SSRG International Journal of Mechanical Engineering
ISSN: 2348 – 8360 /doi:10.14445/23488360/IJME-V6I7P105

Volume 6 Issue 7, 27-31, July 2019

Magnetic Properties of Borided Fe-Ni Alloys

N. Ucar[*1], C. Ekinci[**2], A. Calik***[3], and M. S. Karakas****[4]

[*] Faculty of Arts and Sciences, Physics Department, Suleyman Demirel University, Isparta, Turkey
[*]Rectorate, Bozok University, Yozgat, Turkey
[***] Faculty of Technology, Mechanical and Manufacturing Engineering Department, Suleyman Demirel University, Isparta, Turkey
[****] Faculty of Engineering and Natural Sciences, Department of Metallurgical and Materials Engineering, Konya Technical University, Konya, Turkey

Abstract

Fe-Ni binary alloys containing 70, 80, and 90 wt% Ni were borided in a solid medium at 1273 K for 2 to 6 h and at temperatures of 1173, 1273, and 1373 K for 5 h. The surfaces of the borided alloys were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS). Magnetic properties were investigated using vibrating sample magnetometry (VSM). X-ray studies of the surfaces revealed the presence of Ni_4B_3 and Ni_6Si_2B phases in the boride layer. A decrease in saturation magnetization was observed with increasing boriding temperature and time due to boride/borosilicide formation at the surfaces. A rapid decrease in M_s was observed with increasing Ni content in the alloy, primarily due to dilution.

Keywords: *magnetic saturation, boriding, boride layer, boride phases*

I. INTRODUCTION

The most important class of magnetic materials are ferromagnets, which mainly include iron, nickel, cobalt, manganese, and some alloys or compounds containing one or more of these elements. The saturation magnetization (M_s) of these materials (especially the iron group) is based on the collective electron or band concept [1, 2]. Iron-nickel (Fe-Ni) alloys belong to soft magnetic materials that possess high permeability and low coercivity under a weak magnetic field. They are widely used in computer storage devices, magnetic shielding, solar cells, etc. [3-5]. In recent years, Fe-Ni films have attracted extensive attention due to their high M_s properties, which are desired in printed circuit boards, constrained core technology, and commercial multilayer circuit boards. In the literature [6-13], there are numerous studies on Fe-based alloys' magnetic properties, many of which have shown that magnetic properties are strongly dependent on microstructure, particularly crystallite size, particle morphology, and structural defects. M_s is found to be linked with crystallite size. Hamzaoui et al. [11] used ball milling to produce nanocrystalline Fe-Ni alloys from powder mixtures. They observed an increase in M_s with grain size reduction, which they attributed to each grain acting as a single domain. However, they noted that the increase could also be partially due to lattice expansion, which affects the density of states at the Fermi level. Conversely, decreasing M_s with crystallite size has also been observed in Fe, Ni, and Co nanoparticles [6-8]. The discrepancies in magnetization behavior can be attributed to the various mechanisms that affect magnetization, such as oxidation, lattice expansion, phase Transformations, grain boundary segregation, disorder, etc.

Alloying additions also influence the M_s. Gopalan et al. [13] reported large M_s values in melt-spun Fe-0.63 at% P ribbons, which they attributed to exchange coupling between α-Fe (Fe solid solution containing P) and Fe_3P. Moustafa and Daoush [14] synthesized Fe-Ni permalloy powders using electroless chemical reduction and compared the powder mixtures' magnetization curves with their sintered compacts. They observed increased M_s in the sintered material and attributed the increase to the formation of $FeNi_3$, and later FeNi, during sintering.

Several studies have been previously conducted on bulk ferromagnetic alloys' magnetic properties, and special focus has recently been given to Ni-Fe alloys [9, 11, 14, 15]. However, there are very few studies on magnetization that focus on thermochemical coatings and borides. The present study aims to investigate how M_s is affected by coating thickness and nickel content in borided Fe-Ni alloys.

