

# Effect of sintering techniques on the microstructure and mechanical properties of niobium borides

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## Abstract

This study reports on the consolidation of niobium boride powders by cold pressing/pressureless sintering (PS, with or without Co addition) and spark plasma sintering (SPS) techniques. Niobium boride powders (containing NbB, Nb<sub>3</sub>B<sub>4</sub> and NbB<sub>2</sub> phases) which were mechanochemically synthesized from Nb<sub>2</sub>O<sub>5</sub>, B<sub>2</sub>O<sub>3</sub> and Mg blends and purified by HCl leaching were used as precursor material. The effects of different sintering techniques on the consolidation behaviour, microstructure, densification rate and mechanical properties (microhardness, wear characteristics, elastic modulus, indentation response and fracture toughness) of the bulk products were investigated. PS with Co addition resulted in superior properties than those yielded after PS without Co addition and SPS. Bulk niobium boride products having relative density of 93-98 %, microhardness of 24-28 GPa, wear volume loss of  $2.8-4.5 \times 10^{-4}$  mm<sup>3</sup>, elastic modulus of 508-552 GPa and fracture toughness of 4.05-4.74 MPa.m<sup>1/2</sup> were obtained by Co (2 or 5 wt.%) activated PS at 1500°C.

**Keywords:** Niobium borides, Cold pressing/pressureless sintering, Spark plasma sintering, Microstructure, Mechanical properties.

## 1. Introduction

The borides of VB group transition metals (V, Nb and Ta) have a unique combination of high hardness, electrical and thermal conductivities, chemical stability as well as good thermal shock resistance and corrosion resistance [1]. This combination of excellent properties permits their

applications in surface and thermal protection systems, cutting tools, refractory crucibles, impact-resistant armours and plasma arc electrodes [1-3]. There are five niobium borides ( $\text{Nb}_3\text{B}_2$ ,  $\text{NbB}$ ,  $\text{Nb}_5\text{B}_6$ ,  $\text{Nb}_3\text{B}_4$ , and  $\text{NbB}_2$ ) that have been experimentally reported and structurally well-determined in the Nb–B system [1, 4-7].

Niobium borides have received a great deal of attention owing to their applications in mechanical industry, chemistry and microelectronics fields [8]. Especially the compound,  $\text{NbB}_2$ , is recognized as the potential candidate for high-temperature structural applications [9]. Niobium borides are known as refractory and coating materials which have excellent oxidation stabilities at high temperatures [10].  $\text{NbB}_2$  has been reported as an electrode for use in the refining of aluminium [11]. Non-stoichiometric compounds of  $\text{NbB}_2$  have been a matter in many reports as potential superconductors [12-16]. For example, Nb-deficient diborides in  $\text{NbB}_2$  showed superconductivity with a transition up to 11 K which makes it to be used as superconducting material [16].

Many production techniques have been applied in the preparation of niobium borides. Various stoichiometries of niobium borides have been fabricated conventionally by high-temperature methods such as borothermal/carbothermal reduction processes, direct solid-phase reactions or arc melting [17-26]. Another traditional technique for the synthesis of niobium diboride is chemical vapour deposition using gas mixtures [10]. In order to obtain single crystals of niobium diboride, floating zone method has been also applied using  $\text{NbB}_2$  starting materials [27-28]. The recent techniques developed for preparing niobium borides are self-propagating high-temperature synthesis (SHS) [29-34], low-temperature synthesis in an autoclave [9, 35], milling-assisted reduction methods and mechanochemical synthesis [8, 36-39].

The application of high temperature, the use of expensive starting materials (elemental Nb or B) and/or the use of complicated equipment may restrict the fabrication process to obtain niobium borides for the demanded applications. Conventional techniques triggered by high-temperature have some general disadvantages such as formation of by-products, reduction in purity and grain growth during processing. Thus, it is necessary to find an effective technique that can overcome these limitations and represent the advantages of time and energy savings and simplicity of the equipment. Furthermore, considering the control over the microstructure (shape, size, etc.), refinement of the resultant products is essential for many application areas.

Even though many studies are available for the fabrication of niobium boride powders, sintering processes of them have not been a well-discussed topic in the archival literature. Recent studies are mainly focused on the sintering of niobium borides using various techniques including high-

pressure sintering and spark plasma sintering (SPS) of elemental Nb and B powder mixtures [13,25,40] and pressureless sintering using  $\text{NbB}_2/\text{B}/\text{Nb}$  starting materials [15-16]. Sintering studies have been mostly carried out to investigate the superconducting behaviour of niobium borides, in which any microstructural or mechanical properties of bulk products have not been reported [13,15-16]. The high-pressure synthesis of superconducting  $\text{Nb}_{1-x}\text{B}_2$  ( $x=0-0.48$ ) phase was carried out from the powder mixtures of Nb and amorphous B by heating to temperatures between 900 and 1300°C in 10 min duration and sintering in a BN tube under a pressure range of 1-5 GPa for 0.5-2 h [13]. Polycrystalline bulk samples of  $\text{NbB}_{2+x}$  were obtained by sintering of  $\text{NbB}_2$  and B powders in a tubular furnace at 1100°C for 20 h in order to perform the magnetic susceptibility measurements [16]. Another example for sintering of commercial  $\text{NbB}_2$  (at 600 and 1400°C for 72 h) was conducted by using  $\text{NbB}_2$  and B or Nb to control Nb/B composition and to obtain superconductive niobium- or boron-deficient phases of niobium borides [15]. Only few studies reported the mechanical properties (e.g. microhardness, fracture toughness, elastic modulus) of the sintered niobium boride bodies [25,40]. Among them, bulk  $\text{NbB}_2$  with a relative density of 98 % was prepared by sintering at 1600°C under a pressure of 4 GPa [25]. Moreover,  $\text{NbB}_2$  compact with a density of 97.7 % was obtained by SPS of the  $\text{NbB}_2$  precursors at 1900°C for 15 min under a pressure of 70 MPa [40]. On the basis of reported studies, it should be noted that the utilized precursors are commercially available and expensive raw materials (Nb, B,  $\text{NbB}_2$ , etc.).

