# Production and Characterization of Animal Waste Reinforced Composite Materials By Powder Metallurgy

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# Abstract

Boron carbide is a product used for reinforcement in composite production and frequently used in the defense industry. The fact that boron carbide behaves similarly to the mechanical properties of bone and that titanium is strengthened with boron carbide, which is used as a biomaterial, causes it to be preferred among composite materials. It also makes it attractive to use in industrial applications at high temperatures. It is known that Fe-B4C composites are used together with Fe matrix materials to improve the properties of the group in addition to elements such as Cr, especially Ti, Co, Mo and Fe in various application areas. This makes it frequently used in the sintering process.

In this study, 98,33%Fe-1,66%$B_4C$, 96.66%Fe-1,66%$B_4C$-1,66%eggshell powders, 95%Fe-1,66%$B_4C$-3,32%eggshell powders, 93,33%Fe-1,66%$B_4C$-5%eggshell powders and 91,66%Fe-1,66%$B_4C$-6,66% eggshell powder samples were prepared using the compositions of. It is formed in a single axis press under 400bar pressure. When the mechanical and metallographic properties of the samples produced after sintering at 1400 °C were examined, the effects of eggshell powders on composite samples produced by adding Fe-$B_4C$ composite and eggshell powders in different compositions were observed. 1,66% to 6,66% eggshell powders additive was used in the compositions and mechanical properties were determined in the produced samples. Structural features were tried to be determined by looking at metallographic analyses. The densities of the produced samples were calculated and their hardness and strength were determined. According to the analysis results, 3,33% Egshelters composition and 3,71 gr/cm3 density and 285,5 HV hardness values at 1400 °C were obtained.

# 1. Introduction

Materials formed by the combination of two materials in order to obtain superior properties than the materials they have are called composites(Shuhadah S. and SupriA.G.,2009). Composites are produced in three different structures as metal matrix, ceramic matrix and polymer matrix composite. Synthetic or natural fibers are used in composites. Synthetic or natural fibers can be used separately or together in composites(Azwa, et al. 2013, Chandrappa and Kamath, 2021). The eggshell is composed of calcite and 4% by weight of collagen, sulfated polysaccharides and other proteins. The eggshell is composed of 96% by weight of calcium and magnesium carbonate. The presence of a significant amount of waste with very good structure makes the eggshell a potential resource and can be used efficiently as a reinforcement material(Prabhakar et. al.,2016). Nowadays, the rapid progress of Industry 4.0, the use of new materials in the automotive, defense and aerospace sectors and engineering applications improve the properties of the machinery and equipment produced. Recently, research has been carried out on the improvement of the mechanical properties of the materials with the lightening of the materials and the production of new materials by evaluating the wastes. Research on agricultural wastes is concerned with the use or effective evaluation of the energy potential of wastes as the first target (Ling and Teo, 2012; Surip et al., 2012; Zakaria et al. 2010; Peng et al., 2000). It has been stated that the use of eggshell powders in the production of metal matrix composites improves mechanical properties (Yonetken et. al., 2020).Drawing pens used in different branches of the industry are used as shaping and strength enhancers. Many methods have been developed for the sintering of Ceramic-Metal composites (McCandlish et al., 1992; McCandlish etal., 1993) Ceramic-metal composites have an important place in the production of such materials. It can be designed to have superior properties in ceramic-metal matrix composites. Metal materials are also used to facilitate the machinability of ceramic materials. Direct fabrication methods have been tried to be developed for the production of high-strength ceramic materials (Rajan et al. 1998., Lee et al. 2008, Frage et al. 2002). To improve the mechanical and functional properties of ceramic materials, ceramic matrix composites with metal particles have been developed. Egg shells are a rich source of minerals. Calcium is an important mineral for biomaterials. It is necessary for the human body to function. It makes up 2% of body weight. About 99% of total Ca skeleton and the rest are stored in teeth and body tissues. It is thrown into the environment after use. Excipient from egg shells as a base material for the development of medicine and dental implants or as a food additive and calcium supplement, a component of agricultural fertilizers and an ingredient for bone implants (Murakami et al., 2007). There is still a significant amount of eggshell is considered as waste. (Boron, 2004),2

In the study, the composite physical, mechanical and metallographic effects of added egg shelter powders in the production of metal-matrix ceramic composites were investigated and the produced samples were characterized.

## 2. Materials And Methods

Metallic powder properties used in this study are given below. The 99.8% purity and particle size Fe powders less than 70 µm, were obtained from Sigma Aldrich. $B_4C$ powders having 99.9% purity and a particle size less than 100 µm from Egg Shelter powders were used. Composition of 98,33%Fe-1,66%$B_4C$, 96,66%Fe-1,66%$B_4C$-1,66% egg shelter, 95%Fe-1,66%$B_4C$-3,32% egg shelter, 93,33%Fe-1,66%$B_4C$-5% egg shelter and 91,66%Fe-1,66%$B_4C$-6,66% egg shelter, powders were prepared. Powder samples were shaped with 30g circular uniaxial press. After weighing, the composition mixture was mixed in a mixer for 24 hours to ensure that the composition was homogeneous. The mixture was shaped by uniaxial cold hydraulic pressing using a high-strength steel mold. It was made under a pressure of 400 bar to compress all powder mixtures. Cold pressed samples were sintered at 1400°C for 2 hours in a conventional tube oven using an Argon gas atmosphere. After sintering, the samples were allowed to cool naturally under argon atmosphere in the oven. Micro hardness and shear strength of the samples were measured by METTEST-HT (Vickers) micro hardness tester, respectively. LEO 1430 VP equipped with the Oxford EDX analyzer in TUAM, was used for SEM microstructure and EDX analysis as a scanning electron microscope.

The density changes of the composite samples produced in 98,33&Fe-1,66%$B_4C$, 96,66%Fe-1,66%$B_4C$-1,66% egg shelter, 95%Fe-1,66%$B_4C$-3,32% egg shelter, 93,33%Fe-1,66%$B_4C$-5% egg shelter and 91,66%Fe-1,66%$B_4C$-6,66% egg shelter composites were calculated using the sintering composite samples (d = m / V) formula (Figure 1). The volume of sintered samples was measured by the Archimedes principle. All percentages and ratios were given in percent by weight. The minerals contained in the eggshell powders were analyzed and determined in Table 1 (Yawar et al. 2020).

Table 1
Mineral composition of eggshell powders (Yawar et al. 2020)

| Mineral | Egg Shelter powder |
|---|---|
| Calcium | 39.62 ± 0.12 (%) |
| Magnesium | 0.41 ± 0.01 (%) |
| Phosphorus | 0.11 ± 0.00 (%) |
| Potassium | 0.07 ± 0.00 (%) |
| Sodium | 0.13 ± 0.00 (%) |
| Zinc | 2.02 ± 0.00 (ppm) |
| Manganese | 13.06 ± 0.01 (ppm) |
| Iron | 1120 ± 4.5 (ppm) |
| Copper | 0.96 ± 0.00 (ppm) |

## 2.1 Experimental Results and Discussion

## 2.2 Characterization of specimens

The density-composition graph of the composite samples produced with metal martis and ceramic additives is given in figure.1. In the production of composite samples, the additive of eggshell powders was used atomically at different rates between 0% and 6,66%. The density was calculated as 5.28g/cm$^3$ when eggshell powder was not added in the produced composite. When the eggshell powder was added 6,66% atomically, the density value was calculated as 5.93g/cm$^3$. It was observed in SEM images that the addition of eggshell powder reduced the porosity in the composite.