II. MATERIALS AND METHODS

Fe-Ni alloys containing 70, 80, and 90 wt% Ni were cut to 5 × 10 × 10 mm dimensions from a 5-mm-thick plate. The specimens were borided in a solid medium using the powder pack method. The specimens were divided into three groups. The first group, labeled Group 1, consisted of 70 wt.% Ni alloys borided at temperatures of 1173 to 1373 K for 5 h. The second group, labeled Group 2, consisted of 80 wt% Ni alloys borided in for 2 h, 4 h, and 6 h at a constant temperature of 1223 K. The last group, labeled Group 3, were Fe-Ni alloys containing 70 to 90 wt% Ni borided at 1273 K for 5 h. The three alloy groups and their boriding parameters are summarized in Table 1.

Table 1. The three groups of binary Fe-Ni alloys and their boriding parameters.

Group	Alloy	Boriding temperature	Boriding duration
1	80 wt% Ni	1173 K, 1273 K, 1373 K	5 h
2	70 wt% Ni	1223 K	2 h, 4 h, 6 h
3	70 wt% Ni, 80 wt% Ni, 90 wt% Ni	1273 K	5 h

X-ray characterization of the surfaces was performed using a Rigaku D-MAX 2200 X-ray diffractometer (XRD) with Cu-Kα radiation of 0.15418 nm wavelength. Microstructural details were observed using a JEOL-5600LV scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy
(EDS) detector. The thicknesses of boride layers were measured employing a digital thickness measuring instrument attached to
an optical microscope (Nikon MA100). The average thickness of the boride layers (total, including all phases in the coating) was determined at twelve different locations by measuring the heights of valleys and boride/silicide pins peaks. Magnetization measurements for three specimens in each group were made using a Cryogenic Q-3398 vibrating sample magnetometer (VSM). The magnetic hysteresis loops were recorded at 295 K with applied magnetic fields of up to ± 0.95 T.

III. RESULT AND DISCUSSION

Boriding (surface coating) is a thermochemical surface hardening process used for improving the service life and performance of metals or alloys. The process is used to improve resistance to corrosion and abrasive wear, decrease the coefficient of friction, and, of course, greatly increase surface hardness [15-17]. Many studies have been conducted to investigate the effect of boriding on M_s as well as on the mechanical properties of metals and alloys [10, 18-20]. These studies show that the coating's thickness and the type of boride/borosilicide phases within the coating significantly affect Mrs. Longer's boriding times, resulting in increased boride formation and hence thicker coatings. It is well known that boron (B) is diamagnetic and that the magnetization in iron borides FeB and Fe_2B is lower than that of Fe [21]. Information regarding the magnetic properties of nickel borides, on the other hand, is limited [22,23]. Calik et al. [20] showed that M_s and initial permeability in the borided low carbon micro-alloyed steel decreases with increasing boriding time due to the increase in boride layer thickness. Chabi et al. [10] found that M_s decreases with increasing B content in mechanically alloyed Fe92−xNb8Bx powders. The drop in M_{rs} was attributed to the formation of the hard magnetic phase Fe2B and structural disorder, which was introduced during the milling process. The current literature, therefore, suggests decreasing M_s with increasing boron content.

A. Microstructures

A sample cross-section SEM micrograph showing the layers grown on the Fe-Ni substrate's surface is presented in Fig. 1 along with EDS spot analyses from three different regions marked on the micrograph. The layers' morphology is similar to the typical sawtooth morphology of borides observed in plain carbon steels, albeit smoother. The presence of Au signals in the EDS spectra is due to the gold plating on the specimen, which was applied to prevent electrostatic discharge.

