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# Microstructural and hardness characterisation of sintered low alloyed steel

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**Materials**

## ABSTRACT

**Purpose:** The purpose of the present study is to produce low ally PM steel without any addition and with addition of ferro-boron addition by conventional PM manufacturing route at the different sintering temperature.

**Design/methodology/approach:** Fe-Ni-Cu-Mo-C sintered steel containing 0.5 percent ferro-boron addition was used in this study. The compacts were prepared by powder metallurgy method involving powder mixing, cold pressing at 700 MPa pressure and sintering at temperatures of 1180, 1200 and 1250°C in nitrogen+% 4 $H_2$ atmosphere for 30 minutes. The influence of sintering temperature and boron addition on the hardness and microstructure of P/M steels were investigated. Optical and scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) techniques were used for characterization of the sintered steels.

**Findings:** The results show that increasing sintering temperature resulted in increase in hardness values; however, those values were dropped after sintering temperature higher than 1180°C. On the other hand, Boron addition contributed to hardness values at sintering temperature of 1200°C. Those values were decreased with increasing sintering temperature.

**Research limitations/implications:** The composition of the sintered steels effect on the density values. The composition of the grain boundaries were affected from sintering temperature. Boron, carbon, molybdenum were seen in the grain boundaries of the specimen having the highest hardness values. It is thought that those compositions strongly effects on hardness values of the specimens.

**Originality/value:** Fe-Ni-Cu-Mo-C base powder with and without boron addition low alloy sintered steel were produced. The effects composition and sintering temperature were investigated.

**Keywords:** Powder metallurgy; Steel; Hardness; Microstructure

## 1. Introduction

Powder metallurgy (PM) production method of steel materials having complex shape is cheaper way comparing to the other manufacturing methods [1]. PM has advanced significantly over the past 30 years as a cost effective and efficient processing technique to produce near net shape parts [2].

New PM materials having high performance have been required due to necessity in the various industrial applications. There are many ways to increase the performance of the material including new alloy systems, increasing density using new compaction techniques, increasing sintering temperature and heat treatments. Pre-alloyed diffusion PM has been developed as high performance materials [3-5]. Many performances enhancing pre-alloyed element such as molybdenum, manganese, nickel, chromium have been used. Fe-Ni-Cu-Mo-C sintered low alloy steel has received great attendance by several researchers [4, 6-10].

Porosity in powder metallurgy materials must be reduced to a minimum and density of those materials must be enhanced. After that, those materials can be considered for high performance applications. To fulfill that, various techniques have been used during production process of those PM materials. Employing high sintering temperature is one alternative way to produce PM materials having desired microstructural and mechanical properties.

Table 1.
Chemical composition of the powders used [18, 19]

| Powders | (wt. %) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | C | Cu | Ni | MnS | S | P | Mo | B | Amide wax | Fe |
| Distaloy (gradeAE) | 0.61 | 1.47 | 3.95 | 0.5 | - | - | 0.5 | - | 0.9 | balance |
| Ferro-boron | 0.39 | - | - | - | 0.006 | 0.04 | - | 18 | - | balance |

Another method to improve the properties of those materials is the usage of the element addition such as boron. During production of PM steels, modification of sintering behavior is fond attractive by researchers. Enhanced sintering activity provides to obtain high density materials. Boron as carbon increase hardenability in the steel. Although its effect is limited due to its low solubility in iron, boron is ideal sintering activator and addition of it to powder metallurgy steels provides liquid phase formation that contributes higher density [11-13]. According to binary Fe-B phase diagram, $Fe_2B$ forms an iron rich low melting eutectic at about 1174 or 1177°C. It is thought that higher amount of eutectic were obtained with increasing boron content in the powder and rounded pores. An increase of eutectic amount resulted in better mechanical properties. The percentages of boron content in powder and sintering temperature is crucial parameters, if chosen correctly, almost fully density PM steels may be produced. Boron is used as a sintering activator in the Fe- Cu-Ni- Mo-C low alloyed PM steels [12, 13]. In several investigations, boron as a sintering additive has been used to in low alloyed steels and stainless steels [10, 12-17]. Different boron additions can be used for full density and higher performance.

