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EFFECT OF Fe-Ni SUBSTITUTION IN FeNiSiB SOFT MAGNETIC ALLOYS PRODUCED BY MELT SPINNING

ABSTRACT

Alloys of FeNiSiB soft magnetic materials containing variable Fe and Ni contents (wt.%) have been produced by melt spinning method, a kind of rapid solidification technique. The magnetic and structural properties of FeNiSiB alloys with soft magnetic properties were investigated by increasing the Fe ratio. X-ray diffraction analysis and SEM images shows that the produced alloy ribbons generally have an amorphous structure, together with also partially nanocrystalline regions. It was observed that the structure became much more amorphous together with increasing Fe content in the composition. Among the alloy ribbons, the highest saturation magnetization was obtained as 0.6 emu/g in the specimen with 50 wt.% Fe. In addition, the highest Curie temperature was observed in the sample containing 46 wt.% Fe.

Keywords: Alloy design; Curie temperature; FeNiSiB alloys; melt spinning; saturation magnetization

INTRODUCTION

Amorphous materials show significantly different physical and chemical properties compared to their crystalline counterparts. This is due to their disordered and metastable short-range atomic arrangement. In fact, such materials have excellent mechanical and physical properties such as high strength [1], high hardness and superior corrosion resistance [2–5]. Additionally, iron-nickel based amorphous alloys lacking of crystalline structure exhibit superior soft magnetic properties including high saturation magnetic flux density (B_s), low coercivity (H_c), high magnetic susceptibility (χ) [6]. Thanks to their excellent magnetic properties and other superior mechanical properties, Fe-Ni based amorphous alloys find various applications in critical industrial areas such as power transformers and magnetic sensors [2,7,8]. The first production of amorphous materials was carried out by P. Duwez et al., about 60 years ago, by rapidly cooling of the molten alloy by quenching [9]. Duwez’s work has been accepted by many researchers. In order to save energy and further
miniaturization in electromagnetic devices, many researchers have conducted serious studies in this field to enhance materials having high B, and excellent magnetic softness [10–12]. It is known that cooling rates higher than $10^8$ K/s are needed for occurrence of amorphous regions in the microstructure of iron, cobalt and nickel based amorphous alloys discovered before the 1990s [3,13]. The strength and hardness of the amorphous alloys at room temperature are higher than their crystalline counterparts with the same chemical composition; this is related to lack of dislocation, grain boundaries and other crystalline defects [14]. Generally, although there are certain methods for the production of the amorphous alloys, rapid solidification process (RSP) [15–17] and mechanical alloying (MA) are known to give more effective results than others [18].

It has become easier to obtain amorphous structures by means of melt spinning method, which is known to be effective and inexpensive among the rapid solidification processes recently. Many researchers doing research on the amorphous structures have preferred using the melt spinning method [12,19–21]. It is possible to produce the amorphous and/or nanocrystalline ribbons with a thickness of about 20-50 µm by cooling the molten alloy at cooling rates in range of $10^6$-$10^9$ K/s with melt spinning process [5]. Molten metal alloy is sprayed onto the surface of rotating cold copper disc and loses its heat rapidly. As a result, unlike a controlled cooling, the molten metal alloy, which cannot find enough time to crystallize, solidifies in an amorphous structure [22,23].

It is seen that the researchers have intensively discussed many different material groups with iron-based soft magnetic properties [24–27]. Thus, they revealed that the amorphous or nanocrystalline structures exhibit superior properties than their conventional crystalline counterparts. Luciano et al., showed that metallic glass FeSiB alloy outperforms silicon steel in 1997 [28]. In the following years, FeSiNBuC alloy, which is known by the trade name FINEMET, was developed [29,30]. However, it is known that expensive and hard-to-find rare elements such as Nb in this alloy increase the price of the material. Wang et al., examined the magnetic properties of FeNiSiN alloys and showed that they are superior to FINEMET alloy on their study in 2019 [31]. The saturation magnetization value ($M_s$) obtained by Wang was higher than the FINEMET. As can be seen, many researchers in the literature have carried out different studies to improve the magnetic and mechanical properties and reduce the cost of commercially used soft magnetic materials.