The hardness values measured in the samples produced in Figure.2 were measured from 10 different points and given by taking the average. The lowest hardness value of 178,25HB was measured in the composite sample without eggshell powder added. Different compositions were obtained by increasing the eggshell powder atomically up to 6.66% in the sample composition. Among the produced samples, the highest hardness value was measured in the sample belonging to 204.12HB and 91.66%Fe-1,66%B4C-6,66% composition.

The maximum compressive strength change values of the produced compositions are given in Figure 3. Among the composite samples produced, the lowest compressive strength was measured at 210.52 Mpa in Fe-$B_4C$ composition. In the compressive strength test, the highest strength was measured at 274.18 Mpa in the samples belonging to the 91.66%Fe-1,66%$B_4C$-6,66% eggshell composition. Density, hardness and microstructure pictures confirm these values.

# 3. Metallographic Analysis

Figure 4. The microstructure of the Fe-$B_4C$ composite sample sintered at 1400 °C produced without adding eggshell powder is given in the SEM picture. It is seen that $B_4C$ is homogeneously distributed in the microstructure. It is understood that intergranular neck formation takes place. In addition, it is seen that the porosity in the microstructure is higher than the samples with egg powder added. The hardness and density values of this sample also confirm the excess of porosity.

Figure 5. In the SEM picture, the microstructure of the 96.66%Fe-1,66%B4C-1,66%eggS composite sample sintered at 1400 °C by adding egg shelter powder is given. It is seen that the $B_4C$ particles in the microstructure maintain their homogeneous distribution in Fe, where the appearance is reduced. It is understood that intergranular neck formation takes place. In addition, it is seen that the porosity in the microstructure is less than the sample without egg shelter powders. The hardness and density values of this sample also confirm that the porosity is less than the sample without egg shelter powders.

Figure 6. The microstructure of the 95%Fe-1.66%B4C-3.32% egg shelter composite sample sintered at 1400 °C is given in the SEM picture. It is seen that the appearance of $B_4C$ particles in Fe in the microstructure decreases and starts to disappear. Porosity decreased due to grain coarsening in the sample of this composition. It turns out that sintering takes place much better. Grain boundaries are clearly observed in the microstructure. The hardness and density data of this sample also confirm the microstructure properties.

Figure 7. The microstructure of the 93.33%Fe-1.66%B4C-5%egg shelter composite sample sintered at 1400 °C is given in the SEM picture. It is seen that $B_4C$ particles and eggshell powders in the microstructure disappear in Fe and turn into gray and black colors. Acicular particles are seen in the microstructure. In the sample of this composition, the porosity decreased a lot with grain coarsening. It is understood that sintering takes place much better in this composition. Grain boundaries are clearly observed in the microstructure.

Figure 8. The microstructure of the 91.66%Fe-1.66%$B_4C$-6.66% Egg shelter composite sample sintered at 1400 °C is given in the SEM picture. In addition to the homogeneous distribution of the microstructure, it is observed that it turns into gray and black colors. Acicular particles are seen in the microstructure. The co-porosity in the sample of this composition was much reduced compared to the other compositions. It is understood that the sintering that takes place in this composition takes place much better than other compositions. The highest hardness value was measured in this composition.

Linear SEM-EDX analysis of 98.33%Fe-1,66%B4C composite sample is given in Figure 9. In general, there are peaks belonging to Fe and C elements. There are Fe and Carbon elements along the linear line. Since the purity of the powders used is 98% and 99%, Si, Al and Manganese elements were also encountered.

Linear SEM-EDX analysis of 91.66%Fe-1.66%B4C-6.66%EggS composite sample is given in Figure 10. In the composite sample, in which eggshell powder is added atomically 6.66%, there are peaks of Fe Al, Mg and Ca elements. Calcium and Iron as well as Al and Mg elements were detected along the linear line in the sample, where linear analysis was made. In the analysis of egg shell powders, it was determined that these elements were in the majority.

In Figure 11, X-Ray analysis results of the sample belonging to the composition of 98.33%Fe-1,66%B4C are given. According to the results of the analysis, the phases formed were determined as Fe and B4C. The lowest density and hardness were measured in this composition. By adding eggshell powders to the composition, improvements were achieved in the material microstructure and mechanical properties.

In Figure 12, X-Ray analysis results of the sample of 91.66%Fe-1,66%$B_4C$-6,66%EggS composition are given. According to the results of the analysis, the phases formed were determined as Fe, $B_4C$, $Fe_2B$ and CaO, respectively. The formation of the $Fe_2B$ phase is thought to be effective in increasing the hardness. Unlike the phases formed in the sample without egg shell powders, a peak of $Fe_2B$ and CaO phases was formed.

# 4. Conclusion

In this study, five different compositions, these are 98.33%Fe-1.66%B4C, 96.66%Fe-1.66%B4C-1.66% egg shelter, 95%Fe-1.66%B4C-3 ,32% egg shelter, 93.33%Fe-1,66%B4C-5% egg shelter and 91.66%Fe-1,66%B4C-6.66% egg shelter, sintered at 1400 °C and besides its Physical and Mechanical properties Characterization was done by examining the metallographic properties.

Egg shell wastes, which are out of use from chicken egg processing facilities, are a source of raw materials for different industries. Reuse of eggshell ingredients. It can reduce the risk of microbiological problems and environmental pollution. most of the recommendations for possible uses of eggshell waste Proposals for sustainable economic and environmental benefits can form the basis for pilot studies. This article proposes an alternative with the use of eggshell powders in the production of composites by powder metallurgy method.

# Declarations

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### Author Contributions

Conceptualization, A.Y., A.E and G.P.; methodology, A.Y. and A.E.; software, A.Y.; validation, A.Y. and G.P.; formal analysis, A.Y. and A.E.; investigation, A.Y.; resources, A.Y. and VÖ.B.; data curation, A.Y; writing—original draft preparation, A.Y., A.E and G.P.; writing—review and editing, A.Y. and A.E.; visualization, A.Y. and A.E.; funding acquisition, A.Y; All authors have read and agreed to the published version of the manuscript.

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### Institutional Review Board Statement

Not applicable.

### Informed Consent Statement

Not applicable.

### Data Availability Statement

The processed data necessary to reproduce these findings are available upon request with permission.

### Conflicts of Interest

The authors declare no conflict of interest.

