Microstructure, Wear and Corrosion Properties of NiB-TiC Composite Materials Produced By Powder Metallurgy Method

Mehmet Akkaş, Serkan Islak
Department of Mechanical Engineering, Faculty of Engineering and Architecture, Kastamonu University, 37150, Kastamonu, Turkey

Abstract:
In this study, NiB-TiC composite materials were produced using powder metallurgy. In the Ni-TiC-B powder mixture, TiC was fixed at a rate of 5 %, 5, 10 and 15 % boron was added and mechanical alloying was carried out. The prepared powder mixtures were cold pressed under pressure of 400 MPa and sintered in an argon atmosphere at 800 °C for 2 hours. Microstructure, phase formation, hardness, wear and corrosion properties of the samples were investigated in detail. Scanning electron microscopy (SEM) was used for microstructure analysis and X-ray diffractogram (XRD) was used for phase formation detection. The hardness measurements of the samples were measured by a microhardness measuring device. Densities of the samples were determined by Archimedes' principle. The corrosion tests were performed potentiodynamic polarization curves of the composite materials in 3.5 % NaCl solution. Wear tests were carried out the composite materials under a load of 10 N. Results showed that by increasing the amount of B, the wear and corrosion resistance increased.

Keywords: NiB-TiC composites; Powder metallurgy; Sintering; Mechanical alloying; Corrosion.

1. Introduction

Nickel is an element capable of alloying with various elements such as high-resolution iron, chrome, and cobalt. It is used in various industrial applications such as Ni-based alloys, gas turbine parts, medical applications and nuclear systems [1]. These alloys can solve wear resistance, corrosion, and thermal fatigue problems. These properties lead to the development of new Ni-based alloys. It is vital to develop machine parts such as bearings, gears, and cam that are in contact with each other and are subject to wear. Nowadays, there is a need to develop new materials to reduce wear rates. On the other hand, tribology studies focus on different ways to reduce friction and wear of machine parts by analyzing and investigating events involving friction events, lubrication and wear [2-6]. Ni-B alloys have several advantages, including hydrogenation processes and catalytic activities. Furthermore, Nickel 1455 °C and Boron have a melting temperature of 2076 °C. In addition, electrolytic Ni-B coatings have been used to reduce wear and friction in a wide range of applications in corrosive environments. Ni3B intermetallic phases are well known for their high hardness, high chemical, and thermal stability [7-9].

Big differences have between the melting temperatures of nickel and boron, therefore, it is difficult to produce Ni-B based alloys by melting-based methods. Mechanical alloying can be used to overcome this difficulty. In this way, Ni-B intermetallics can be produced

*) Corresponding author: mehmetakkas@kastamonu.edu.tr
which have lower melting degrees than nickel and melting degrees of the pipe [10, 11]. Among the nickel and boron, there are many intermetallic phases such as Ni₃B, Ni₂B, Ni₄B₃, and NiB. These are hard and wear resistant phases. Production of nickel-based alloys by powder metallurgy methods is common. Powder metallurgy involves the production of powders, mixing and converting into a final product that is more suitable for the production of materials with weakness and machinability. This method has been replaced by powder metallurgy because the high strength alloys used in the construction of gas turbine discs are difficult to be forged. Further advantages of this method are the ease of dust particle size control and minimization of errors such as gas gap [12]. Mechanical alloying of powder metallurgy methods, production of nano-sized powders and melting temperature are the methods that are applied as an economical and versatile production technique for obtaining various metallic alloys. The alloying process in the alloying process, the alloying time, the powder-grinding ball ratio affect the final microstructure, particle size, average surface area. In addition, the elemental powder mixtures can be produced as solid, intermetallic and amorphous phases. Mechanical alloying is often used in manufacturing processes with powder metallurgy [13, 14].

In this study, NiB-TiC alloys were prepared by adding TiC and B into the Ni matrix in different ratios using a cold pressing and sintering method (powder metallurgy). The microstructure, corrosion, wear and hardness properties of these composites were investigated.

2. Materials and Experimental Procedures

NiB-TiC alloys with powder metallurgy method and NiB-TiC alloys were used for experimental production. Nickel powder with 99.5 % purity and 45 micron size range was purchased from Sigma-Aldrich Company. TiC powder with 98 % purity and 44 micron size range was purchased from Sigma-Aldrich Company. Boron powder with 99-97 % purity and 0.4 micron size range was purchased from Pavezyum Chemical Industry Company. In the Tab. I results of chemical analysis (composition) are given.

| Sample No | Ni (wt.%) | B (wt.%) | TiC (wt.%) |
|-----------|-----------|----------|------------|
| 1         | 100       | 0        | 0          |
| 2         | 95        | 0        | 5          |
| 3         | 90        | 5        | 5          |
| 4         | 85        | 10       | 5          |
| 5         | 80        | 15       | 5          |

In the NiB-TiC powder mixture, 5 %, 10 and 15 % boron were added to keep the TiC content at 5 % and mechanical alloying was performed by stirring at 350 rpm for 5 hours. The prepared powders were placed in the cold pressing mold. In the cold pressing process, a pressure of 400 MPa was applied as the pressing pressure. Sintering process was carried out at argon atmosphere at 800 °C for 2 hours. After pressing and sintering, metallographic sample preparation methods were applied to the materials produced in 10 mm diameter and 6 mm height. SEM, EDS, XRD, microhardness, density, wear and corrosion analyzes were performed for the obtained samples.

