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Microstructure, hyperfine interaction and magnetic transition of Fe-25%Ni-5%Si-x%Co alloys

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Abstract Morphological and magnetic properties in Fe-25%Ni-5%Si-x%Co (x = 0, 10, 15) alloys are investigated. Scanning electron microscopy (SEM), Mössbauer spectroscopy and AC magnetic susceptibility measurements are used to determine the physical properties of alloys. The martensite morphology changed depending on the Co content. The Mössbauer study shows that the volume fraction and hyperfine field of martensite increases while isomer shift values decrease with increasing Co content. On the other hand; AC susceptibility results showed that; Co is an effective element which can be used to control both the magnetic transition and martensitic transformation temperatures.

Keywords AC susceptibility · Mössbauer spectroscopy · Fe-Ni-Si-Co alloys · Hyperfine magnetic field

1 Introduction

The martensitic phase transition from austenite to martensite, i.e., from basically non-magnetic FCC structure to the BCC or tetragonal structure which is in magnetic order usually occurs when austenite is supercooled. It is also well known that the plastic deformation of austenite can induce martensitic transformation in Fe based alloys and martensitic transformation can be also induced under different external forces such as hydrostatic pressure and magnetic field [1–3]. The elements constituting the alloy is one of the important factors affecting the characteristics of martensitic transformation such as hardness of austenite, morphology of martensite, effect of shape memory and magnetic properties of alloys

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[4–7]. For instance, even a small amount of Si, Mo or Co addition changes the martensite morphology, magnetic properties and hardness of the alloy [4, 6, 8, 9]. Additionally, increasing Si content causes the martensite morphology to change from lath to twinning martensite plate and the volume fraction of martensite decreases according to a previous study of Gungunes et al. [4].

Phase transformations from austenite to martensite in Fe based alloys effects the magnetic behavior of alloys [10]. In the austenite phase formed as a result of martensitic transformations, many ferrous alloys and steels which are ferromagnetic in the martensite phase display paramagnetic behavior as Shimizu and Kakeshita previously reported [11]. Noteworthy to mention here, for the magnetic characterization of the materials, Mössbauer spectroscopy is one of the most efficient and precise methods which enables the determination of some properties like the isomer shift values, the hyperfine magnetic field and the volume fraction of austenite and martensite phases [4, 9, 12].

According to the study of Tanaka et al., the addition of Co promotes the formation of thin-plate martensite and also improves the Shape Memory (SM) effect in FeNiSi alloys [2]. However, there is no sufficient information about the effect of Co addition on magnetic properties of FeNiSi alloys in the literature. For this reason, this study was conducted to investigate the influence of Co content on morphological, magnetic and mechanical properties of Fe-25%Ni-5%Si-x%Co alloys.

2 Experimental method

Arc melting technique was employed to prepare the Fe-25%Ni-5%Si-x%Co (x = 0,10,15) alloys by using 99.9 % pure Fe, Ni, Si and Co elements under a protective argon atmosphere. Investigated alloys were austenitized at 1100 °C for 24 h in evacuated silica capsules prior to quenching in ice water. In order to thermally induce martensite, the alloys were immersed in liquid nitrogen as a final step of the process. Bulk samples were polished with a 2–3 μm diamond paste and etched in a solution containing 80 ml H_2O_2, 5 ml HF and 15 ml H_2O to prepare for the SEM (JEOL JSM-5600 Scanning Electron Microscope) investigation. 60 μm thick foil specimens were prepared for Mössbauer spectroscopy by mechanical and chemical thinning processes. ^{57}Fe Mössbauer spectra were recorded at room temperature in the standard transmission geometry using 25 mCi ^{57}Co source diffused in Rh and the chemical isomer shifts were quoted relative to α-Fe. The parameters and relative volume fractions of the austenite and martensite phases were determined using a Normos-90 computer program. In order to measure the magnetic susceptibility, samples in the form of discs having 1.5 mm radius and 1.5 mm thickness were prepared from the bulk material. A computerized AC susceptometer (LakeShore 7130) with a closed cycle refrigerator between 300 K and 20 K was used to conduct the experiments. The magnitude of the applied AC field is 80 A/m and the frequency is 111 Hz.