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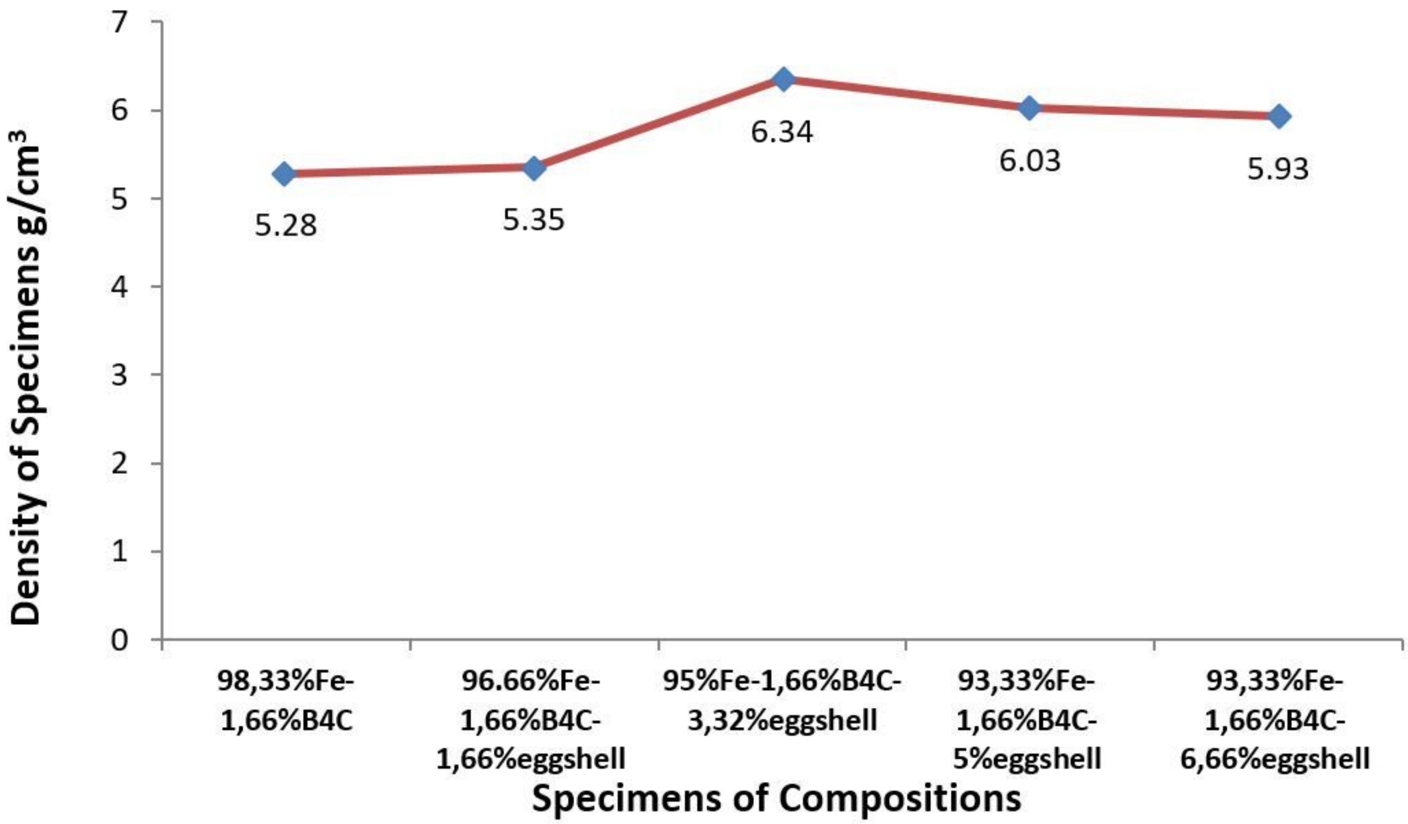
# Figures




## Figure 1

Composition-density