On the other hand, another important issue is that the ribbons are amorphous throughout their thickness. Accordingly, whether the structure can be completely or partially amorphous depends on several parameters such as the cooling rate of the molten alloy and distance of nozzle to the copper disc [32]. For example, it has been demonstrated by many researchers that the structure is completely amorphous on the surface of the ribbon in contact with the copper disc, but a certain part of its outer surface crystallizes [24,29,31]. Reason for this is that the heat transfer on the surface of the copper disc is faster than in the air [33]. Rotational speed of the copper disc is one of important parameters affecting the cooling rate [34]. In other words, the rotational speed of the copper disc plays a critical role in formation of the amorphous structure.

In this study, the Fe-Ni based soft magnetic alloy ribbons were produced by using the melt spinning method. Changes in the magnetic and the crystalline structure were investigated by adding Fe element to the alloy instead of Ni, which is relatively expensive in the alloy composition. Thus, it is aimed to reduce costs by enhancing soft magnetic alloys by means of the melt spinning method. In the study, Fe$_{50}$Ni$_{42}$Si$_6$B$_2$ alloy showed the best magnetic property and the saturation magnetization was as high as 0.6 emu/g. Therefore, the Fe$_{50}$Ni$_{42}$Si$_6$B$_2$ alloy can be nominated as a cheap candidate for use in applications such as the soft magnetic power transformers and the magnetic sensors.
MATERIALS AND METHODS

Chemical composition of the alloys studied within scope of the study is given in Table 1. The alloys whose compositions were determined within scope of the study were first melted twice in a high-frequency vacuum induction furnace to be more homogeneous. Before starting melting process, the furnace atmosphere was reduced to a vacuum level of $10^{-4}$ mbar twice, and inside of the furnace was cleaned of harmful gases such as oxygen and finally 500 g of ingot was produced by the melting in a high purity argon atmosphere. For production of the alloys, alloying elements of Fe (99.98% purity), Si (99.99% purity), Ni (99.97% purity) and B (95% purity) procured from Alfa Aesar were used.

A visual summarizing the experimental work done is given in Fig. 1. Accordingly, ingots produced in an appropriate composition were melted again under the argon atmosphere by the melt spinning method and sprayed on the copper disc. The molten metal was sprayed by means of the 0.5 mm thick nozzles, onto the copper disc rotating at 25 m/s with the 400 mbar argon pressure [35]. A ribbon of approximately 10 mm width and 25 µm thickness was produced.

![Image](image_url)

**Fig. 1.** Schematic of the production process for the ingots and the ribbons

In X-ray diffraction (XRD) (Bruker D8) analyzes, graphite monochromator and high energy Cu-Kα radiation ($\lambda=1.5406$ Å) were used and the 2θ angle was kept between 3° and 90° for measurements. Magnetic saturation analyzes (VSM, LAKE SHORE 7407) were applied under 500 kA/m magnetic field. Curie temperature determination tests were checked by means of a vibrating sample magnetometer (VSM, LAKE SHORE 7407) under the argon atmosphere at a speed of 2.5 °C/s under 4 kA/m magnetic field. In addition, SEM and EDX mapping analyzes were performed on the TESCAN MIRA 3 brand device. In this way, the homogeneous distribution of alloying elements in the samples, the thickness of the ribbons and whether microcrystals were formed or not [36,37].

RESULTS AND DISCUSSION

In Fig. 2, the X-ray diffraction (XRD) patterns of the alloy ribbons of F1, F2 and F3 by the melt-spinning of Fe-Ni-based alloys having soft magnetic properties are shown. As can be seen, from the XRD analysis of each alloy, it is seen that the alloys are generally in amorphous structures and also partial nanocrystalline phases are obtained within these
amorphous structures. Accordingly, a distinct sharp Bragg peak is observed at 2\(\Theta\)=44° in the XRD pattern representing alloy F1 (Fe\(_{42}\)Ni\(_{50}\)Si\(_{6}\)B\(_2\)).

![XRD patterns for alloys F1, F2, and F3](image)

**Fig. 2.** The XRD patterns for the alloy ribbons of F1 (black), F2 (red) and F3 (blue) produced by the melt spinning method.