The objective of the present study is to produce low ally PM steel without any addition and with addition of ferro-boron addition by conventional PM manufacturing route at the different sintering temperature. Later, the effect of sintering temperature and boron addition on the hardness and microstructure of sintered low alloy steels were investigated. Optical and scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) techniques were used for characterization of the sintered steels.

## 2. Experimental procedure

Fe-Ni-Cu-Mo-C powder was used in this study. The powder was prepared from diffusion alloyed distaloy AE™ produced by Höganos, Sweden and graphite and lubricant were added (Table 1). This powder has density values of 3.10 $gcm^{-3}$ without compaction and density of 7.12 $gcm^{-3}$ after pressed at 600 MPa [18]. Two different compositions were used, the one is as received distloy powder and the other is the base powder with addition of ferro-boron. Ferro boron was ground and seized with the practical size of 53 µm. It was added to as received distaloy powder to obtain sintered low alloyed steel having 0.2 weight % percentage of boron. Low alloyed sintered steels were produced by the conventional powder metallurgy route. The mixed powders were compacted using single action press at 700 MPa. Later, those compacts were sintered at 1120, 1180, 1200 and 1250°C for 30 minutes in nitrogen + 4 % hydrogen atmosphere, and then cooled in the furnace.

Density measurements were performed by the water displacement method using an SHIMADZU model electronic weighing balance of 0.001 mg accuracy. Brinell hardness measurements were performed using BMS-200RB model hardness tester. Before hardness measurements, the specimens were ground at 1200 grid silica carbide paper. A load of 187.5 kg and duration of 30 seconds were used during measurement. At least three hardness measurements from different areas of the specimens were preformed for each specimen and then average values were calculated.

For microstructural examination, the specimens were ground on successively finer grades of SiC abrasive paper with the grit from 120 to 1200 and the samples were then polished using 1µm alumina slurry. After that the samples were washed in water for one minute. The Specimens were etched with 2 % nital and %4 picral solution. Microstructural examination of the specimens were performed using an NIKON LP 1200 ELIPSE model optical microscope and an JEOL JSM 6060 LV scanning electron microscope and EDS analysis were performed on them by an energy dispersive spectroscope, model IXRF 500.

## 3. Results and discussions

The density values of the sintered steel without and with boron addition as a function sintering temperature are given in Figure 1. The density values of the all specimens increase with sintering temperature up to 1200°C for both distaloy AE and the distaloy AE with 0.5 wt. % boron addition. However, the density values of both types of sintered steels decrease after sintering temperature higher than 1200°C. The density values of the distaloy AE increase with the sintering temperature because the grain size is getting higher at higher sintering temperature. Similar trend was seen for the specimens with boron addition. Higher sintering temperature resulted in lower density values due to presence high gap between the grains. As expected, the density of the base materials increases with the concentration of alloying elements. Copper enhances sintering due to the formation of a liquid phase. Nickel and graphite in sintered materials produce shrinkage; therefore, increasing the density of low alloyed PM steels [3, 4, 20]. The density values of the specimens having no additive have higher than that of the specimen with boron addition. This contradicted with the values obtained in earlier study [12, 13]. The density increased with increasing boron addition to rich the maximum with 0.6 wt % boron addition in the FeNiMo systems [12, 13]. On the other hand, ferro alloys addition to PM materials resulted in lower density values due to purity problem of those powders. Similar trends in Fe-Ni-Cu-Mo-C with addition of Ferro-titanium and Ferro- molybdenum [21]. Swelling after sintering was observed for the materials with boron addition. In an earlier study, it was explained that boron alloyed stainless steel absorbs lower amounts of oxygen and carbon. Boron behaves as inhibitor during sintering [21]. When nitrogen was used as sintering atmosphere, BN can be formed due to nitrogen absorption. Nitrogen absorption is detrimental during sintering process of the low alloy steels under hydrogen atmosphere, therefore, higher density may not be achieved [12, 13]. Formation of nitrides, borides and carbides cause grain separates. Therefore, lower density values of PM steels may be obtained.