change curve of Ceramic Metal Composite

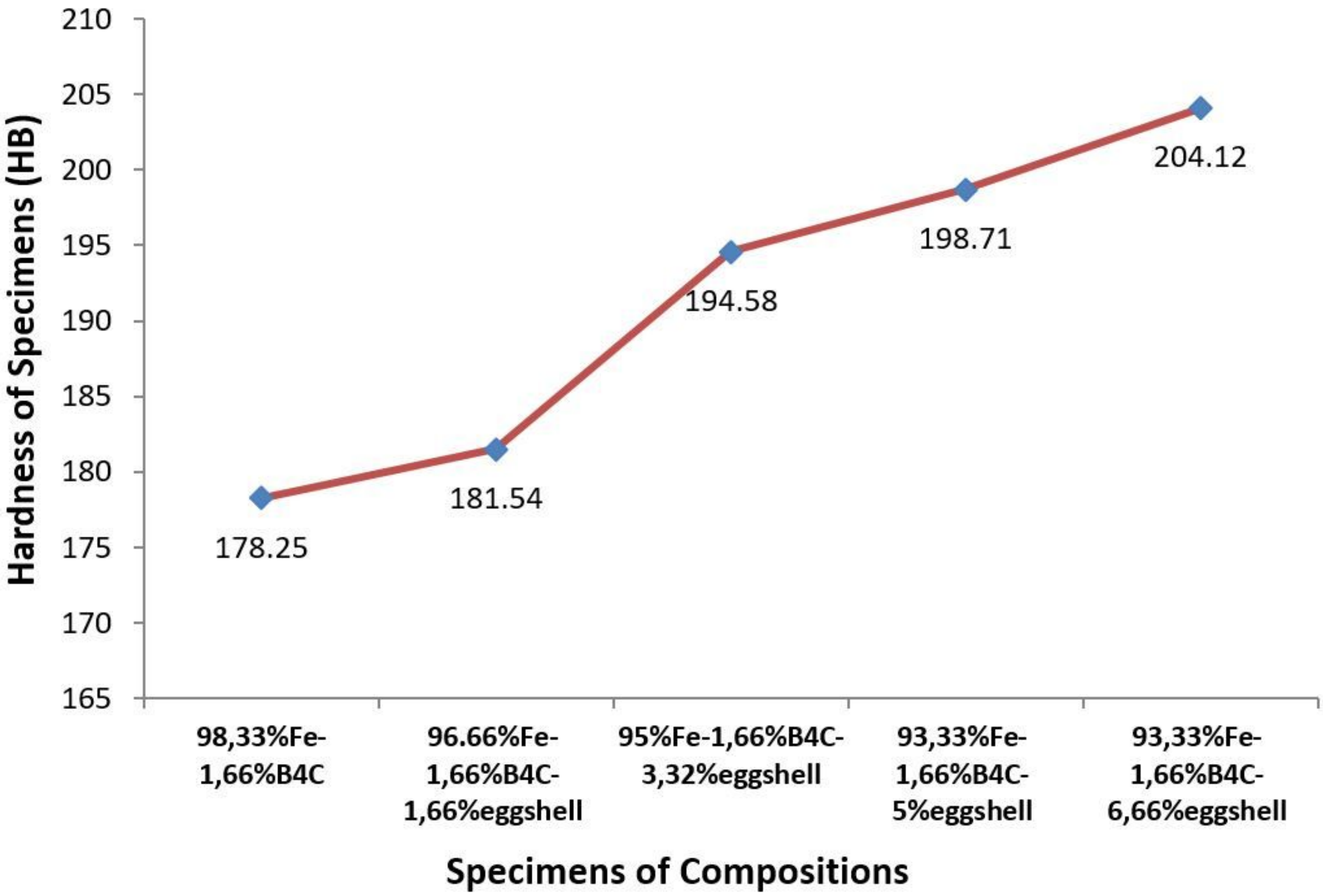
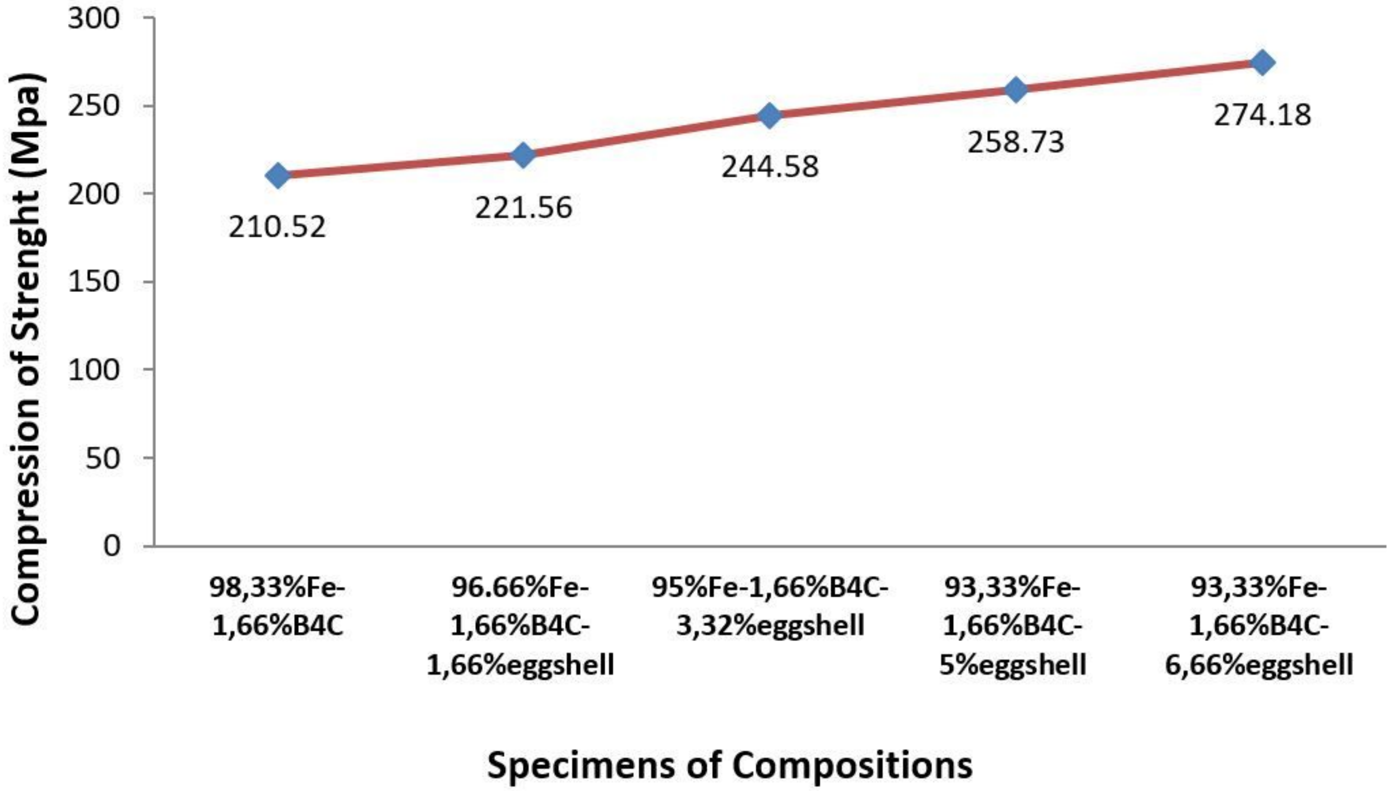