The SEM images and EDS analyzes of the materials were obtained from the “FEI” brand “Quanta FEG 250” in model device at Kastamonu University Central Research Laboratories. The XRD analyzes of the samples were taken from “Bruker” brand “D8
Advance” model device at Kastamonu University Central Research Laboratories. The hardness measurements of the materials were done by using “SHIMADZU” brand “HMV-G21” model microhardness measurement device under 15 g waiting time and 200 g load. The densities of the samples were calculated by using the Archimedes’ principle. Corrosion tests of the produced materials were made by “Gamry” brand Potentiostat/Galvanostat device. The wear tests of the produced samples were carried out in accordance with ASTM G133 standard with “UTS Tribometer T10 Test Device” in Karabük University Iron and Steel Institute.

3. Results and Discussion

The SEM images of the NiB-TiC composites produced by the powder metallurgy method (Fig. 1) were taken and evaluations were made according to the obtained images. When the SEM images are examined, the Ni structure of the sample containing 100 % Ni is clearly seen. In addition, it is seen that TiC particles are distributed homogeneously in the interior of the sample containing Ni+5 % TiC. Samples produced are non-cracked and partially porous. As the addition of B increases, the pore amount decreases and it is seen from SEM photographs. It is observed that the boron is distributed homogeneously in the given SEM images. The homogeneous dispersion may be sufficient due to the mechanical alloying process and the sintering temperature [15].

![SEM images of Ni-B-TiC alloys produced by powder metallurgy method.](image_url)

Fig. 1. SEM images of Ni-B-TiC alloys produced by powder metallurgy method.
EDS analyzes of the samples produced are shown in Fig. 2. The EDS analysis given in Fig. 2a shows that the structure is 100 % Ni. The EDS analysis given in Fig. 2b is the result of EDS analysis of Ni + 5 % TiC alloy and supports the produced sample. Fig. 2c is the result of EDS analysis of the NiB-TiC composite and contains 66.31 % Ni, 5.57 % Ti, 6.68 % B, 10.43 % C and 11 % O in the structure.

![Fig. 2. EDS analysis of samples produced: (a) Ni, (b) Ni + 5 % TiC, and (c) Ni + 5 % TiC + 10 % B.](image)

The XRD graph of NiB-TiC composites produced by powder metallurgy is given in Fig. 3. Ni, Ni₂B, Ni₅B, NiTi and NiC₃B₁₅ phases were formed in the samples. When the graph is analyzed, it is clear that Ni and Ni₂B phases are dominant. During the sintering process, Ni₂B and Ni₅B phases occurred between the Ni and B elements. Very little amount of NiC₃B₁₅ triple phase occurred. As the addition amount B increased, the intensity of Ni₂B and Ni₅B phases increased [16].
Ni-B and Ni-Ti phase diagrams are given in Fig. 4, respectively. In the given phase diagrams, it is clearly seen at which ratios the phases can occur. Ni$_2$B, Ni$_3$B and NiTi phases are formed in phase diagrams. Ni$_2$B, Ni$_3$B, NiTi phases were formed in the samples. The EDS analysis and XRD analysis results are supported in the produced samples.

Before corrosion and after corrosion surfaces of specimens were examined by SEM to understand corrosion mechanism (Fig. 5). More homogeneously corrosive surface and pitting formations in some regions can be observed for the unreinforced sample. However, corrosion occurred at grain boundaries for TiC-B reinforced composite. It is likely that there is a galvanic corrosion between TiC-B materials and Ni. Hence the Ni might be dissolved continuously and reinforcements were separated from the composite.
Fig 5. SEM-EDS images and analysis results of the NiB-TiC alloys produced before and after corrosion.

The potentiodynamic polarization curves of composites determined in 3.5 % NaCl solution are shown in Fig. 6. Potential was applied between -0.5 mV and 0.5 mV (with a scanning rate of 5 mV/s) versus open circuit potentials (OCP) which were determined after 15 min of immersion periods. The $E_{corr}$ values of the TiC and B reinforced composites shifted to anodic region. This is a strong indication for degraded corrosion performance of reinforced...
composites. Yet, the relation between corrosion performance, TiC and B contents of reinforced samples is not clear from the figure. This is mostly because of very different potentiodynamic behavior in the cathodic and anodic portions of scanning for different TiC and B contents.