3 Results and discussion

3.1 Microstructure characterization of martensite

The effect of Co content on martensite morphology was investigated. According to our previous study, different martensite morphologies were observed in Fe-%24.5Ni-%4.5Si alloy which are shown in Fig. 1. [12]. We also collected the TEM micrographs of

Fig. 1 SEM Micrograph of martensite plate in Fe-24.5%Ni-4.5%Si alloy (12)

Fe-%24.5Ni-%4.5Si alloy with electron diffraction pattern in another previous study and the observed martensite morphologies were determined to be martensite plates and twinned martensite from the TEM micrographs [13]. It is well known that the lenticular martensite in ferrous alloys consists of the following three distinctive regions: midrib, twinned region and untwinned region [14, 15]. The midrib is localized in the middle of the lenticular martensite plate [15]. Additionally, lenticular martensite which forms at intermediate temperatures between lath martensite and thin plate martensite is plate-like with curved interfaces [15]. Figure 2 shows the morphologies of the martensites formed in the Fe-25%Ni-5%Si-10%Co alloy which are in line with the figures presented in the literature on lenticular martensite in ferrous alloys [14, 15]. The martensite morphology formed in the Fe-25%Ni-5%Si-15%Co alloy is shown in Fig. 3. which is mainly composed of lenticular martensite. As seen in the figure, the lenticular martensite formation is facilitated by increasing Co content. It is well known that the martensite morphology of ferrous α martensite is classified into several kinds, i.e. lath, butterfly, lenticular and thin plate shapes [4]. Amongst them, the substructure of lath martensite consists of high density dislocations [16] while lenticular martensite consists of three distinct regions: fine transformation twins in the midrib, the twinned region and the untwinned region, respectively [14]. The lath martensite has advantages of strength while twin martensite displays high strength but a brittle character [17].

Tanaka et al. investigated the effect of Co addition on the microstructure, shape memory effect and mechanical properties in Fe–28Ni–6Si and Fe–28Ni–6Si-10Co alloys and reported that both were composed of lenticular martensite in non ausaged alloys [5]. In our study however, we could observe no lenticular martensite in the Fe-%24.5Ni-%4.5Si alloy which may be attributed to the amount of Ni used in our previous study [12]. This is in good agreement with the results of Shibata et al. and others which report that the martensite morphology in the Fe–Ni alloy containing about 28.5–33 mass% Ni is lenticular [14, 15, 18]. In this study, we added %10 Co to Fe-%25Ni-%5Si alloy which caused formation of lenticular martensite and increasing the amount of Co to %15 increased the amount of lenticular martensite as well. From this result, we can say that addition of Co to Fe-%25Ni-%5Si alloy causes the formation of lenticular martensite.

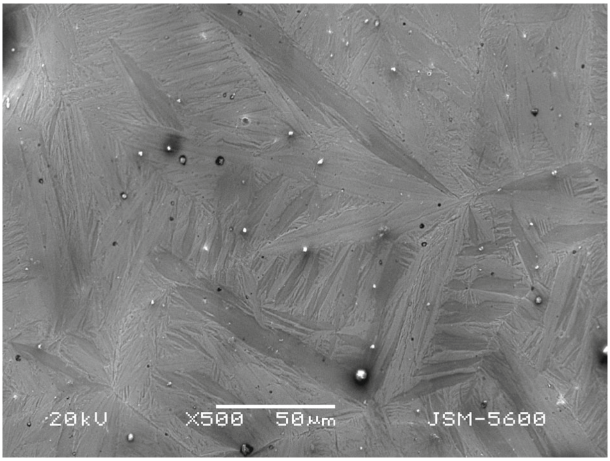

Fig. 2 SEM Micrograph of martensite plate in Fe-25%Ni-5%Si-10%Co alloy

It is well accepted that the martensite morphology is dependent on many factors, such as alloy composition [4, 5, 7], austenite grain size [19], ausaging [2, 20], and martensite formation temperature [7, 16], however no one has shed light on the reason why morphology exists in ferrous α martensite so far.