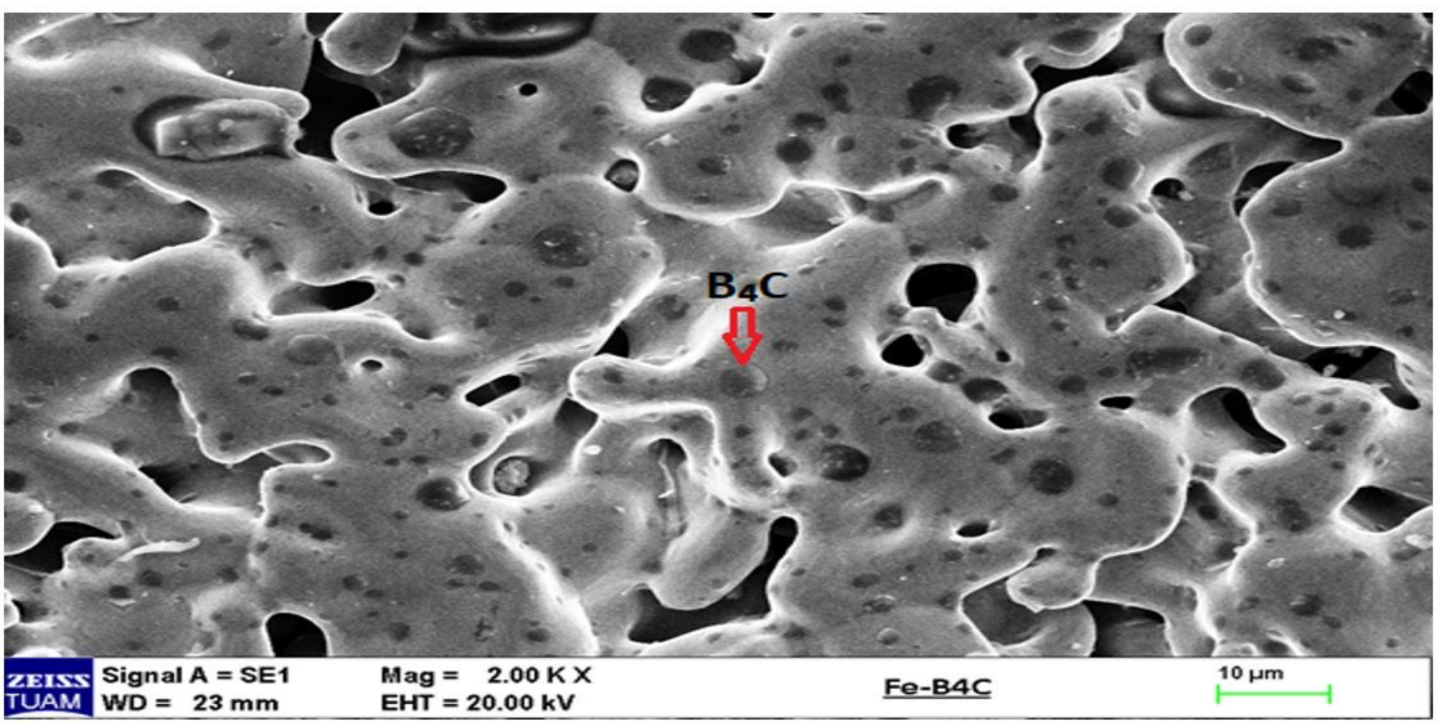

Figure 2

Composition-hardness change curve of Ceramic Metal Composite



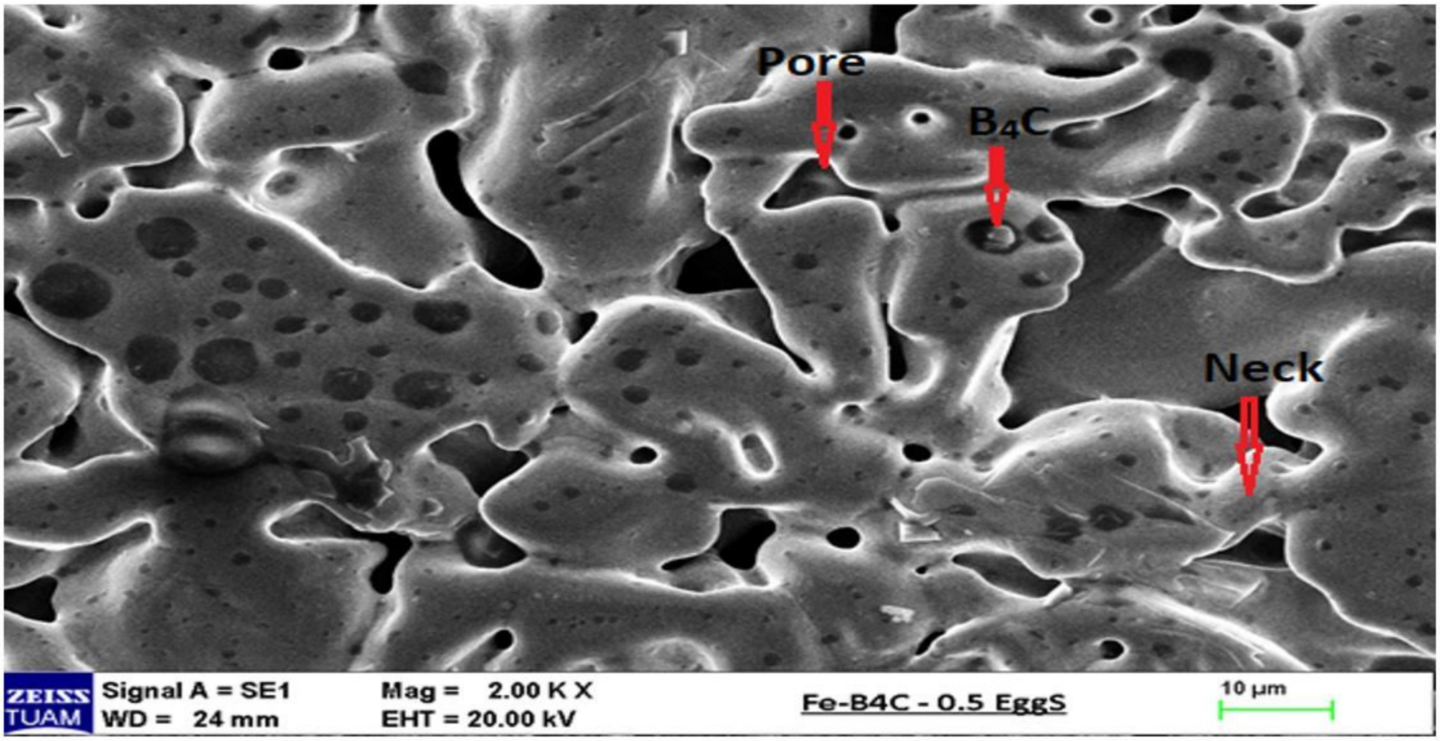

## Figure 3

Composition-Strenght change curve of Ceramic Metal Composite



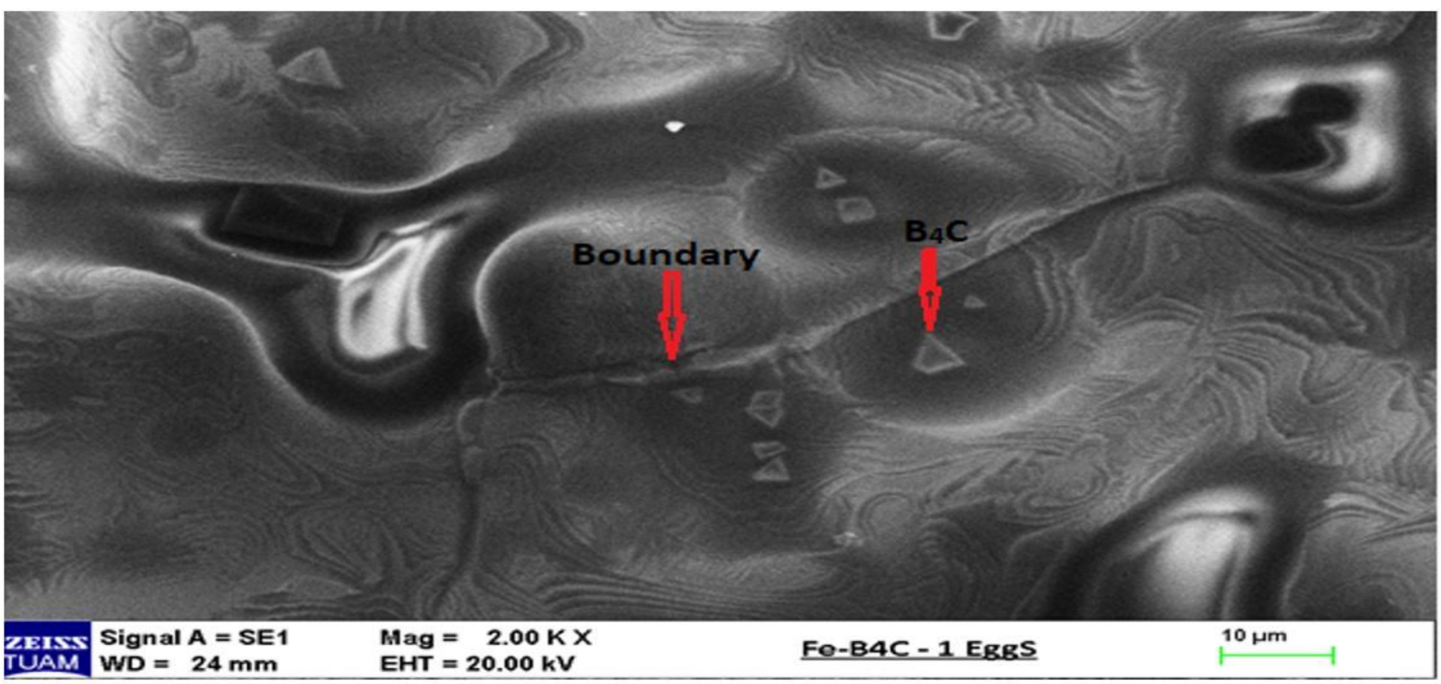