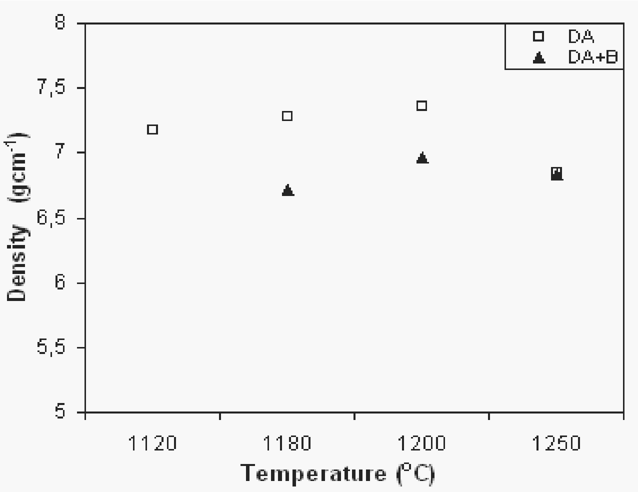


Fig. 1. The effects of composition and sintering temperature on densities of sintered low alloy steels (DA: Distaloy AE; DA+B: Distaloy with 0,5 wt % boron addition)

Hardness values of the sintered steels with and without boron addition are shown in Figure 2. Hardness values increases with increasing sintering temperature. However, the values sharply decrease after sintering temperature higher than 1200°C. On the other hand, the sintered steel with boron addition has the highest hardness value for the specimen sintered at 1200°C. The hardness of Fe-B matrix grain was not influenced by boron addition; which proved in solubility of boron in iron. The hardness values of the PM compacts with boron addition were in the range of 295-443 kgmm$^{-2}$, depends on sintering temperature. Those values are almost 2-3 times higher than that of PM compact without boron addition sintered at 1120°C, which is generally used sintering temperature of these types' materials. By increasing temperature from 1120°C to 1180°C hardness values is increased substantially for sintered steel without addition. This is primarily due to more developed sintering necks, rounder pores and change microstructure from upper bainite to lower bainite. The material may shrink slightly at higher sintering temperature; therefore, the density is increased slightly [22]. As seen from the figures, PM materials having higher density values also exhibit higher hardness values. There is a parallelism between the hardness and density values of the sintered low alloy steels produced. In this study, specimen was heated to sintering temperature at 5°C min$^{-1}$. This value is to slow and cooling rate was kept the same. The phases formed in this type material are strongly depended on cooling rate. Therefore, lower hardness values were obtained than that of the materials produced with higher cooling rate in earlier study [10].

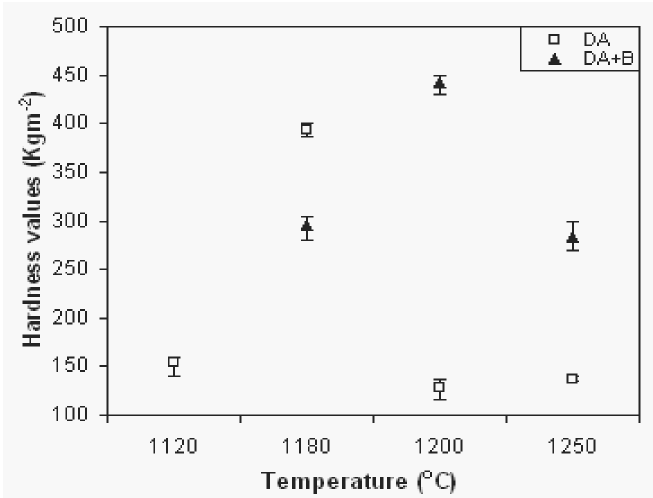


Fig. 2. Hardness variation as a function of sintering temperature and compositions