Fig. 6. Potentiodynamic polarization curves of composites.

All curves exhibit active/passive behavior. The results of the corrosion measurements are summarized in Tab. II. Among the samples, the largest corrosion potential has unreinforced Ni+TiC sample (-188 mV). The lowest corrosion potential among the other samples was measured as -347 mV for Ni+TiC+B (10 %). Among the measured corrosion current values, the smallest value belongs to Ni+TiC sample (12.5 μAcm⁻²). In corrosion science, the general approach to corrosion is that low corrosion current and high corrosion potential means low corrosion rate or high corrosion resistance [18, 19]. According to this approach, it is the Ni+TiC sample which is the most resistant to corrosion among the composites. Corrosion rate and corrosion resistance values in Tab. II also support this approach. As the amount of TiC increased, the resistance of the composite to corrosion decreased. The presence of the TiC and B particle in the Ni matrix caused a second passivation peak to occur. In addition, with the increase in the amount of TiC and B, the amount of porosity increases. Total and number surface of pores expands the corrosion area and reduce corrosion resistance [17-18].

Therefore, explicit calculation of corrosion current density (icorr) which can be applied through Tafel extrapolation to corrosion data is required. I_corr values determined from extrapolations can also be used to calculate corrosion rates of the samples according to following equation [19]:

$$\text{Corrosion Rate (mm/year)} = \lambda \cdot I_{\text{corr}} \cdot (\text{E.W.)} / d.$$ 

where;

$$\lambda = 3.27 \times 10^{-3} \text{(mm. g)/(mA. cm. year)}$$ is a metric conversion factor

E.W. = Equivalent Weight

$$d = \text{Density (g/cm}^3)$$
Tab. II Electrochemical results of Materials.

| Materials          | $E_{corr}$ (mV) | $I_{corr}$ (µAcm$^{-2}$) | $B_a$ (mV) | $B_c$ (mV) | Corrosion rate (mpy) | Corrosion resistance (kΩ.cm$^2$) |
|--------------------|-----------------|---------------------------|------------|------------|---------------------|-------------------------------|
| Ni                 | -251            | 666                       | 87,60      | 73,20      | 180,2               | 279,3                        |
| Ni+TiC             | -188            | 12,5                      | 303        | 121,6      | 3,393               | 1,156                        |
| Ni+TiC+B (5 %)     | -254            | 136                       | 381,2      | 228,6      | 36,92               | 4,178                        |
| Ni+TiC+B (10 %)    | -347            | 102                       | 201,6      | 164,4      | 27,65               | 157,8                        |
| Ni+TiC+B (15 %)    | -345            | 47,20                     | 148,9      | 178,4      | 12,76               | 3,016                        |

The results derived from individual fittings have been presented in Tab. III. It seems that very low concentration (Ni+TiC) of TiC leads to a large gradation increase of corrosion performance. This is much clearer from the data shown in the inset of Fig. 6, as one can deduce an exponentially stabilized behavior of corrosion rate with extra additions of TiC+B. Therefore larger addition of TiC+B into these composites will not degrade overall corrosion performance. This is important information which will be very useful in case for larger addition of TiC+B is mandatory in improving mechanical properties.

As a result, there is a reaction between Ni and TiC+B. TiC+B acts as effective anodes to accelerate corrosions. So corrosion rate is decreased for NiB-TiC composites. Same results are taken for TiC-B reinforced nickel composite in literature [17, 18].

The microhardness graph of the samples produced in Fig. 7 is given. Hardness measurements were taken from the sample surface along a line at 50 µm intervals. The hardness of the sample with 100 % Ni is about 117 HV0.02. The hardness value of the sample containing Ni + 5 % TiC changed to 120 HV0.02. The hardness of the samples with 5 %, 10 % and 15 % addition according to addition B is 157, 171 and 188 HV0.02, respectively. The hardness of the B doped samples is higher than the 100 % Ni sample. This increase is associated with the presence of carbide and hard phases formed. Addition of B caused the formation of the Ni$_2$B and Ni$_3$B phase and consequently contributed to the increase in hardness [20, 21].