In addition to the sintering of niobium borides, some studies have been conducted on the consolidation of niobium boride-based composites such as  $\text{NbC-NbB}_2$  [41],  $(\text{Nb}_x\text{Zr}_{1-x})\text{B}_2\text{-SiC}$  [42] and  $\text{B}_4\text{C-NbB}_2$  [43].  $\text{NbC-NbB}_2$  composite compacts were fabricated by SPS of  $\text{NbC-NbB}_2$  precursor powders at 1600-1800°C for 10-30 min under a vacuum of 6-10 Pa [41].  $(\text{Nb}_x\text{Zr}_{1-x})\text{B}_2\text{-SiC}$  composites were obtained by pulsed electric current sintering (PECS) of  $\text{NbB}_2$  and SiC in vacuum of 4 Pa at 2000°C [42].  $\text{B}_4\text{C-NbB}_2$  composites were produced by SPS using  $\text{NbB}_2$  and  $\text{B}_4\text{C}$  powders at 1800-2200°C for 1 min with a pressure of 60 MPa [43]. It is significant to improve an effective fabrication technique of the sintered boride bodies and to investigate their consolidation behaviour and mechanical properties for determining their application areas.

In this study, niobium boride powders (containing NbB,  $\text{Nb}_3\text{B}_4$  and  $\text{NbB}_2$  phases) which were mechanochemically synthesized from  $\text{Nb}_2\text{O}_5$ ,  $\text{B}_2\text{O}_3$  and Mg blends were used as precursor material due to obtain sintered bodies. Niobium boride powders were consolidated by cold pressing/pressureless sintering (with or without metallic Co addition) and spark plasma sintering (SPS) techniques. The effects of sintering techniques on the consolidation behaviour,

microstructure, densification rate and mechanical properties of the bulk samples were firstly investigated via different routes conducted on the laboratory-synthesized pure niobium boride powders. The physical and microstructural characterizations of the sintered samples were determined by using an X-ray diffractometer (XRD) and scanning electron microscope (SEM) and by utilizing Archimedes density method. Mechanical properties of the bulk products were described in terms of microhardness, wear characteristics, elastic modulus, indentation response and fracture toughness.

## **2. Experimental Procedure**

### **2.1. Preparation of niobium boride powders**

Niobium boride powders used in this study were synthesized from their related oxides in the presence of a strong reducing agent by using a combined method of mechanochemical synthesis and selective acid leaching, in our laboratory facilities. Mechanochemical synthesis which is based on high-energy ball milling process enables to initiate, accelerate and complete the chemical (reduction and/or displacement) reactions between the active powder particles without any external applied heat [44]. The subsequent acid leaching treatment provides to remove undesired products from the mechanochemically synthesized powders and yields resultant products with high purity. Previously, different kinds of boride products were synthesized in our laboratory facilities with the same combined method [45-48].

The utilized raw materials were Nb<sub>2</sub>O<sub>5</sub> (Alfa Aesar<sup>TM</sup>, 99.5 % purity, 150 μm average particle size), B<sub>2</sub>O<sub>3</sub> (ETI Mine, 98 % purity, 467 μm average particle size) and Mg (MME, 99.7 % purity, 112 μm average particle size) powders. They were blended in stoichiometric amounts with a total batch amount of 6 g according to the theoretical reduction reaction [49]. Powder blends were milled for 5 h by using a Spex<sup>TM</sup> 8000 D Mixer/Mill with a rotational speed of 1200 rpm. Milling was performed with a ball-to-powder weight ratio (BPR) of 10:1 using hardened steel balls (6 mm diameter) in a hardened steel vial (50 ml capacity). Both sealing of milling vials and sample unloading were carried out in a glove box (Plaslabs<sup>TM</sup>) under Ar (Linde<sup>TM</sup>, 99.999 % purity) atmosphere in order to prevent interaction of particles with atmospheric conditions. Afterwards, selective HCl (Merck<sup>TM</sup>, in concentration of 37 %) leaching was applied on the mechanochemically synthesized products under the effect of ultrasonic stirring (Bandelin Sonorex<sup>TM</sup> RK-100 H) in order to eliminate undesired MgO phase and other impurities released from the milling media. The leaching parameters such as concentration and solid-to-liquid ratio of the solution and duration were fixed respectively at 4 M, 1 g/10 cm<sup>3</sup> and 15 min. The solutions containing insoluble solids were centrifuged

(Hettich<sup>TM</sup> Rotofix 32A, at 3500 rpm for 30 min), supernatant liquids were decanted and residual solids were washed with distilled water. After a series of centrifugation-decantation-washing treatments, residual solids were dried under air (FN 500 stove, at 120 °C for 24 h). The detailed information on the preparation of niobium boride powders by mechanochemical synthesis and HCl leaching was described and published elsewhere [49]. According to the reported characterization results [49], niobium boride powders containing NbB, Nb<sub>3</sub>B<sub>4</sub> and NbB<sub>2</sub> phases were obtained with high purity and with an average particle size of ~200 nm by the combined method of mechanochemistry (for 5 h) and leaching (with 4 M HCl). These pure powders are hereafter referred to as N5.