The microstructure of Fe-Ni-Cu-Mo-C PM steel sintered at 1120°C consists of upper bainite, perlite and some ferrite (Fig. 3a). This is the explanation for moderate hardness value. On the other hand, percentage of lower bainite phase increased after high temperature sintering such as 1180°C (Figure 3b). This is consisted with earlier study [3, 4, 20, 22]. Grain coarsening occurs with sintering temperature increase (Figure 3 a, b, c). The optical microstructures of the specimens with boron addition are given in Figure 3 e-f. Ferritic microstructure is dominated and grain growth was also seen with sintering temperature rise. Differences of the microstructure between specimens with and without boron addition are seen in Figure 4 a-d. As clearly seen from the figures, microstructures are totally different and grain coarsening was dominant for the specimens with boron addition after higher sintering temperature.

Boron is well known sintering activator in the iron based materials by formation the liquid phase, produced by the following eutectic reaction [2, 12-15, 23]:

$Fe_2B + \gamma Fe \longrightarrow$ Sıvı (1)

This reaction was occurred at 1177°C [15]. The sintering temperature must be higher than 1177°C for effective liquid phases sintering occurred by contributions of boron. The liquid phase has a very low solubility in iron (0.0002 wt %) provides continuous network between the solid grains and liquid phase sintering. The amount of boron content is very important for obtaining full density of PM materials. The liquid phase remained segregated at the grain boundaries during the sintering and provided a rapid diffusion path for allowing quick densification. The pores are filling by liquid phase occurs on the wetting on the pore surfaces by grain growth, which control the pore filling and densification. The sintering kinetics is determined by grain coarsening [12-13, 23]. Formation of boron carbides borides such as NiB, MoB, $Mo_2B$, $Ni_2B$ at the grain boundary reduces ductility. During the sintering process, those reactions are also occurred:

$$2Fe + B \longrightarrow Fe_2B \quad (2)$$

$$2Mo + 2Fe_2B \longrightarrow Mo_2FeB_2 + 3Fe \quad (3)$$

Those two reactions were occurred in solid state and causes compact expansion. Iron boride $Fe_2B$ starts to form at about 500°C, while $Mo_2FeB_2$ complex boride may form at about 930°C [15]. $Mo_2FeB_2$ is hard phase. The hardness of iron boride grains is 1800 $Hv_{0,1}$ [15].

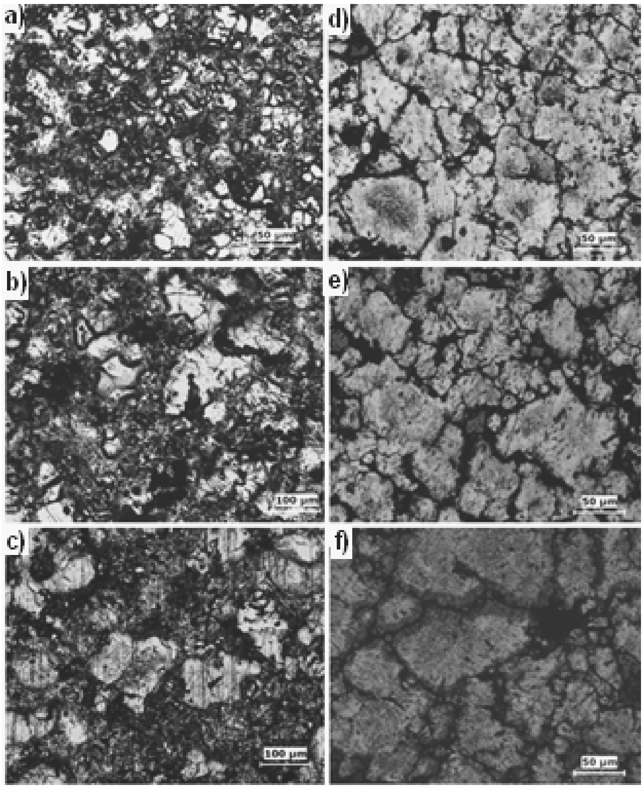

Fig. 3. Optical micrographs of the specimens without boron addition sintered at a) 1120°C b) 1180°C c) 1250°C, the specimens with 0.5 wt % boron addition sintered at d) 1180°C e) 1200 °C f) 1250°C