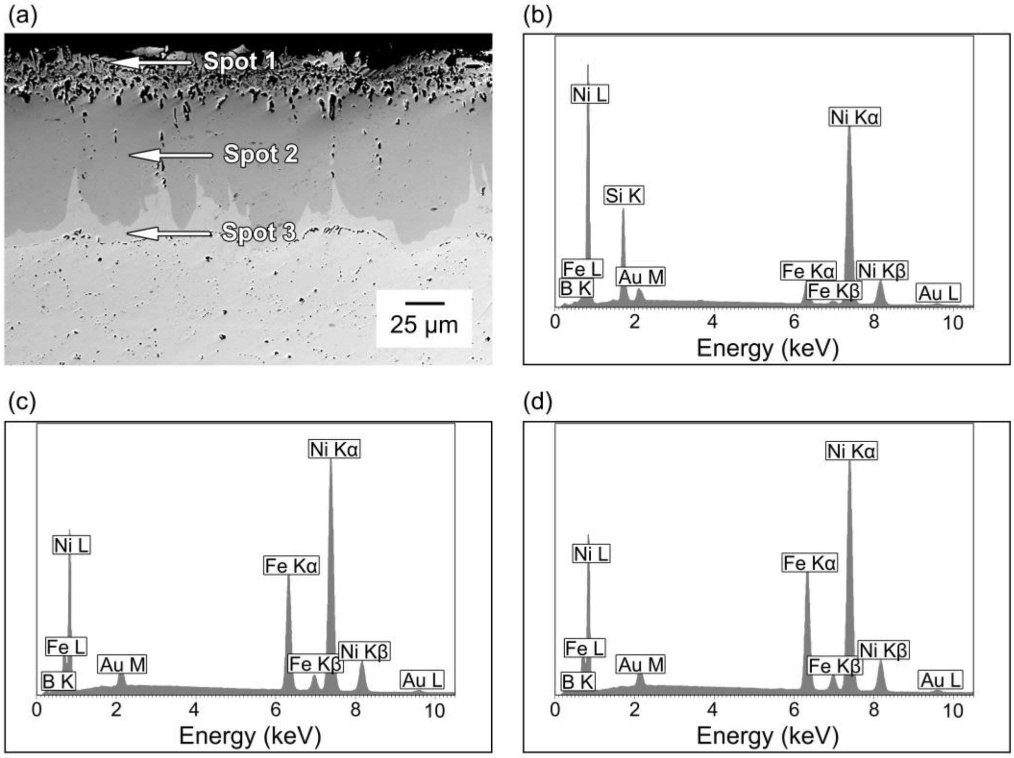

Fig. 1. (a) Cross-section view of Fe-%70Ni alloy borided at 1273 K for 5 h, and the EDS spectrum for (b) Spot 1, (c) Spot 2, and (d) Spot 3 shown in (a).

Through comparisons from XRD analyses shown in Fig. 2, SEM images (Fig. 1a), and EDS microanalyses (Figs. 1b-d), the phases within the boride layer were identified Ni_4B_3 and Ni_6Si_2B. The formation of the borosilicide phase is due to the alloy's high affinity to silicon in the boriding powder. The strong Si peak at 1.74 keV in the EDS spectrum of Fig.1b indicates that the borosilicide Ni_6Si_2B is the outermost phase in the boride layer (note the absence of the Si peak in Figs 1c and 1d), with Ni_4B_3 beneath. The XRD pattern in Fig. 2 suggests that Ni_4B_3 is present in the monoclinic (m-Ni_4B_3) and orthorhombic (o-Ni_4B_3) form. EDS analyses of Spot 2 and Spot 3 in Figs. 1c and 1d also point to the presence of Ni_4B_3 in two different crystalline forms as the two spectra are nearly identical. The coexistence of the two phases was previously reported by Rundqvist [24].

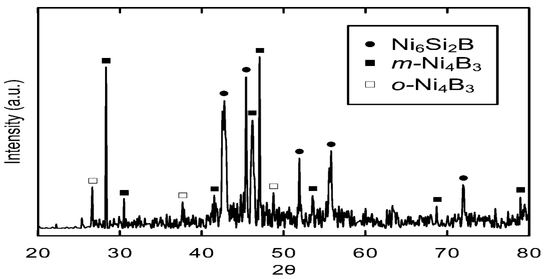

Fig. 2. X-ray diffraction pattern for the Fe-%70Ni alloy borided at 1273 K for 5 h. (*o*: orthorhombic, *m*: monoclinic).