## **2.2. Consolidation and sintering of niobium boride powders**

After the preparation of pure niobium boride powders (N5), they were consolidated and sintered using two different techniques: a-cold pressing/pressureless sintering (PS) and b-spark plasma sintering techniques (SPS). In order to determine the effect of sintering aid on the bulk properties, N5 powders were pressureless sintered with or without use of metallic cobalt. Two different amounts of Co (Alfa Aesar<sup>TM</sup>, 99.5 % purity, 44 μm average particle size) sinter additives such as 2 and 5 wt. % were incorporated into the N5 powders by milling for 5 min in a Spex<sup>TM</sup> 8000 D Mixer/Mill. The milling parameters such as milling media, atmosphere and ball-to-powder weight ratio were used as the same with those employed during the preparation of the powders. As the first step of cold pressing/pressureless sintering process, N5 powders were compacted in a 10 ton capacity MSE<sup>TM</sup> MP-0710 uni-axial hydraulic press under a pressure of 800 MPa. Cylindrical-shaped green bodies with a diameter of ~6.3 mm were pressureless sintered at 1500°C for 4 h in a Linn<sup>TM</sup> HT-1800 high-temperature controlled-atmosphere furnace with a heating and cooling rate of 10°C/min under Ar gas (N5-PS). Pure niobium boride powders with the addition of metallic Co were also consolidated at the same conditions (N5-2CoPS and N5-5CoPS) with those of the N5-PS sample. Furthermore, SPS experiments were conducted on the N5 powders using a FCT Systeme<sup>TM</sup> HP D 25 SPS equipment. Powders were loaded in a graphite die with an inner diameter of 20 mm and sintered at 1500°C for 15 min with a heating and cooling rate of 100°C/min under an applied holding pressure of 60 MPa (N5-SPS). Table 1 summarizes the consolidation and sintering conditions of the niobium boride samples with abbreviated code names.

## **2.3. Characterization investigations**

Phase analyses of the N5 powders and sintered samples were carried out using a Bruker<sup>TM</sup> D8 Advanced Series powder diffractometer with CuK<sub>α</sub> radiation ( $\lambda=0.154$  nm, 40 kV and 40 mA)

in the  $2\theta$  range of  $20-90^\circ$  at a step size of  $0.02^\circ$  and at a rate of  $2^\circ/\text{min}$ . The International Center for Diffraction Data<sup>®</sup> (ICDD) powder diffraction files were utilized for identification of the crystalline phases. Microstructural characterizations of the sintered products were performed using a Hitachi<sup>™</sup> TM-1000 scanning electron microscope (SEM) operating at 15 kV. The densities of the sintered samples were measured in ethanol using the Archimedes method and the results were reported as the arithmetic mean of three different measurements taken from the same sample. In order to obtain scratch-free mirror finish for SEM analyses, Vickers microhardness measurements, indentation tests and reciprocating sliding wear tests, all sintered samples were subjected to a typical metallographic preparation procedure. Sintered samples were hot-mounted in a Struers<sup>™</sup> LaboPress-1, ground and polished in a Struers<sup>™</sup> Tegrapol-15 instrument.

Vickers microhardness measurements of the sintered samples were conducted using a Shimadzu<sup>™</sup> HMV Microhardness Tester under a load of 200 g for 15 s. Microhardness test result for each sample includes the arithmetic mean of twenty successive indentations and standard deviation. All sintered samples were subjected to reciprocating sliding wear tests at room temperature in a laboratory atmosphere by a Tribotech<sup>™</sup> Oscillating Tribotester using a 6 mm alumina ball under an applied force of 4 N, with a sliding speed of 6 mm/s and a stroke length of 2 mm for a total sliding distance of 200 m. Friction coefficients were recorded during wear tests. Wear tracks of all the sintered samples were imaged by using the same SEM utilized in microstructural characterization and examined by a Veeco<sup>™</sup> Dektak 6M Stylus profilometer. Wear test results in terms of wear volume loss values are the arithmetic mean of three different measurements for each sample. Relative wear resistance values were calculated as the ratio of highest wear volume loss to the wear volume loss of each sample. Depth-sensing indentation measurements of the samples were performed at a peak load of 250 mN, using a CSM<sup>™</sup> International MHT SN 06-0212 instrumented Vickers indenter. The applied load versus penetration depth curves were obtained at a loading and unloading rate of 500 mN/min with a holding time of 2 s at the peak load. In addition, elastic modulus of the samples was obtained according to the Oliver-Pharr method [50]. The fracture toughness of the samples was estimated from the cracks obtained by the Vickers indentation technique (Shimadzu<sup>™</sup> HMV microhardness tester) using 2 kg load for 15 s. The indentation mark was evaluated with the relation given in Eq.(1):

$$K_{IC} = 0.016 (E/H)^{1/2} (P/c^{3/2}) 10^{-6} \quad (1)$$

where  $K_{IC}$  is the fracture toughness ( $\text{MPa}\cdot\text{m}^{1/2}$ ),  $E$  is the modulus of elasticity (GPa);  $H$  is

Vickers hardness (GPa);  $P$  is the indentation load (N); and  $c$  is  $1/2$  of the crack length (m) [51]. Although Eq. (1) is an empirical approach for the fracture toughness measurement by indentation which takes into account of the Young's modulus, it should be noted that it is still a rough estimation. Vickers hardness values determined in this study were used in the calculation of fracture toughness. Fracture surface analysis (e.g. indentation cracks) was monitored using a Leica<sup>TM</sup> ICC50HD optical microscope (OM).