Figure 5 shows the microstructure of the PM steels with addition boron and corresponding EDS line analysis. As seen from the figure, distinct grain boundary separation was not seen and the elements present in the material were distributed homogeneously in the grain. Copper provides liquid phase sintering and density increase, therefore, the hardness increase of the low alloy steels. Copper diffuses in to grains. Actually, cupper ($D = 1.5x10^{-11}$ $cms^{-1}$) diffuses slowly but it is helped initially by the presence of the liquid phase [4]. Addition copper to this type of materials having nickel increases strength and hardness values. Elevated temperature sintering also increases diffusion of the admixed element which enhances materials strength. Nickel and copper additions enhance strength by solid solution alloying with hardenability [20].

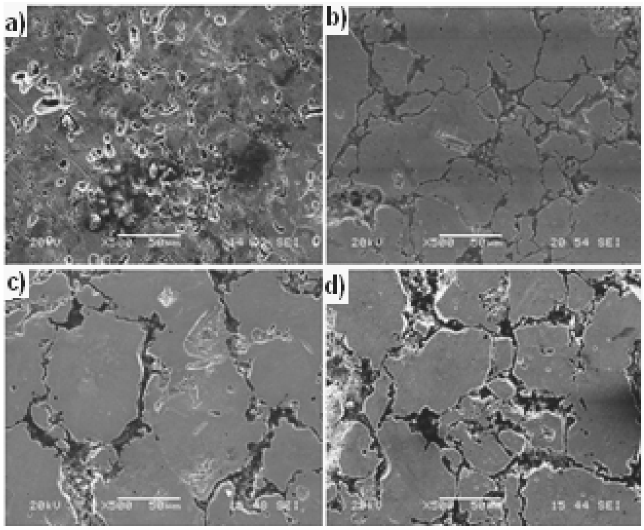

Fig. 4. SEM micrographs of the specimens without boron addition sintered at a) 1180°C, the specimens with 0.5 wt % boron addition sintered at b) 1180°C c) 1200 °C d) 1250°C

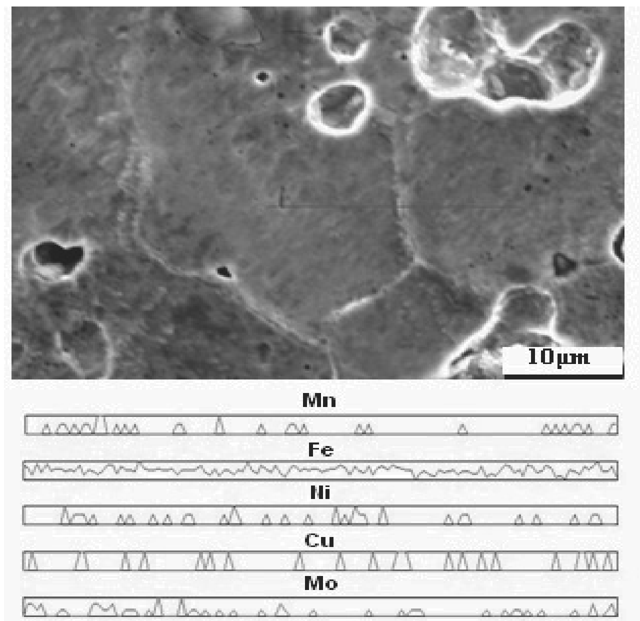


Fig. 5. Micrographs and EDS line element analysis for the specimen without boron addition sintered at 1180°C