The Ni_6Si_2B layer contains significant porosity, probably due to B's rapid diffusion from the Ni_6Si_2B layer to the Ni_4B_3 layer during the boriding treatment. The formation of Ni_6Si_2B has been reported in powder metallurgy products containing nickel, boron, and silicon [25-27]. Formation of Ni_6Si_2B is often considered undesirable due to its low hardness, which has compelled manufacturers of boriding powders to developing new, Si-free boronizing powders, such as Ekabor-Ni [29].

B. Boride Layer Thickness

As expected, an increase in boriding temperature and time in the Group 1 and Group 2 specimens result in an increase in the layer thickness, from 13 µm to 96 µm and from 7 µm to 105 µm and, respectively. The diffusion of boron atoms explains the substrate's increase by increasing temperature and time [17,20,30]. On the other hand, the thickness of boride layers formed on the Fe–Ni binary alloys decreased with increasing Ni content. This is probably due to the hindering of boron diffusion by boride/borosilicide phase formation. Azakli et al. [31] reported that some alloying elements as titanium, nickel, and chromium resulted in decreased thickness in the boride layer, forming a diffusion barrier.

C. Magnetic Properties

It is well known that M_s is one of the most important magnetic properties of a material; it determines whether the material can be either used as a hard or soft magnet. Hysteresis loops obtained from this study, as a function of boriding time, temperature, and Ni content, are shown in Fig. 3. The figures indicate that the effects of boriding magnetic properties cannot be ignored. As expected, decreases with increasing boriding temperature and time, but also decreases with increasing Ni content. The obtained results for Fe-Ni alloys are similar to results previously obtained for low carbon micro-alloyed steels and $Fe_{92-x}Nb_8B_x$ powders [10, 20]. Borosilicide phases obstruct the magnetic domains' movement in the boride layer under the external magnetic field. M_s, therefore, decreases with increasing boride layer thickness.

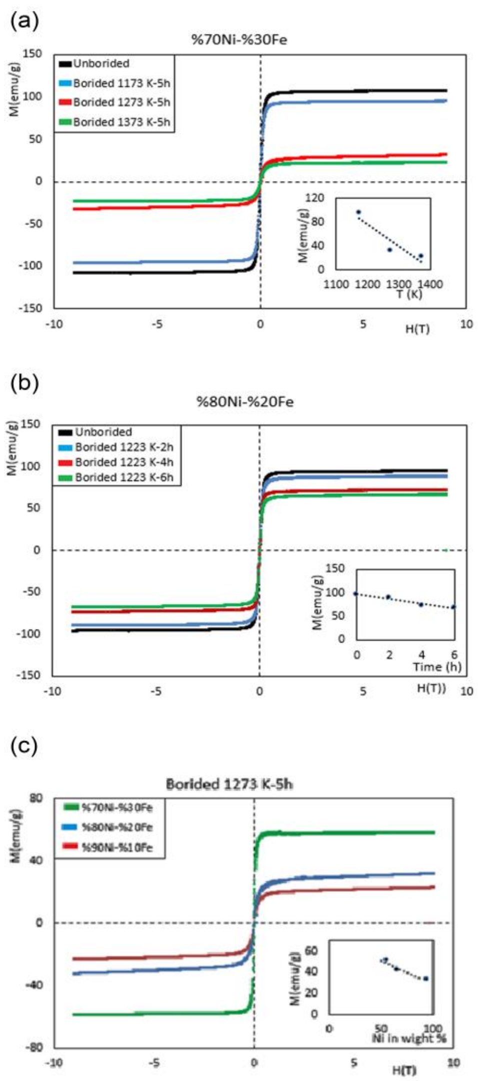

Fig. 3. Room temperature magnetization hysteresis loops of the borided Fe-Ni alloys as a function of boriding temperature (a), boriding time (b), and Ni content (c).