### **3. Results and discussion**

#### **3.1. Microstructural analyses of the sintered products**

The sintered samples of niobium borides consolidated with or without Co sinter additive by PS or consolidated by SPS do not have any shape deformation in their upper and lateral surfaces but they display dimensional changes compared to their green bodies. The maximum dimensional change is about 1.5 % in the sintered samples consolidated by PS and SPS without the Co additive. However, this change reaches to a maximum of about 9.5 % in the samples sintered in the presence of the Co aid. On the basis of observed considerable decrease in the dimensions of the samples after sintering with Co additive, it is possible to predict more shrinkage and hence higher densification than those without the Co additive.

Figures 1(a)-(d) show the back-scattered electron (BSE) SEM images taken from the sintered niobium borides consolidated by PS (with or without Co addition) and SPS techniques. At first sight, it can be obviously seen from the BSE SEM images that the sinterability of the niobium boride samples was improved by changing the sintering conditions and methods from pressureless sintering to activated pressureless sintering and spark plasma sintering. BSE SEM image in Figure 1(a) does not show a flat surface of a successful sintering process and reveals lots of pores throughout the microstructure. Thus, pressureless sintering at 1500°C for 4 h without Co addition is inadequate to obtain dense body from the high-purity niobium boride powders. On the other hand, the sintering of the powders at the same conditions with the presence of different amounts of Co additive (N5-2CoPS, N5-5CoPS) provides the fine microstructures without any observable pore and segregation in the BSE SEM images (Figures 1(b) and (c)). On the basis of the working principle of the BSE imaging, the dark particles are assumed to comprise a secondary phase between the particles. As seen from Figure 1(b), secondary phase particles ranging in sizes between 500 nm and 4  $\mu$ m are uniformly distributed throughout the microstructure. It is obvious from Figures 1(b) and (c) that the increase in the Co content from 2 to 5 wt. % resulted in the cluster formations or regional agglomerations of this secondary phase particles and probably in the formation of Co-rich and/or Nb-rich regions

throughout the microstructure. It can be said that densification of niobium boride samples could be feasible at the same temperature with the pressureless sintering, by using of metallic sintering aid and by increasing of its amount. Moreover, the size and distribution of the pores in the pressureless sintered sample without aid (N5-PS) decreased substantially in the SPS sample (N5-SPS), which indicates the significant contribution of SPS on the densification process (Figure 1(d)). Also, there are colour contrasts on the microstructure of the N5-SPS sample which are possible to determine with further phase analysis.

### 3.2. Phase analyses of the sintered products

In order to determine the probable contaminations, secondary phase formations and/or phase transformations occurred during sintering, bulk products were subjected to the XRD analyses. Figure 2(a) and (b) show the XRD patterns of the pure niobium boride powders (N5) and their pressureless sintered product (N5-PS). Figure 2(a) reveals the structure of the precursor powders consisting of NbB (ICDD Card No: 32-0709, Bravais lattice: base-centered orthorhombic,  $a=0.330$  nm,  $b=0.872$  nm,  $c=0.317$  nm), Nb<sub>3</sub>B<sub>4</sub> (ICDD Card No: 03-065-2553, Bravais lattice: body-centered orthorhombic,  $a=0.330$  nm,  $b=1.408$  nm,  $c=0.314$  nm) and NbB<sub>2</sub> (ICDD Card No: 35-0742, Bravais lattice: primitive hexagonal,  $a=b=0.311$  nm,  $c=0.327$  nm) phases. According to the semi-quantitative Rietveld refinement method based on the XRD patterns of the synthesized N5 powders, the amounts of NbB, Nb<sub>3</sub>B<sub>4</sub> and NbB<sub>2</sub> phases in the overall powder are 43.2, 34.7 and 22.1 vol. %, respectively [49]. Figure 2(b) clearly shows that after pressureless sintering at 1500°C for 4 h of the mechanochemically synthesized and leached niobium boride powders, NbB, Nb<sub>3</sub>B<sub>4</sub> and NbB<sub>2</sub> phases completely transform to the NbB phase which was already dominant in the structure before sintering. Based on the XRD analyses, it can be said that there is no contamination or other undesired phases in the structure of the N5-PS sample (Figure 2(b)).

On the other hand, SPS of the N5 powders resulted in a variation on the phase distribution of the bulk samples. Figure 3 shows the XRD pattern of the spark plasma sintered niobium boride sample (N5-SPS). Unlike the pressureless sintered sample (N5-PS) containing single phase NbB (Figure 2(b)), spark plasma sintered products comprise of dominant NbB phase, with the presence of small amounts of Nb<sub>3</sub>B<sub>4</sub> and Nb<sub>5</sub>B<sub>6</sub> phases. Already, the formation of NbB, Nb<sub>3</sub>B<sub>4</sub> and NbB<sub>2</sub> phases were experienced after powder processing. However, the emergence of Nb<sub>5</sub>B<sub>6</sub> phase is very surprising after SPS since it is an unstable phase with an undefined melting temperature between the stability region of NbB and Nb<sub>3</sub>B<sub>4</sub> phases, in the Nb-B binary phase diagram [4-5,7]. The non-achievement of the single phase NbB can be attributed to the short holding time (15 min) during SPS which is not sufficient to complete the whole phase

transformation. Nevertheless, there is a significant increase in the XRD peaks of NbB phase after SPS (Figure 3), compared with those of the N5 precursor powders given in Figure 2(a). This shows the effectiveness of SPS technique which exhibit a local increase in the temperature at the particle contacts due to the applied high electric current through powders. This local temperature rise which significantly enhances the diffusivity of the powders accelerates the phase transformation in a very short time [40]. Additionally, the presence of different stoichiometries of the niobium boride phases (NbB, Nb<sub>3</sub>B<sub>4</sub> and Nb<sub>5</sub>B<sub>6</sub>) confirms the colour contrasts in the BSE SEM image of the N5-SPS sample (Figure 1(d)).