This indicates that the specimen is partially crystallized. It has been determined that the alloy F1 is generally amorphous, but peaks of orthorhombic FeB, Ni\(_3\)B and rhombohedral B\(_{31}\)Si\(_{11}\) nanocrystalline intermetallic phases with high melting point are also observed. The XRD results obtained in the alloy F1 agree with Wang’s work in 2019 [31]. No sharp Bragg diffraction peaks were observed in the XRD patterns representing alloys F2 (Fe\(_{46}\)Ni\(_{46}\)Si\(_{6}\)B\(_2\)) and F3 (Fe\(_{50}\)Ni\(_{42}\)Si\(_{6}\)B\(_2\)). The XRD peak, which is sharp in the alloy coded as F1 at approximately 2\(\Theta\)=44°, has a diffuse characteristic in the alloys F2 and F3. According to these results, it is seen that the alloys F2 and F3 are mostly amorphous. In the XRD pattern representing the alloy coded as F3, Fe\(_2\)Si nanocrystalline intermetallic phase is encountered at approximately 2\(\Theta\)=44°. It was determined that intensity of the peak of FeB nanocrystalline phase increased due to increase in the amount of Fe and decrease in the amount of Ni in the alloys F3 compared to the alloy F2. In the study of Jia et al. in 2020, amorphous forming ability (AFA) of the alloys increased with increase of the Ni content in the range of 0-20% by
weight [10]. However, in our study, a different result was obtained because the amount of Ni was quite high. According to the obtained results, it is seen that the AFA of the alloy increases with the substitution of the Ni by Fe in the alloy composition and almost the entire structure turns into amorphous. The reason of this, it is thought that it may be caused by similarity in atomic packing of Fe and Ni elements, whose atomic radius are 1.26 Å and 1.24 Å, respectively. Atomic size differences do not change much, with replacement of the Ni and Fe elements in the alloy. On the other hand, it is known that the atomic size differences affect crystallization process [38]. According to Inoue, in order to obtain an amorphous structure in the alloy composition, the atomic size difference between the elements forming the alloy should be above 12 wt.% [39–41]. In addition, it has been proven in previous studies that Si atoms in magnetic alloys play a supporting role in forming the amorphous structure [39,42]. Although atomic radii of the Fe and Ni elements are close, it can be said that amorphous forming ability (AFA) of the Fe element with the Si element is slightly better. Also, it is known that the B element used in the alloy improves the AFA, like the C element [41,43]. This is explained by similar atomic radius (0.85 Å and 0.86 Å, respectively), valences, and electronegativity of the B and C elements [39,44]. It is thought that with replacement of the Ni element with the Fe element, the atomic size difference increases a little more and the AFA ability increases.

Fig. 3 shows the M-H measurement results and typical hysteresis curves of the alloy ribbons of F1, F2 and F3 by the melt spinning made via vibrating sample magnetometer (VSM) analysis of the soft magnetic ribbons of three different compositions. Accordingly, the highest saturation magnetization value was observed in the alloy F3. Increase in the amount of Fe significantly affected the saturation magnetization (Ms) value of the alloy, and the Ms value increased from 0.4 emu/g to 0.6 emu/g. Depending on the increase in Fe content in the alloy composition, the soft magnetic property of the material increased significantly. This situation can be explained by the following mechanism: Based on the energy band theory, magnetic moment of the Fe atom is 2.2 μB, and the magnetic moment of the Ni atom is 0.6 μB. Hence, it is thought that replacement of the Ni atom by the Fe atom in the alloy composition will increase the saturation magnetization value of the alloy [32,45,46]. From the inset hysteresis curve in Fig. 3, coercivity values of the soft magnetic alloy ribbons were calculated as 3.0 A/m, 4.1 A/m and 3.1 A/m for the alloy ribbons of F1, F2 and F3 respectively. Table 1 shows the saturation magnetization (Bs), the magnetic coercivity (Hc) and Curie temperature (Tc) values calculated for F1, F2 and F3 samples. As shown in the Table 1, the Hc value slightly increased from 3.0 A/m for the alloy F1 to 4.1 A/m for the alloy F2, with the increase in the Fe content. However, it decreased to 3.1 A/m at the 50 wt.% Fe ratio. These coercivity values are well below the studies in the literature [32,47]. Because it is known that annealing process applied to the soft magnetic materials increases the coercivity values [32,47].