In the literature, it has been shown that the M_s of an alloy decreases progressively with increasing Ni content due to atoms distributed in the grain boundaries [32]. In the present study, the decrease of M_s with the increase of Ni content is attributed to the dilution of Fe the Fe-Ni alloy and the formation of boride and silicide phases with lower magnetic moments. The results show no evidence of exchange coupling between the coating and the Fe-Ni substrate.

IV. CONCLUSION

Magnetic properties of borided Fe-Ni samples have been measured as a function of boriding time, boriding temperature, and nickel content. Significant changes in M_s were observed with changes in boriding parameters and with Ni content. Higher boriding temperatures and longer boriding durations resulted in decreased M_s values due to the formation of nickel borides and silicides. Boriding of Ni-Fe alloys with higher Ni content only resulted in lower M_s values, partly due to boride/silicide formation and partly due to the dilution of iron in the substrate. While the results show disadvantageous effects of boriding in regard to M_{rs}, they may prove useful in applications where a compromise must be made between surface hardness and high M_s.

REFERENCES

[1] W. Heisenberg, Zur Theorie des Ferromagnetismus, Z Phys. 49 (1928) 619–636.

[2] E.C. Stoner, Collective electron specific heat and spin paramagnetism in metals, Proc Roy Soc. A 154 (1936) 656–678.

[3] H. Gavrila, V. Ionita, Crystalline, and amorphous soft magnetic materials and their applications, J. Optoelectron. Adv. M. 4 (2002) 173–192.

[4] U.C. Ozogut, A. Cakir, Temperature-dependent Young's modulus change in Si-doped Fe65Ni35 Invar alloy, IMMC 2016, 18th International Metallurgy and Materials Congress, Istanbul, Turkey.

[5] O. Ikeda, Y. Himuro, R. Kainuma, K. Ishida, Phase equilibria in the Fe-rich portion of the Fe–Ni–Si system, J. Alloy Compd. 268 (1998)130–136.

[6] A. Tasaki, S. Tomiyama, S.N. Lida Wada, R. Uyeda, Magnetic properties of ferromagnetic metal fine particles prepared by evaporation in argon gas, Jpn. J. Appl. Phys 4 (1965) 707–711.

[7] I.P. Yu, I. Fedorov, Electromagnetic properties of a colloidal suspension of nickel in paraffin, Zh. Tekhnich, 37 (1967) 726–728.

[8] A.E. Petrov, A.N. Kostygov, V.I. Petinov, Magnetic properties of Sn spherical particles of iron at a temperature 4.2-300 K, Fiz. Tverd. 15 (1973) 2927–2931.

[9] F.O. Schumann, Magnetic properties of Fe-based alloys, J. Appl. Phys. 87 (2000) 5460–5462.

[10] T. Chabi, N. Bensebaa, S. Alleg, S. Azzaza, J.J. Sunol, E.K. Hill, Effect of the Boron Content on the Amorphization Process Magnetic Properties of the Mechanically Alloyed Fe92−xNb8Bx Powders, J. Supercond. Nov. Magn. 32 (2019) 893–901.

[11] R. Hamzaoui, O. Elkedim, E. Gaffet, Friction mode and shock mode effect on magnetic properties of mechanically alloyed Fe-based nanocrystalline materials, J. Mater. Sci. 39 (2004) 5139–5142.

[12] B. Węgliński, J. Kaczmar, Effect of Fe_3P Addition on Magnetic Properties and Structure of Sintered Iron, Powder Metall. 23 (1980) 210–216.

[13] R. Gopalan, Y.M. Chen, T. Ohkubo, K. Hono, High saturation magnetization and microstructure in melt-spun Fe–P ribbons, Scripta Mater. 61 (2009) 544–547.