Figure 4(a) and (b) show the XRD patterns of the pressureless sintered niobium boride samples with the addition of Co (N5-2CoPS, N5-5CoPS). As seen from Figure 4(a) and (b), Nb<sub>3</sub>B<sub>4</sub> as a dominant phase and a small amount of NbCo<sub>2</sub> (ICDD Card No: 15-0499, Bravais lattice: face-centered cubic, a=b=c=0.677 nm) intermetallic phase were obtained after cold pressing/pressureless sintering of the mechanochemically synthesized and leached powders (containing NbB, Nb<sub>3</sub>B<sub>4</sub> and NbB<sub>2</sub> phases) in the presence of 2 and 5 wt. % Co addition. This indicates that a reaction occurred between the dominant phase NbB and Co to form Nb<sub>3</sub>B<sub>4</sub> and NbCo<sub>2</sub> according to the reaction given in Eq. (2) during pressureless sintering.



Formation of NbCo<sub>2</sub> arises from the diffusion of Co melt through niobium boride phases and dissolution of boride phases in the liquid Co, at the sintering temperature of 1500°C which is higher than the melting point of Co (T<sub>m</sub>=1495°C). Taking into account of the phase transformation of NbB, Nb<sub>3</sub>B<sub>4</sub> and NbB<sub>2</sub> containing powders to the single phase NbB at 1500°C for 4 h (Figure 2), it can be claimed that the formation of the reaction given in Eq. (2) and the transformation of NbB<sub>2</sub> and Nb<sub>3</sub>B<sub>4</sub> phases to NbB phase occur simultaneously during the holding time of sintering. It has been reported in many studies that during pressureless sintering with metallic additives, transition metals (Co, Ni, etc.) react with metal borides (TiB<sub>2</sub>, ZrB<sub>2</sub>, etc) to form secondary metallic borides such as Co<sub>2</sub>B, CoB, Ni<sub>2</sub>B, Ni<sub>3</sub>B, etc. [52-54]. Besides, the formation of these extremely brittle secondary borides has negative effects on the fracture toughness and hardness of the sintered boride samples, especially metallic sintering aid was used over a certain limit (> 10 wt.%) in the total powder blend [53]. On the other hand, there is only one study which reported the formation of Ni<sub>3</sub>Zr intermetallic phase during pressureless sintering of ZrB<sub>2</sub> at 1500°C with 10-50 wt. % Ni additive [55]. The hardness and density values of the sintered boride increase with increasing Ni content up to 40 wt. % of the total powder [55]. It is notable to indicate that the precursor powders consist of a mixture of stoichiometric and non-stoichiometric zirconium boride phases (ZrB<sub>2</sub>, ZrB and ZrB<sub>15</sub>) [55]. As mentioned

before, the interaction of single phase metal boride and metallic additive during sintering usually results in the formation of secondary borides. Thus, the reason of the formation of intermetallic phase instead of a secondary boride phase can be attributed to the non-stoichiometric composition of the precursor powders (Figure 2(a)). Furthermore, increasing Co content from 2 to 5 wt. % in the composition causes an increase in the fraction of NbCo<sub>2</sub> phase (Figure 4). This means that the diffusion of higher amount of Co into the niobium borides increases the interaction surfaces of the particles, and hence their tendency to yield NbCo<sub>2</sub> phase. The presence of a secondary intermetallic phase (NbCo<sub>2</sub>) and its increasing amount in the N5-2CoPS and N5-5CoPS samples also confirm their BSE SEM images in Figures 1(b) and (c). Consequently, the unexpected formation of intermetallic phase is considered as an original result in the activated sintering of the metal boride systems.

### **3.3. Density measurements of the sintered products**

Theoretical density values of all sintered samples were recalculated by taking into account of their different phase contents and theoretical, Archimedes and relative densities are given in Table 2. Pressureless sintered sample (N5-PS) without any additive exhibits the lowest relative density of around 81 %. The low relative density of the N5-PS sample is due to the insufficient sintering conditions such as absence of pressure and metallic additive in addition to the low temperature. It has been reported that in solid-state sintering of the nanoceramics, grain growth/coarsening may dominate the densification process and results in poor density [56]. Moreover, high density values for the sintered pure metal borides are almost impossible to be achieved due to their high melting point and low bulk diffusivity using pressureless sintering [54,57]. It is well known that densification can be enhanced with small additions of metallic additives to form the liquid phase [52]. Thus, the highest relative density was obtained as 97.61 % in the sintered N5-5CoPS sample. The high relative densities (93.74 and 97.61 %) of the N5-2CoPS and N5-5CoPS samples are due to the effect of liquid-phase sintering by means of Co addition. The relative density of the sintered sample with 5 wt. % Co addition increases by about 4 % from the sample containing 2 wt. % Co, indicating that a liquid phase and increase in its amount can improve the densification by higher wetting rate of the boride particles. On the other hand, the relative density increases as SPS is used instead of pressureless sintering without aid: The relative density of N5-PS sample increases from 81.11 to 83.75 %. This high densification in a very short time (15 min) during SPS can be explained by the applied mechanical pressure (60 MPa) which keeps the powder particles in larger contact during sintering and by means of the high-intensity pulsed direct current passing through the powder compacts [40]. It has been reported that SPS of NbB<sub>2</sub> powders at temperatures of 1700 and

1900°C for 15 min respectively resulted in relative densities of 84.9 and 97.1 % [40]. This indicates that SPS of niobium boride powders needs elevated temperatures than 1500°C to obtain nearly full densification. Nevertheless, Co addition during pressureless sintering contributes to the density values of the samples more than SPS at the same temperature (1500°C). All the relative density values conform well to the microstructures presented in the BSE SEM images of the samples (Figure 1). It can be also interpreted that both the use of sintering temperature higher than 1500°C and the use of Co sintering aid during PS and SPS processes will yield the highest relative density values for the samples.