<table>
<thead>
<tr>
<th>Properties/Alloys</th>
<th>Saturation Magnetization, B_s (emu/g)</th>
<th>Coercivity, H_c (A/m)</th>
<th>Curie Temperature, T_c (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>0.4</td>
<td>3.0</td>
<td>700</td>
</tr>
<tr>
<td>F2</td>
<td>0.3</td>
<td>4.1</td>
<td>730</td>
</tr>
<tr>
<td>F3</td>
<td>0.6</td>
<td>3.1</td>
<td>680</td>
</tr>
</tbody>
</table>
Fig. 3. The magnetization curves of the alloy ribbons of F1 (black), F2 (red) and F3 (blue) produced by the melt spinning.

Fig. 4 shows M-T curves of the alloy ribbons of F1, F2 and F3 by the melt spinning, which give variation of the magnetization with the temperature. As seen from the curves, the Curie temperature increased from 700 K to 730 K with the increase of the Fe content in the alloy ribbons from 42 wt.% to 46 wt.%. When the amount of Fe in the alloy composition rises to 50 wt.%, a decrease to 680 K was observed in the Curie temperature. This situation can be explained by the following reasons: It is known that exchange interaction of 3d-electrons affects the $T_c$ temperature and is directly related to associated bond electron density [48]. Accordingly, localized electrons in the 3d-shell can interact only over an atomic distance. However, non-localized electrons in s-shell are known to interact over six atomic distances [49]. Therefore, since the Fe and Ni atoms have 6 and 8 electrons in the 3d-band, respectively, the electron exchange here decreases with the increase in Ni content. On the other hand, with the increase in the Ni content, contribution of the s-shell electrons to the $T_c$, increases [50]. Consequently, change in the $T_c$ is determined by cooperative contribution of the 3d-electrons and the s-electrons [45]. Effect of the localized or the non-localized electrons in the 3d- and s-shells on the magnetic properties was clearly seen. Indeed, the change in the Fe and Ni contents has a significant effect on the magnetic properties of the alloys.

Fig. 4. Thermo-magnetic (T-M) curves of the alloy ribbons of F1 (black), F2 (red) and F3 (blue) produced by the melt spinning.
Figure 5 shows the SEM and EDX mapping analysis results of the samples. It is seen that the ribbons thicknesses vary between about 40-50 µm. It is seen that our results are compatible with the studies in the literature [18,51]. It is known that the disc rotation speed indirectly affects the strip thickness and cooling rate in order to form an amorphous structure. Therefore, it is understood from both XRD and SEM images that the structure can attain an amorphous form at the disk rotation speed of 25 m/s we have chosen. As can be seen from the SEM results in Figure 5, no crystal structure was found. On the other hand, in the EDX maps in Figure 5, it is seen that the elements in the samples show a homogeneous distribution.

**CONCLUSIONS**

The soft magnetic alloy ribbons with three different chemical compositions were produced by the melt spinning method, which is one of the rapid solidification methods. According to this;
- In the results of the XRD analysis of the alloy ribbons, it was clearly seen that the structure turned into a much more amorphous form with the increase of the Fe content. Although there are partial nanocrystalline phases in the alloy ribbons with high Fe content, the structure was found to be substantially amorphous.
- According to the results of the VSM analysis, it was observed that the saturation magnetization increased with the increase of the iron content in the alloy ribbons.
- From the M-T curves of the alloy ribbons, it was observed that the amount of Fe increases up to 46 wt.% increased the $T_c$ temperature.
- The magnetic coercivity value slightly increased with the increase of the Fe content up to 46 wt.%.

According to these results, it is thought that increasing the Fe constituent, which is cheaper than Ni, in the Fe-Ni soft magnetic materials used in sensitive electrical and electronic components, may be effective in terms of both economic and magnetic properties.
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