3.2 Mössbauer studies

Mössbauer spectroscopy was utilized for the depiction of magnetic properties of austenite and martensite phases. The spectra collected from the measurement of the samples at room temperature are given in Fig. 4. Heat treatment transforms the Mössbauer spectra of the alloys to a typical six-line spectrum of the ferromagnetic or antiferromagnetic structure and also a singlet corresponding to the matrix austenite [4, 12, 13]. Table 1 is comprised of the Mössbauer parameters such as isomer shift and hyperfine magnetic field with the calculated volume fraction of each phase. The hyperfine magnetic field H determined by the Mössbauer results are 30.09 ± 0.42 [12], 31.64 ± 0.033, 32.74 ± 0.021 T for the alloys containing 0%Co, 10%Co, 15%Co, respectively. When the results of the measurements are analyzed, it can clearly be seen that, the addition of Co to the related FeNiSi alloy increases the average hyperfine magnetic field gradually as the amount of Co added to the alloy increases.

As stated in the report of Ishikawa et al., the hyperfine magnetic field is primarily proportional to the magnetic moment of iron atoms [21]. Accordingly, hyperfine field in Fe-Ni-Si-Co alloys increase with the addition of Co and the main reason for this is the increase in the magnetic moment of Fe. Likewise, findings of Qin et al.is stating that the increasing amount of Si in Fe-Mn-Si alloys as well increases the hyperfine magnetic field [22]. The change of the exchange "potential" influences primarily transition temperature, while the saturation field may change either way and the spin density is considered to be responsible of the increase in the hyperfine magnetic field [23, 24]. In contrast to these studies, our previous study showed that increasing Si content decreases the hyperfine magnetic field [4].

The variations in the isomer shift values reveal the changes of the s-electron charge density at the Fe nucleus. Our current Mössbauer results indicate that the value of isomer shifts