Diffusion of boron into matrix grains is also effect on hardness due to formation hard phases such as carbides, nitrides and borides. Diffusion rate of addition elements enhances with increasing sintering temperature, which contributes formation of various phases. The highest hardness values were obtained for the specimen sintered at 1200°C. As seen from the figures of EDS line analysis, (Figures 6, 7, 9) almost the same microstructure of grain boundaries were obtained. However, slight differenced were also available. Size of grain boundaries were increased with increasing sintering temperature. When the compact with boron addition sintered at 1200°C, boron, oxygen and molybdenum were increased at the grain boundary (Figure 7), which proves formation of $Mo_2FeB_2$ phase, which is hard and brittle and cause high hardness of the compacts as given in equation 4. Ni and Cu were distributed homogeneously. It is attributed that higher sintering temperature provides to increase diffusion rate of the elements into grains. On the other hand, EDS analysis of the specimen sintered at 1200°C showed that typical element of those materials were seen in the grain (Fig. 8a), while oxygen, carbon and boron present in the grain boundary due to affinity of boron to those elements (Figure 8b). The grain boundary size increased when the specimen sintered at 1250°C (Figure 9). This means that the gap between the grains increase at higher sintering temperature. According to EDS line analysis, composition of the grain boundary is slightly different (Figure 9). Boron and oxygen were seen at the boundary; however boron were not seen in the grain, as it is seen in the compact sintered at 1200°C. Boron and carbides accumulated in the grain boundaries, while oxygen is dispersed along the line on the grain boundary and grain. The grains surrounded by hard and brittle phases was not allowed its plastic deformation during hardness measurements, therefore higher hardness values of the PM steel with boron addition were obtained. Key factor here for higher hardness values obtained strongly depends on composition of the grain boundaries.

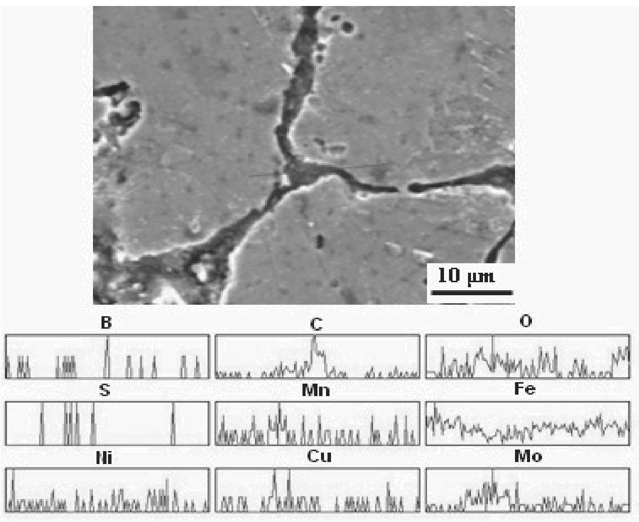


Fig. 6. Micrographs and EDS line element analysis for the specimen with boron addition sintered at 1180°C

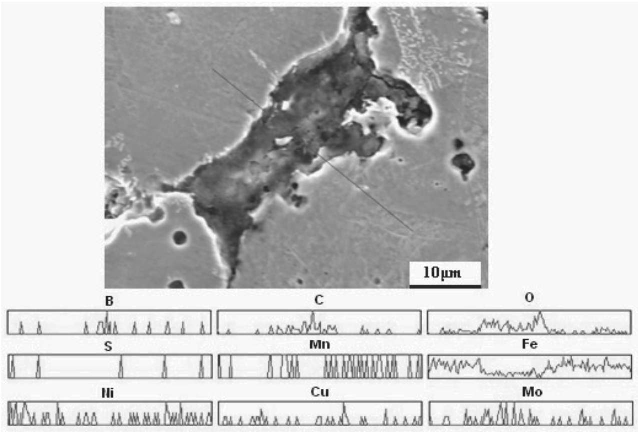


Fig. 7. Micrographs and EDS line element analysis for the specimen with boron addition sintered at 1200°C