## Figure 4

SEM picture of Fe-$B_4C$ composite



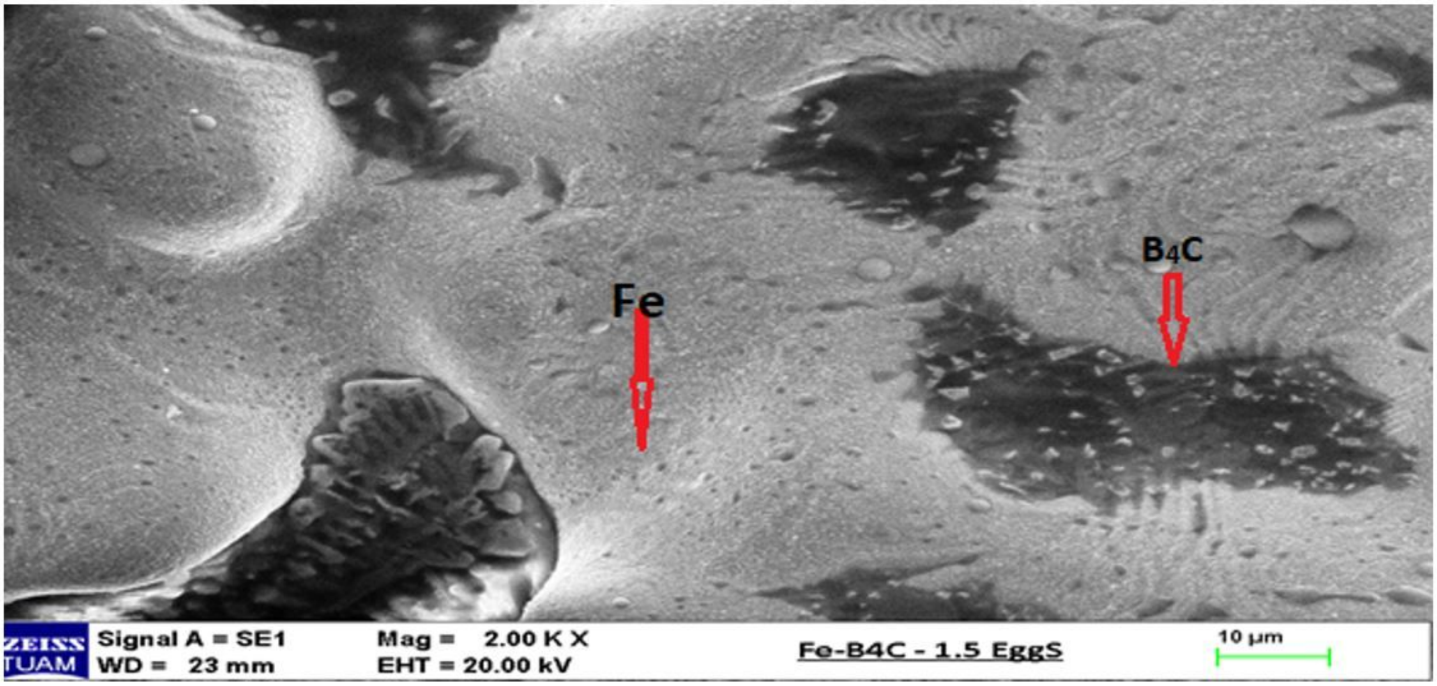

## Figure 5

SEM picture of 96.66%Fe-1,66%B4C-1,66%EggS composite



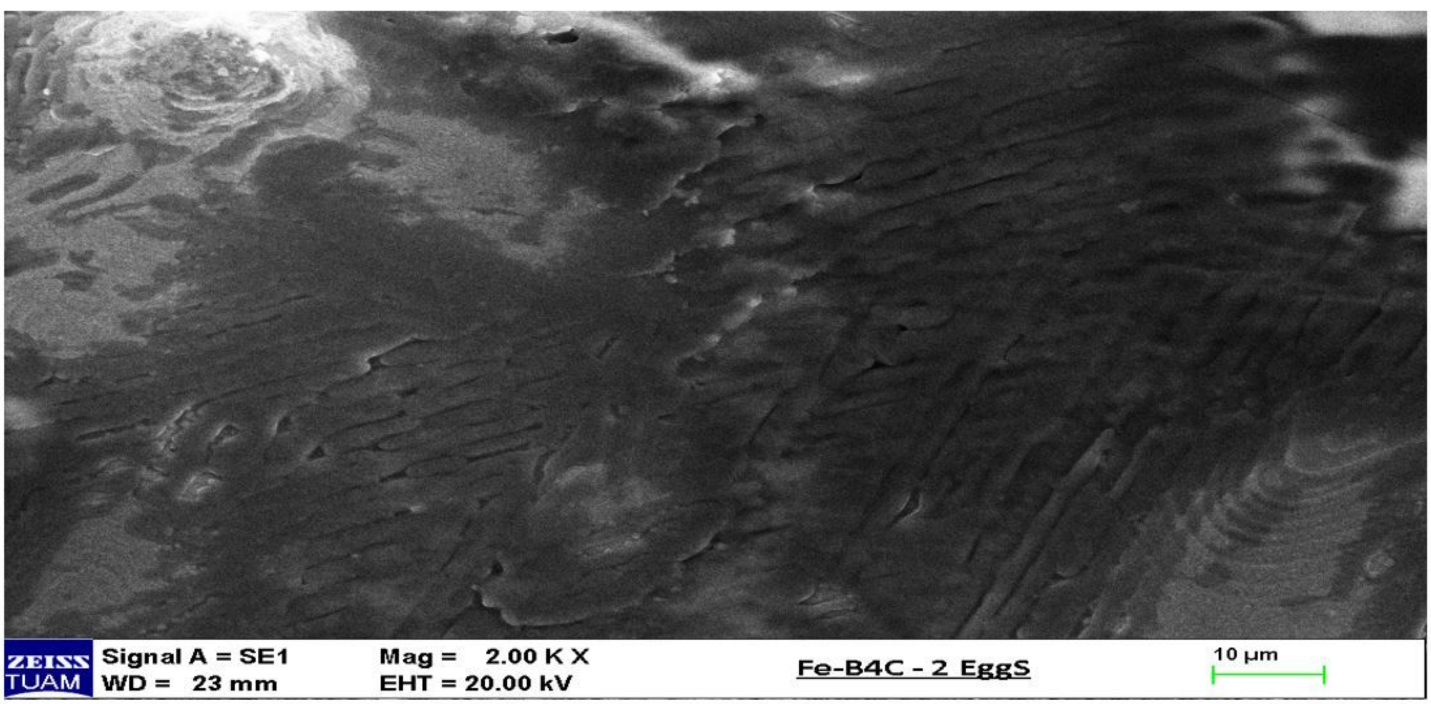
### Figure 6

SEM picture of 95%Fe-1.66%$B_4C$-3.32EggS composite