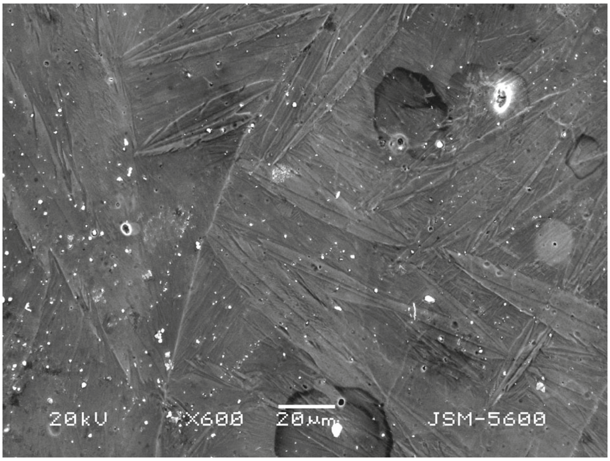

Fig. 3 SEM Micrograph of martensite plate in Fe-25%Ni-5%Si-15%Co alloy

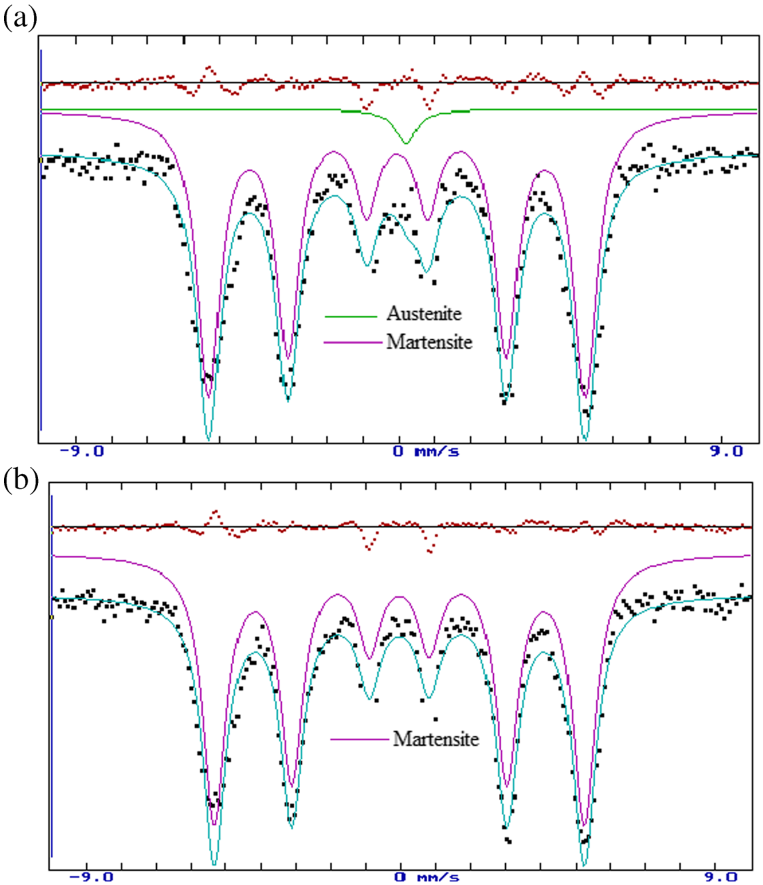

Fig. 4 Mössbauer spectra for **a** Fe-25%Ni-5%Si-10%Co **b** Fe-25%Ni-5%Si-15%Co alloys

Table 1 Mössbauer parameters of the studied alloys

Alloys	Martensite morphology	M_s (K)	T_c (K)	δ_A, mms^{-1}	δ_M, mms^{-1}	%M	%A	$H(T)$
Fe-24.5%Ni-4.5%Si (12)	Plate+ twinned	230	243	0.093 ± 0.018	0.09 ± 0.05	58.31	41.69	30.09 ± 0.42
Fe-25%Ni-5%Si-10%Co	Lenticular+ other type	276	–	0.077 ± 0.005	0.195 ± 0.007	94.59	5.41	31.64 ± 0.028
Fe-25%Ni-5% Si-15%Co	Lenticular+ other type	251	–	0.063 ± 0.002	–	100	0	32.74 ± 0.021

M_s is the martensite start temperature, T_c is the curie temperature, H(T) is the magnetic field in Tesla, δ is the isomer shift, %M and %A are the volume fractions of martensite and austenite, relatively

decreases with increasing Co content. The decrease in the isomer shift value indicates an increase in the 4s electron density at Fe nucleus [23]. This decrease in isomer shift with increasing Co content can be a result of a change in the occupation of the Fe 3d shell. According to Qin et al. [22] the electrons in the 3d shell of Fe have a screening effect on the Fe nucleus from 3s and 4s electrons which contribute to the s electrons charge density at the nucleus. Therefore, when Co is added to Fe-Ni-Si alloys, the 3d electron density falls and the s electron density at the Fe nucleus increases. Blachowski and Wdowik investigated the effect of impurity of transition metals on charge and spin density in binary iron alloys. Additionally, Mössbauer experimental results are discussed in their study. According to their results, the average electron density on the iron nucleus generally decreases with the increasing number of the impurity outer shell electrons. The average spin density versus the number of the outer shell electrons of the impurity (N_e) changes linearly for 4d and 5d metals, however 3d metals have oscillatory character. Correlation between average electron and spin density indicates that the electron density is lowered with the increasing spin density. The correlation between these two quantities is the weakest for 3d metals [24].

3.3 Magnetic susceptibility

To investigate the magnetic phase transition and the martensitic transformation temperature, the temperature dependence of the magnetic susceptibility for each sample was measured. Results are shown in Fig. 5. As seen in the Fig. 5a, at 243 K (T_c; Curie temperature) the AC- susceptibility increased sharply during phase transition from paramagnetic to ferromagnetic in Fe-25%Ni-5%Si alloy. It is well known that a large number of ferromagnetic domain forms in the ferromagnetic region which are aligned in the direction of applied AC field. The magnetization is essentially defined as the rearrangement of these domains [12]. During the cooling process, the magnetic susceptibility values suddenly changed at 230 K (M_s; Martensite start temperature) because of athermal martensitic transformation. Here the magnetic transition temperature is higher than the crystallographic phase transition. As seen in the Fig. 5b and c, there is no magnetic phase transition in Fe-25%Ni-5%Si-10%Co and Fe-25%Ni-5%Si-15%Co alloys, respectively. AC- susceptibility of Fe-Ni-Si alloys with Co gradually decreased as the temperature decreased and suddenly changed at 276 K and 251 K for 10% Co and 15% Co, respectively. According to these results, M_s increases with addition of Co in Fe-25%Ni-5%Si alloy but M_s decreases with increasing Co content

