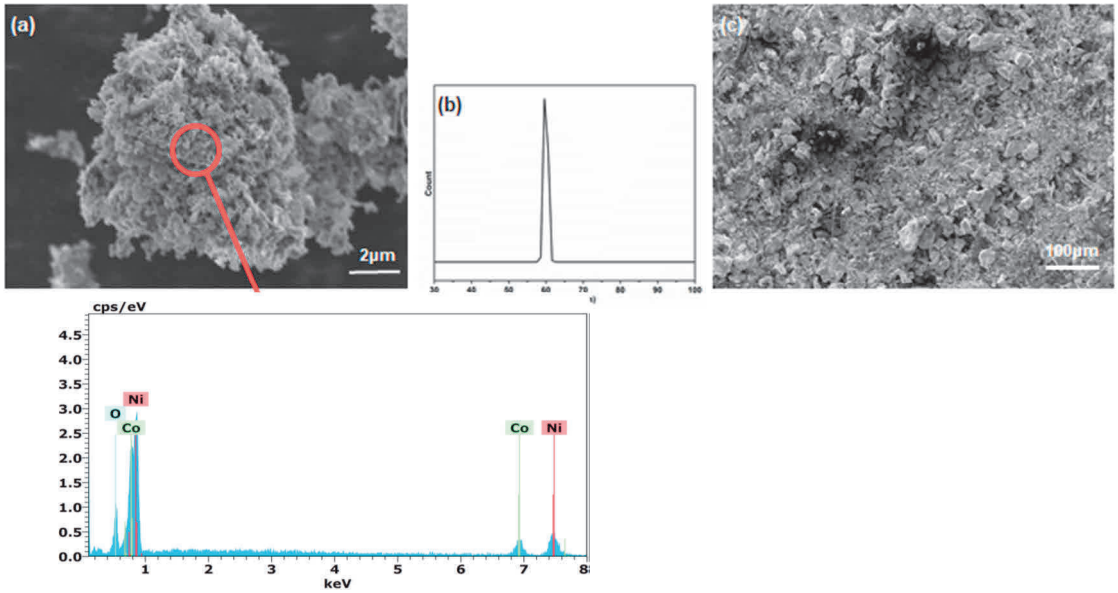

Figure 5 SEM and DLS analyses of the powder mixtures in presence of eutectic phase (a) SEM image and EDX analysis and (b) DLS analysis after a reaction at 750 °C, and (c) SEM image after annealing at 1100 °C

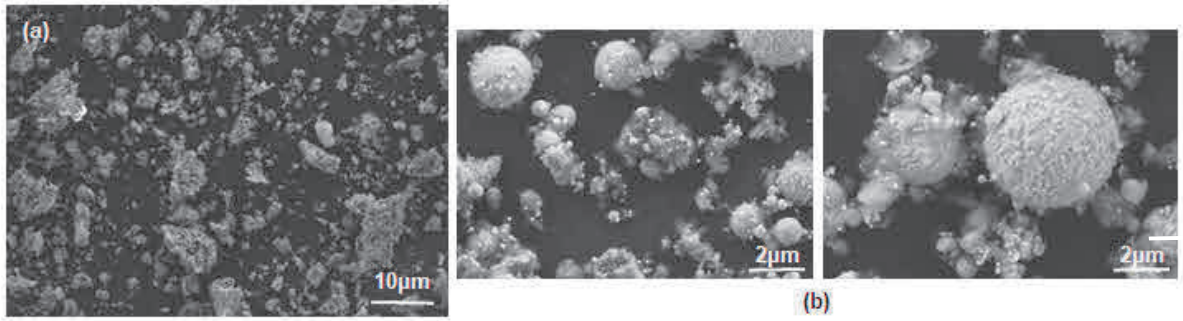

Figure 6 SEM images of the powder mixtures in presence of eutectic phase (a) after a reaction at 850 °C, and (b) after annealing at 1100 °C

4. CONCLUSION

In this study, using metal chloride powder blends, cobalt-nickel-boron composite powders were successfully synthesized via low temperature synthesis method. After reaction at 750 °C, the powder mixtures had Co_2B, CoB, Ni_2B, $Ni_4B_{2.81}$ phases present. Increasing the reaction temperature for 100 °C resulted in removal of the unstable phases and obtaining Ni_2B, CoB_x and CoNi phases. After annealing of the resulting powders of the reaction carried out at 750°C, Co_2B-CoB-Ni_2B composite powders were obtained with an average particle size of 60 nm. Presence of KCl/LiCl eutectic mixture resulted in the reaction taking place from liquid phase and at a low temperature and also prevented the impurities coming from the reaction tubes.

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