[14] S.F. Moustafa, W.M. Daousch, Synthesis of nano-sized Fe-Ni powder by the chemical process for magnetic applications, J. Mater. Proc. Technol. 181 (2007) 59–63.

[15] C. Xu, J.K. Xi, W.Gao, Improving the mechanical properties of borided layers by superplastic boriding, J. Mater. Process. Technol. 65 (1997) 94–98.

[16] P.X. Yan, X.M. Zhang, J.W. Xu, Z.G. Wu, Q.M. Song, High-temperature behavior of the boride layer 45# carbon steel, Mater. Chem. Phys. 71(2001)107–110 .

[17] A.H. Ucisik, C. Bindal, Fracture toughness of boride formed on low-alloy steels, Surf. Coat. Technol. 94-95 (1997) 561–565.

[18] Y. Wang, Q. Zhou, Q. Zhong, A Magnetic Properties and Corrosion Resistance of Fe-Si Alloy Coating Prepared on Mild Steel, Mater. Sci. 20 (2014) 1–5.

[19] A. Yang, H. Imrane, J, Lou, J. Kirkland, C. Vittoria, N. Sun, V.G. Harris, Effects of boron addition to the atomic structure and soft magnetic properties of FeCoB films, J. Appl. Phys. 103 (2008) 1–5.

[20] A. Calik, M.S. Karakas, N. Uçar, Ö.B. Aytar, The effect of boriding on the magnetization behavior of low carbon microalloyed steels, J. Mag. 17 (2012) 96–99.

[21] W.Y. Ching, Y-N Xu, B.N. Harmon, J. Ye, T.C. Leung, Physical Review B 42 (1990), Electronic structures of FeB, Fe_2B, and Fe_3B compounds studied using first-principles spin-polarized calculations, 4460-4470.

[22] J.B. Goodenough, A. Hamnett, G. Huber, F. Hullinger, M. Leiß, S.K. Ramasesha, H. Werheit, Physics of Non-Tetrahedrally Bonded Binary Compounds III, Springer, 1984, p. 52.

[23] T. Lundstrom, "Transition Metal Borides," in V.I. Matkovich (ed.), Boron and Refractory Borides, Springer-Verlag, 1977, p. 351.

[24] S. Rundqvist, An X-Ray Investigation of the Nickel-Boron System, Acta Chemica Scandinavica 13 (1959) 1193-1208.

[25] S. Rundqvist and F. Jellinek, The Structure of Ni_6Si_2B, Fe_2P and some related phases, Acta Chem. Scand. 13 (1959) 425-432.

[26] E. Lugscheider, H. Reimann and O. Knotek, "Das Dreistoffsystem Nickel–Bor–Silicium", Monatshefte für Chemie (Monat. Chemie) 106 (1975) 1155-1165.

[27] T. Tokunaga, K. Nishio, H. Ohtani, and M. Hasebe, "Phase Equilibria in the Ni–Si–B System," Materials Transactions 44 (2003) 1651-1654.

[28] D. Mu, B. Shen, C. Yang, X. Zhao, Microstructure Analysis of Borided Pure Nickel using Boriding Powders with SiC as Diluent, Vacuum 83 (2009) 1481–1484.

[29] N. Makuch, M. Kulka, M. Paczkowska, "Nanomechanical properties of gas-borided layer produced on Nimonic 80A-alloy", Ceramics International 43 (2017) 8255-8261.

[30] I. Ozbek, H. Akbulut, S. Zeytin, C. Bindal, A. H. Ucisik, The characterization of borided 99.5% purity nickel, Surf. Coat. Technol. 126 (2000) 166–170.

[31] Y. Azakli, S. Cengiz, M. Tarakci, Y. Gencer, Characterisation of boride layer formed on Fe–Mo binary alloys, Surf. Eng. 32 (2016) 589–595.

[32] R.Z. Valiev, D. Vishnyakov, R.R. Mulyukov, G.S. Fainstein, On the decrease of Curie temperature in submicron-grained nickel, Phys. Stat. Sol. 117 (1990) 549–553.