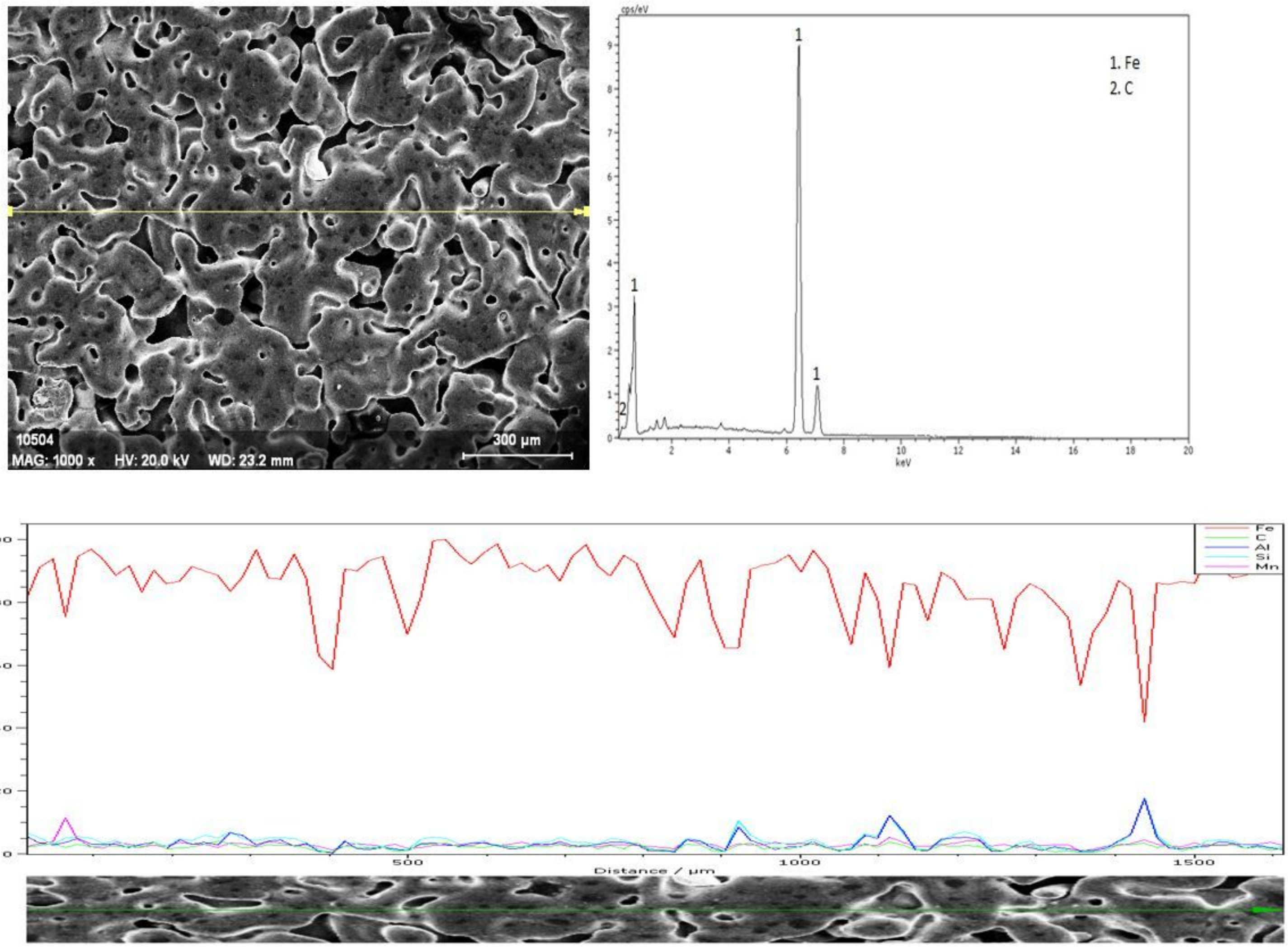

### Figure 7

SEM picture of 93.33%Fe-1.66%$B_4C$-5%EggS composite



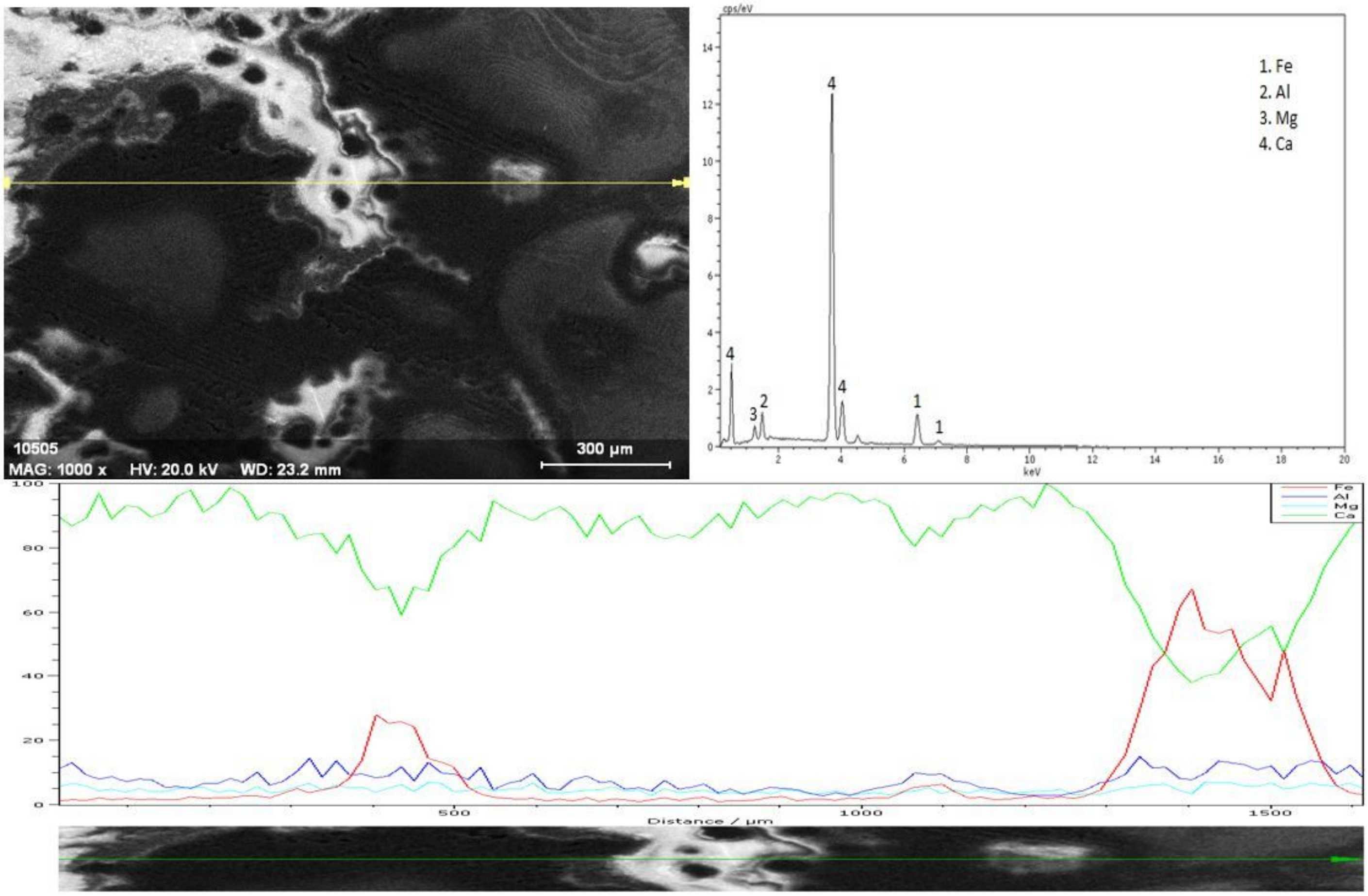
## Figure 8

SEM picture of 91,66%Fe-1,66%$B_4C$-6,66%EggS composite




## Figure 9

EDX analysis of 98,33%Fe-1,66%$B_4C$ composite