### **3.4. Mechanical properties of the sintered products**

Microhardness values ( $HV_{0.2}$ ) of the sintered niobium borides are presented in Table 3. As expected from its lowest density value, pressureless sintered niobium boride sample (N5-PS) exhibits the lowest microhardness value of  $1.92 \pm 0.31$  GPa among the sintered samples. As seen from Table 3, microhardness of N5-PS sample incredibly increases with Co addition during pressureless sintering and reaches to  $24.82 \pm 2.06$  and  $27.17 \pm 1.85$  GPa for the N5-2CoPS and N5-5CoPS samples, respectively. This phenomenon can be attributed to finer microstructures and higher densities of the N5-2CoPS and N5-5CoPS samples which consist of  $Nb_3B_4$  as the major phase and  $NbCo_2$  as an intermetallic phase. It has been previously reported that intermetallic phases distributed in a major boride phase contribute positively on the hardness values of the sintered products [55]. Furthermore, spark plasma sintered niobium boride sample (N5-SPS) demonstrates much higher microhardness value as  $13.68 \pm 0.73$  GPa when compared to that of pressureless sintered sample without Co addition. Among all samples, the N5-5CoPS sample has the highest microhardness value of  $27.17 \pm 1.85$  GPa, along with the highest relative density value of 97.61 %. Thus, the microhardness values of the samples are in the same trend with their density values: They increase when sintering technique was changed from PS to SPS and they exhibit the highest values when Co was added in the case of using PS. In the literature, there are some studies which reported the microhardness values of the bulk  $NbB_2$  structures prepared via different synthesis methods or with different sintering conditions: Bulk  $NbB_2$  prepared by sintering of Nb and B powders at 1600°C for 15 min under 4 GPa resulted in a microhardness value of 25.5 GPa [25].  $NbB_2$  crystals produced by the floating zone method exhibited the Vickers hardness values in a range of  $HV_{0.2}=19.1-21.7$  GPa [28]. The Vickers hardness of high-density (with a relative density of 97.7 %)  $NbB_2$  compacts, which prepared by SPS technique (at 1900°C for 15 min under 70 MPa) from Nb and B powders, was reported as  $HV_{0.1}=20.2$  GPa [40]. Additionally, there are some investigations reporting the hardness values of the  $NbB_2$ -based composites:  $NbC/NbB_2$  compacts obtained from the MA-

SHS and SPS at 1800°C for 10 min exhibited a microhardness value of 19.8 GPa with a relative density of 94 % [41]. NbB<sub>2</sub> grains in the B<sub>4</sub>C-NbB<sub>2</sub> composites produced by SPS at 1800 and 2200°C exhibited the microhardness values of HV<sub>0.1</sub>~27 GPa and HV<sub>1.0</sub>~22 GPa, respectively [43]. Thus, SPS processes for the preparation of NbB<sub>2</sub> or NbB<sub>2</sub>-based bulks in the literature were applied in the temperature range of 1800-2200°C and the maximum microhardness was obtained as about 27 GPa. It can be stated that bulk niobium borides may have many different hardness values, depending on the method of synthesis, consolidation technique, the process parameters, and the relative density achieved. Comparing the reported hardness values of niobium borides with those of the present study, it can be stated that the achieved microhardness values are considerably high for the utilized consolidation processes and parameters (pressureless sintering with Co or SPS at 1500°C).

Wear volume loss, relative wear resistance and mean friction coefficient values of the sintered niobium boride samples are presented in Table 4. As seen from Table 4, N5-PS sample has the highest wear volume loss of 125×10<sup>-4</sup> mm<sup>3</sup> and a relative wear resistance of 1 as the reference. Relative wear resistances of the samples were calculated by dividing the wear volume loss of the N5-PS sample to those of the other samples. When Co is used as an aid of pressureless sintering (N5-2CoPS, N5-5CoPS), the relative wear resistances significantly increase to 44.6 and 27.8, along with the increase in the microhardness from 1.92 GPa to 24.82 and 27.17 GPa, respectively. The utilization of SPS also increases the relative wear resistance of the niobium boride sample from 1 to 10.9. On the basis of these results, it is clear that wear resistances of the sintered samples are in the same increasing trend with their microhardness values, excepting the N5-5CoPS sample. The relation between wear volume loss and microhardness has been investigated by several researchers [58,59]. The highest wear resistance was obtained for the N5-2CoPS sample among the samples and this is most likely due to the NbCo<sub>2</sub> particles which restrict the flow of the material during sliding under an applied load. However, higher amount of NbCo<sub>2</sub> particles in the N5-5CoPS sample than the N5-2CoPS sample causes a decrease in the wear resistance probably due to the contribution of third body wear of the released particles on the sliding surface. The decrease in the wear resistance of N5-5CoPS sample also indicates that wear volume loss is strongly dependent to the amount of intermetallic phase and this dependency limits the amount of addition of Co sintering aid, unlikely to the density and microhardness values. On the other hand, mean friction coefficient of the N5-PS sample sliding against alumina counterface is about 0.30 and the Co addition, which were independent of wt.% content, let to an increase in the mean friction coefficient of the samples (0.48 for both of the N5-2CoPS and N5-5CoPS samples). The highest mean friction coefficient value among the

samples was obtained as 0.532 for the N5-SPS sample. The results showed that pressureless sintering process without aid obviously reduced the mean friction coefficient during sliding action. Unfortunately, there is no study about the wear behaviours of the sintered niobium borides in the archival literature. Although many studies have been carried out on the wear properties of the boride-dispersed metal matrix composites, there are only few studies on the wear properties of the sintered metal borides [48,60,61]. The wear volume loss of the N5-PS sample ( $0.0125 \text{ mm}^3$ ) exhibits almost similar value to those of the pressureless sintered samples originated from the mechanochemically synthesized and leached  $\text{SmB}_6$  powders ( $0.0193 \text{ mm}^3$ ) [48]. The values in Table 4 are also comparable to the wear volumes of the hot-pressed  $\text{ZrB}_2$ - $\text{TiB}_2$  ceramics which changed with varying amount of  $\text{TiB}_2$  and were reported between  $0.312 \times 10^{-4}$  and  $10.8 \times 10^{-4} \text{ mm}^3$  [61].