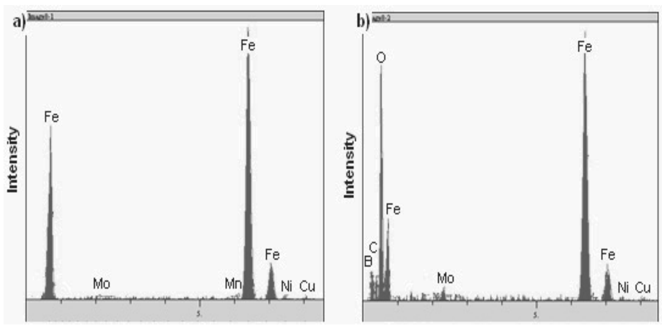


Fig. 8. EDS analysis taken from a) the grain and b) grain boundary for the specimen with boron addition sintered at 1200°C

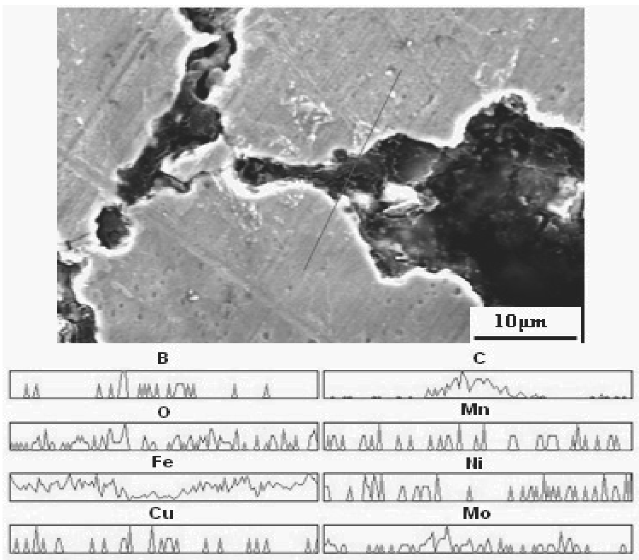


Fig. 9. Micrographs and EDS line element analysis for the specimen with boron addition sintered at 1200°C

## 4. Conclusions

Fe-Ni-Cu-Mo-C base powder with and without boron addition low alloy sintered steel were produced. The effects composition and sintering temperature were investigated. The following results were obtained:

1) The composition of the sintered steels effect on the density values. Both compositions showed similar trends. Sintered low alloyed steels having different compositions increased with increasing sintering temperature up to 1200°C. However, it decreases after sintering temperature of 1250°C. On the other hand, the density values of the specimens decrease with boron addition comparing with that of the specimen without addition.
2) The grain growths of the specimens with and without boron additions were seen with increasing sintering temperature.
3) Hardness values have great influence from sintering temperature for both specimens with without boron additions. The highest hardness values were obtained for the specimen produced from distalloy AE at 1180°C sintering temperature. Sintering temperature higher than 1180°C resulted in lower hardness values. Boron addition contributed to the hardness values of sintered steels and almost three times higher hardness values were obtained comparing with the sintered steels produced at 1120°C.
4) According to grain boundaries SEM EDS analysis of the specimens, different compositions of the grain boundaries were seen depending on both sintering temperature and boron addition. The composition of the grain boundaries were affected from sintering temperature. Boron, carbon, molybdenum were seen in the grain boundaries of the specimen having the highest hardness values. It is thought that those compositions strongly effects on hardness values of the specimens.