## Figure 10

EDX analysis of 91,66%Fe-1,66%$B_4$C-6,66%EggS composite

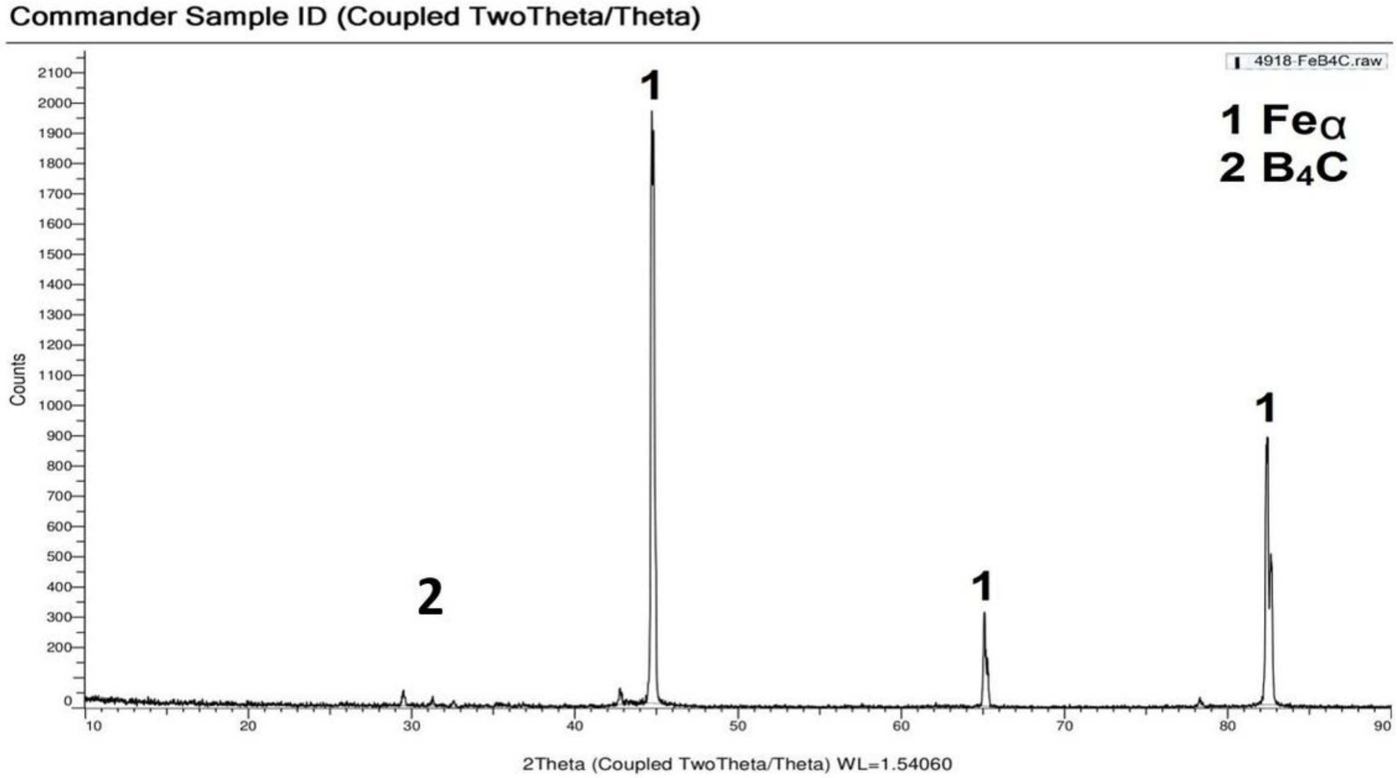
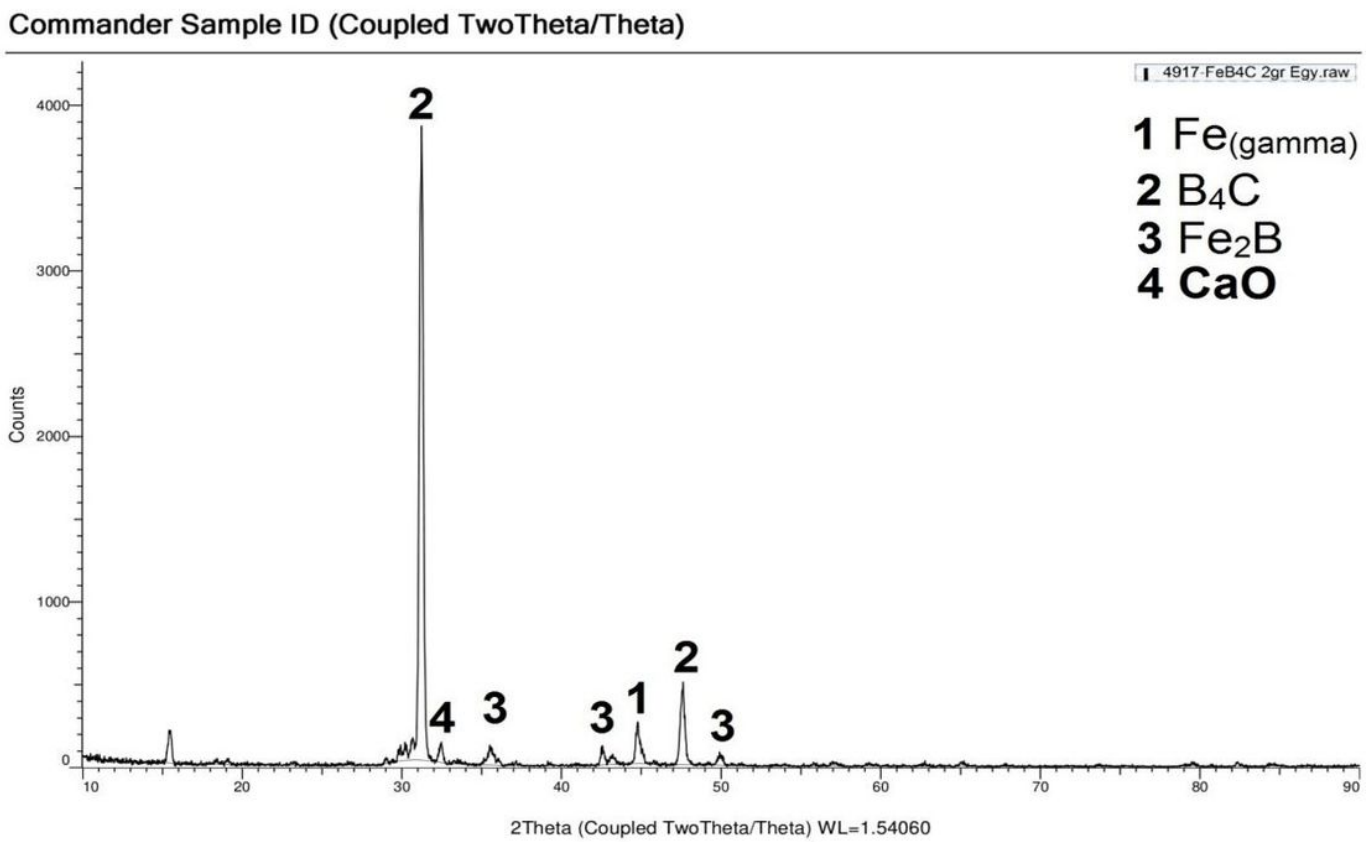



Figure 11

XRD analysis of 98,33%Fe-1,66%$B_4C$ composite



## Figure 12

XRD analysis of 91.66%Fe-1,66%$B_4C$-6,66%EggS composite