Figures 5(a)-(d) show the SEM images of the wear tracks taken at the same magnifications (80X) from the sintered niobium borides. As seen from Figure 5(a), N5-PS sample has a very wide wear track, indicating the higher wear volume loss value than those of other sintered samples (Figures 5(b)-(d)). The high porosity in the microstructure of the N5-PS sample probably lead to severe material loss during sliding due to the sliding motion of alumina ball under the applied load of 4 N. N5-PS sample exhibits some micro-grooves along the sliding direction whereas those of the N5-2CoPS, N5-5CoPS and N5-SPS samples reveal almost smooth wear tracks. As seen from Figure 5(b),  $\text{NbCo}_2$  particles are preferentially aligned along the sliding direction which considerably reduces the ploughing tendency of the counterface. The mean friction coefficients (Table 4) and wear track appearances (Figures 5(b) and (c)) of the N5-2CoPS and N5-5CoPS samples suggest that these samples have similar friction characteristics. Furthermore, the smooth appearance of the worn surfaces of the N5-SPS sample can also be explained by the resistance against material removal in the sliding surface due to its higher density and higher hardness values than those of N5-PS sample.

In order to make a representative evaluation between the highest and lowest wear volume loss among the samples (Table 4), the wear track profiles of the N5-PS and N5-2CoPS samples were compared to each other. Figure 6(a) and (b) show the wear track profiles of the N5-PS and N5-2CoPS samples and the contact surface OM images of the alumina balls slid on their surfaces, respectively. The comparative wear profiles of N5-PS and N5-2CoPS samples clearly reveal the influence of phase and microstructural characteristics on their wear volume loss values. N5-PS sample shows a very high wear track depth which results in high material loss and low wear resistance, whereas a very low wear depth is observed in the N5-2CoPS sample. As seen from OM images in Figure 6(b), the worn surfaces of the alumina balls slid on the surfaces of the

samples contained parallel scratches, which are the main characteristics of micro-abrasion. The contacting surfaces of the balls seem to be flattened along the sliding direction, indicating their wear and adherence to the sample surfaces. Thus, it is also suggested that the worn surface of the N5-PS sample has a higher amount of aluminium and oxygen contaminations than those of N5-2CoPS sample due to the increase of the contact surface of the ball during sliding on the surface of N5-PS sample. The worn surfaces of the alumina balls are seen as compatible with the SEM images of the wear tracks in Figures 5(a) and (b).

Figure 7(a) through (d) illustrates the load versus penetration depth curves of the sintered niobium borides obtained from the depth-sensing indentation measurements which were conducted under a maximum load of 250 mN with a constant loading and unloading rate of 500 mN/min. The curve of N5-PS sample (Figure 7(a)) shifts to lower indentation depths with the addition of Co prior to the pressureless sintering (Figure 7(b) and (c)) and with the utilization of SPS (Figure 7(d)), indicating an increase in the indentation hardness. The area covered by a load-penetration depth curve reveals the amount of the plastic deformation dissipated during indentation, which can be termed as residual plastic work [61,62]. It can be clearly observed in Figure 7 that the N5-PS sample has the highest plastic deformation among the samples and the residual plastic work significantly decreases to lower values for the N5-SPS, N5-2CoPS and N5-5CoPS samples. Additionally, the N5-2CoPS and N5-5CoPS samples show very similar features of load-penetration depth curves (Figure 7(b) and (c)), corresponding that the addition of high amount of Co (5 wt.% instead of 2 wt.%) during sintering has almost no effect on the residual plastic work and the penetration depth of the Vickers indenter. Load versus penetration depth curves of the samples in this study can be comparable with those of pressureless sintered  $TiB_{2-x}$  wt.% Co ( $x=5, 10$  and  $20$ ) samples in the literature [54]: as the Co content increases from 5 to 20 wt.%, the curves of the samples shifts to higher indentation depths, with a decrease in the indentation hardness values. It also indicates that a limited amount of metallic Co as sintering aid could be added into the borides for improving their mechanical properties [54].

Elastic modulus and fracture toughness values roughly estimated by Vickers depth-sensing indentation of the sintered niobium borides are presented in Table 5 in order to compare their responses to a specified indentation load. Increasing indentation derived recovered elastic work (Figure 7) with the utilization of SPS and the addition of Co prior to pressureless sintering is also reflected by the increase in the elastic modulus values as given in Table 5. There is a good correlation between the elastic modulus (Table 5) and the microhardness values of the samples (Table 3). However, the elastic modulus of the N5-5CoPS sample is slightly low considering its higher microhardness value than that of N5-2CoPS sample. The relatively higher amount of