![Microhardness graph of produced samples.](image)

The change in the density values of the produced samples is given in Tab. III. When Tab. III is examined, it was determined that the relative density values of the samples decreased according to the amount of B [21, 22]. In addition, the increase in the amount of B with decreasing density ratios of the samples are supported on the SEM images.
Tab. III. Density values of samples produced.

|                | Theoretical Density (gr/cm³) | Experimental Density (gr/cm³) | Relative Density (%) |
|----------------|-----------------------------|-------------------------------|----------------------|
| Ni             | 8.9                         | 6.7021                        | 75                   |
| Ni+TiC        | 8.7015                      | 5.8339                        | 67                   |
| Ni+TiC+B (5 %) | 8.3795                      | 5.1638                        | 61                   |
| Ni+TiC+B (10 %)| 8.0575                      | 4.5401                        | 56                   |
| Ni+TiC+B (15 %)| 7.7355                      | 4.1476                        | 53                   |

Wear depth values belonging to the composites under load of 10 N. Wear depth values are calculated each 100 m sliding distance up to 100 m for all samples. As expected, wear depth is increased with applied load. There is a great difference between pure nickel and Ni+TiC+B composites. Wear depth decreases with the addition of B. First 100 m, the rise of wear depth is too much especially for Ni+TiC+B 15 % under the load of 10N. At the end of 100 m sliding distance, Ni+TiC+B 15 % composite exhibit best wear performance but there is not a significant difference compared then Ni+TiC+B 10 %. Modest increases can be seen after boron 0.10 wt%.

Fig. 7 shows the variations in coefficient of friction (COF) with loads 10 N for all composites. According to the results, COF decreases when applied load increases for all samples. Nickel displays a lower coefficient of friction compared with other composites under load of 10N. Higher weight percentage can be seen clearly for Nickel. Ni+TiC and Ni+TiC+B 5 % exhibit a similar trend and there is no significance change in COF. Wear rates (weight loss) of samples are presented in Fig. 7. TiC is apparent that wear rates are smaller at the higher boron. On the other hand, addition of boron and TiC on nickel improves the wear resistance. Pure nickel has highest wear rates under load of 10N. Ni+TiC+B 15 % composite show better wear resistance and the wear rate is lower than other composites and pure nickel.

As indicated in Fig. 5, Ni+TiC+B 15 % has the highest hardness value. The hardness of material effects the wear behavior [23]. It is related in literature that, softer materials have
also higher wear rates than harder materials and according to the Archard, wear rate is proportional with applied loads [24]. The results of wear loss/100 m belonging to the composites used in this study demonstrate the relation between hardness and wear rates.

The worn surfaces of specimens under load of 10 N are shown in Fig. 9. SEM was used to determine wear mechanism. Wear mechanisms (oxidation, abrasion and adhesion) can be found in worn surfaces either only or combination [24]. Fig. 8 Scratch marks are parallel to the sliding direction and there are oxidation parts in selected areas. Fig. 8 present the Ni 95 % + TiC 5 % and Ni 80 % + TiC 5 % + B 15 % composites. It is clearly seen that located on the worn surface. Wear rate is lower than other composites and partially scratch marks can be seen in the microstructure. When all microstructures of composites are examined, it can be concluded that Ni 80 % + TiC 5 % + B 15 % show best wear characteristics.

![Fig. 9. Worn surfaces and EDS analysis results of samples.](image-url)
As a result, abrasive wear is a dominant mechanism. Scratch marks are generally parallel to the sliding direction. Adhesion can be significantly less than abrasive for all samples. It is also minimized because of the fact that the wear tests are carried out using low sliding speed.

4. Conclusion

In this study, nanoparticle additive NiB-TiC alloys were produced by powder metallurgy method and SEM-EDS, XRD, microhardness, density, wear and corrosion results were investigated. 400 MPa pressure, 800 °C temperature and 2 hours in argon atmosphere were used as production parameters. As a result of the studies;

✓ The nanoparticle additive NiB-TiC alloys were successfully pressed and sintered.
✓ As a result of XRD analysis, Ni, Ni$_2$B, Ni$_3$B, NiTi and Ni$_3$B$_{15}$ phases were determined.
✓ The highest hardness value was obtained in 15 % B additive sample.
✓ It was determined that the relative density values of the samples decreased due to the increasing amount of B.
✓ Corrosion rate is decreased for NiB-TiC composites
✓ When all microstructures of composites are examined, it can be concluded that Ni 80 % + TiC 5 % + B 15 % show best wear characteristics.

5. References

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Садржај: У овом раду, NiB-TiC композитни материјали су добијени металургијом праха. У Ni-TiC-B смешу, TiC је био фиксан са 5 %, док је 5, 10 и 15 % бора додавано у смешу. Тако припремљене смеше прахова су пресоване под притиском од 400 МПа и синтеровани у атмосфери аргона на 800 °C током 2 сата. Детаљно су испитани микроструктура, формирање фаза, тврдоћа, хабање и корозионе својества. SEM је коришћен за анализу микроструктуре, а XRD за детекцију фаза. Мерења тврдоће су раде на узорцима у 3,5 % раствору NaCl, ради одређивања корозионих својстава. Хабање је мерено под силом од 10 N. Резултати указују на то да са порастом удела бора, хабање и отпорност на корозију расту.

Кључне речи: NiB-TiC композити; металургија праха; синтеровање; легирање; корозија.