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## References

[1] R.M. German, Powder Metallurgy of Iron and Steel, John Willey and Sons, USA, 1998.
[2] KS. Narasimhan, Sintering of powder mixtures and the Growth of ferrous powder metallurgy, Materials Chemical Physic 67 (2001) 56-65.
[3] R.J. Causton, J.J. Fulmer, Sinter hardening low alloy steels, Proceedings of the Advances in Powder Metallurgy and Particulate Materials, San Francisco, California, USA, Volume 5, 1992, 17-52.
[4] V.A. Tracey, Nickel sintered steels: development, status and prospects, Proceedings of the Advances in Powder Metallurgy and Particulate Materials, San Francisco, California, USA, Volume 5, 1992, 303-314.
[5] G.S. Upadhyaya, Sintered metallic and ceramic materials-sintered low-alloy ferrous materials, John Wiley & Sons LTD, West Sussex, England, 2000.
[6] H. Khorsand, S.M. Habii, K. Yoozbasizadea, K. Janghordban, S.M.S. Rihhai, H.R. Serai, M. Ashtai, The role of heat treatment on wear behavior of powder metallurgy low alloy steels, Materials and Design 23 (2002) 667-670.
[7] R. Yılmaz, A. Gökçe, Effect of ferro-titanium addition on ımpact and fracture toughness of low alloyed steel produced by powder metallurgy, Proceedings of the 13th International Metallurgy and Materials Congress, Istanbul, 2006, 903-909 (in Turkish).
[8] R. Yılmaz, A. Gökçe, The effect of ferro-titanium addition on mechanical properties of alloyed sintered low alloyed steel, Proceedings of the 11th International Materials Symposium, Denizli, 2006, 760-766 (in Turkish).
[9] R. Yılmaz, A. Gökçe, H. Kapdıbaş, The effect of molybdenum addition on the microstructure and mechanical properties of sintered steel, Advanced Materials Research, Materials and Technologies 22-23 (2007) 71-74.
[10] R. Yılmaz, Ö. Özgün, The effect of chemical composition on fracture toughness of sintered alloyed steel produced by powder metallurgy, Proceedings of the 14th International Metallurgy and Materials Congress, Istanbul. Submitted. 2008 (in Turkish).
[11] R.M. German, Enhanced Sintering Through 2nd Phase Additions, Powder Metallurgy 28/1 (1985) 7-12.
[12] M. Seleckha, A. Salak, H. Danninger, The effect of boron liquid phase sintering on properties of Ni-, Mo- and Cr-alloyed structural steels, Journal of Materials Processing Technology 141 (2003) 379-384.
[13] M. Selecka, A. Salak, H. Danninger, The effect of boron liquid phase sintering on properties of Ni-Mo and Cr-alloyed structural steels, Journal of Materials Processing Technology 143-144 (2003) 910-915.
[14] M. Sarasola, T. Gomez-Acebo, F. Castro, Liquid generation during sintering of Fe–35% Mo powder compacts with elemental boron additions. Acta Materialia 52 (2004) 4615-4622.
[15] J. Nowacki, T. Pieczonka, Dilatometric analysis of sintering of iron–boron–cobalt P/M metal matrix composites, Journal of Materials Processing Technology 157-158 (2004) 749-754.
[16] H.O. Gülsoy, S. Salman, S. Özbek, Effect of FeB additions on sintering characteristics of injection molded 17-4PH stainless steel powder, Journal of Materials Science 39 (2004) 4835-4840.
[17] H.O. Gülsoy, Enhancing the wear properties of iron based powder metallurgy alloys by boron additions, Materials and Design 28 (2007) 2488-2491.
[18] Höganas Datasheet, 69.02.505, Starmix, 2005.
[19] Marmara Metal, Datasheet. 2006.
[20] J.A. Hamill, R.J. Causton, S.O. Shah, High performance ferrous p/m materials utilizing high temperature sintering, Proceedings of the Advances in Powder Metallurgy and Particulate Materials-1992, San Francisco, California, USA, Volume 5,1992, 193-214
[21] J. Abenojar, D. Esteban, M.A. Martinez, F. Velasco, Sintering stainless steels with boron addition in nitrogen base atmosphere, Materials Science Forum 534-536 (2007) 733-736.
[22] U. Engstrom, A. Klekovkin, S. Berg, B. Edwards at al., , Efficient low alloy steels for high performance structural applications, webpage of Höganas, 2006.
[23] S.M. Lee, S.J.L. Kang, Theoretical analysis of liquid-phase sintering: pore filling theory, Acta Materialia 46/9 (1998) 3191-3202.