NbCo<sub>2</sub> particles dispersed in the N5-5CoPS sample than the N5-2CoPS sample may cause a slight decrease in its elastic modulus (from 552.2 GPa to 508.8 GPa). It has been also reported that the increase in weight percentages of Co, MoSi<sub>2</sub> and TiSi<sub>2</sub> additives in some boride ceramics decreases the elastic modulus [54,57]. Furthermore, NbB<sub>2</sub>-20 vol.% SiC composites prepared by pulsed electric current sintering were reported to have the elastic modulus value of 501 ± 2 GPa [42]. The elastic modulus values for the N5-2CoPS and N5-5CoPS samples are higher than that of NbB<sub>2</sub>-20 vol.% SiC composite. It could be said that the use of metallic Co has more positive effect on the mechanical properties of the NbB<sub>2</sub>-based composites, rather than the use of SiC ceramic material in the sintering process. Moreover, Vickers indents obtained with a load of 0.2 kg did not result in the formation of cracks. However, increasing the indentation load to 2 kg resulted in the extensive crack growth and hence these cracks enabled the evaluation of K<sub>IC</sub>. Indentation cracks of the N5-2CoPS, N5-5CoPS and N5-SPS samples at the load of 2 kg were presented in the OM images given in Figure 8. Fracture toughness tests (using 2 kg indentation load) could not be conducted on the N5-PS sample because the cracks were not obviously observed. As seen from Figures 8(a)-(c), N5-5CoPS sample has lower crack propagation than those of N5-2CoPS and N5-SPS samples. The presence of higher amount of NbCo<sub>2</sub> particles in the N5-5CoPS sample than that of N5-2CoPS can restrict the propagation of the diagonal cracks. Thus, as expected, the highest fracture toughness value of 4.74 ± 0.23 MPa.m<sup>1/2</sup> among the samples was estimated for the N5-5CoPS sample (Table 5). In the literature, there are some reported fracture toughness values for the boride-based composites: spark plasma sintered NbB<sub>2</sub>-B<sub>4</sub>C composites containing 60 mol.% NbB<sub>2</sub> have the fracture toughness of 7.2 ± 1.2 MPa.m<sup>1/2</sup> calculated by Anstis method [43]. Hot-pressed B<sub>4</sub>C-VB<sub>2</sub> composites with a variable amount of VB<sub>2</sub> was found to have the highest fracture toughness value of 8 MPa.m<sup>1/2</sup> [63]. Also, the fracture toughness value of hot-pressed TiB<sub>2</sub>-2.5 wt.% MoSi<sub>2</sub> composites was reported as about 6 MPa.m<sup>1/2</sup> [61]. Dissimilar to the composite structures, the fracture toughness data of the Co<sub>2</sub>B coatings obtained using the Vickers depth-sensing microindentation technique was in the range of 4.6-5.4 MPa.m<sup>1/2</sup> [64]. Considering the reported fracture toughness values for different types of boride-related materials, the measured values for the N5-2CoPS and N5-5CoPS samples in this investigation can be evaluated as high enough to be obtained via powder metallurgy and cold pressing/pressureless sintering with the use of Co additive.

Consequently, addition of Co sintering aid prior to pressureless sintering process enabled to produce sintered niobium borides with superior properties rather than PS and SPS techniques, taking into account of the density, microhardness, relative wear resistance, elastic modulus and

fracture toughness results. The addition of higher amount of Co also results in a minor decrease in the relative wear resistance and elastic modulus values of the samples. However, the need of application area can designate the accurate usage of the Co addition in the samples, for latter investigations.

#### 4. Conclusions

High-purity niobium boride powders which were prepared by mechanochemical synthesis and leaching process were consolidated by using cold pressing/pressureless sintering (with or without Co addition) and spark plasma sintering (SPS) techniques. The results were discussed regarding the effect of different sintering techniques on the consolidation behaviour, microstructure and mechanical properties of the bulk samples. Based on the results of the present study, the following conclusions can be drawn:

- The sinterability of the niobium borides was improved by changing the sintering conditions and methods from PS to SPS and activated PS.
- PS samples without Co addition have a single NbB phase whereas PS samples with Co addition have dominant Nb<sub>3</sub>B<sub>4</sub> phase and a small amount of NbCo<sub>2</sub> intermetallic phase. When SPS was applied on the pure powders, dominant NbB and small amounts of Nb<sub>3</sub>B<sub>4</sub> and Nb<sub>5</sub>B<sub>6</sub> phases were observed.
- Pressureless sintered samples (N5-PS) exhibited the lowest relative density (81.11 %) and the lowest microhardness ( $1.92 \pm 0.31$  GPa) values among the samples. Relative density and microhardness incredibly increased with Co addition during pressureless sintering: 93.74 % and  $24.82 \pm 2.06$  GPa for the 2 wt.% Co (N5-2CoPS) sample; 97.61 % and  $27.17 \pm 1.85$  GPa for the 5 wt.% Co added samples (N5-5CoPS).
- The highest values of the relative wear resistance (44.6) and elastic modulus (552.2 GPa) were obtained for the N5-2CoPS sample. The increase in the amount of Co (from 2 to 5 wt.%) resulted in a minor decrease in the relative wear resistance (27.8) and elastic modulus values (508.8 GPa). However, the highest fracture toughness value of  $4.74 \pm 0.23$  MPa.m<sup>1/2</sup> among the samples was obtained for the N5-5CoPS sample.
- The utilization of Co additive during pressureless sintering resulted in higher physical and mechanical properties than those of obtained after SPS at the same sintering temperature. Activated sintering was found as a more effective way of yielding superior properties at the used process conditions.

## Acknowledgements

This research investigation was financially supported by “The Scientific and Technological Research Council of Turkey (TÜBİTAK)” with the project title of “Synthesis of Refractory Metal Borides via Three Different Production Methods from Solid, Liquid and Gas Raw Materials for Various Application Areas; Sintering, Characterization, Comparison of Process and Final Products” and with the project number of 112M470. Further, the authors wish to express their appreciations to Prof. Dr. Servet Turan for his help with the SPS experiments.

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