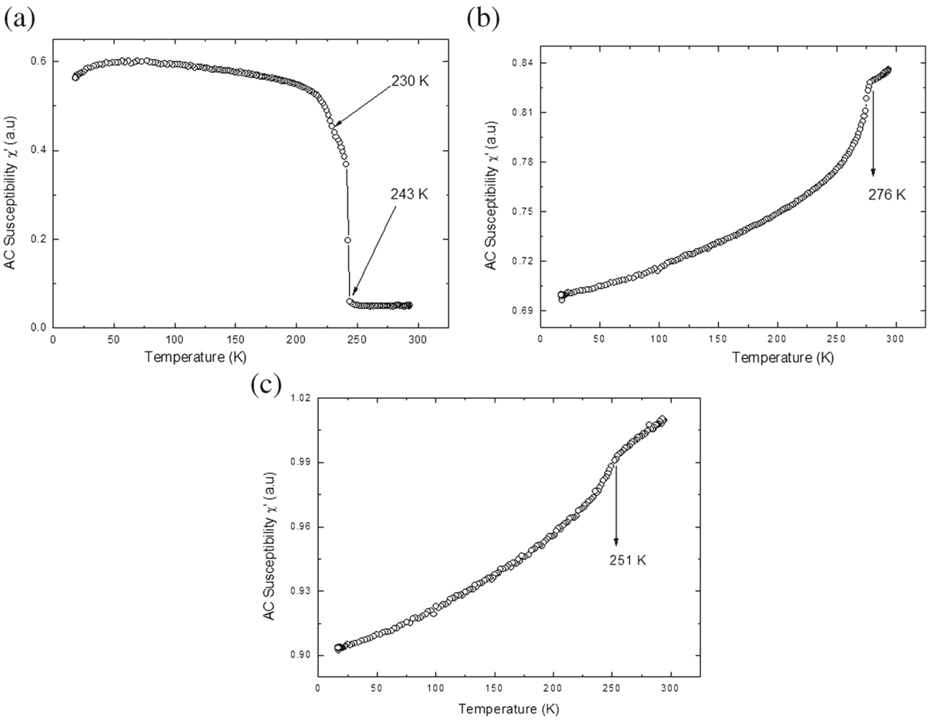

Fig. 5 Temperature dependence of AC- susceptibility for **a** Fe-25%Ni-5%Si, **b** Fe-25%Ni-5%Si-10%Co, **c** Fe-25%Ni-5%Si-15%Co alloys

in Fe-25%Ni-5%Si-x%Co alloys. Figure 5 also shows the temperature dependencies of the magnetic susceptibility in the Fe-25%Ni-5%Si-x%Co alloys. As can be seen in the figure, the magnetic susceptibility values increase with increasing Co content. The martensite phases are composed of high density dislocations and dislocation density of twinned martensite less than other type martensite [25]. The crystal structure defects such as dislocations may prevent the motion of magnetic domains. SEM results of these studies shows the lenticular martensite formation is facilitated by the addition of Co content in Fe-25%Ni-5%Si alloy. Thus, dislocation density decreases with increasing of Co content and the magnetic susceptibility values become relatively bigger.

4 Conclusions

The effect of the addition of Co on the microstructure, microhardness, martensitic and magnetic transitions in the FeNiSi alloys were investigated and the following findings were obtained:

1. According to SEM results, the lenticular martensite formation is facilitated by the addition of Co content in Fe-25%Ni-5%Si alloy. The martensite morphology changes to mainly partial twinned lenticular martensite with increasing of Co in investigated alloys.

2. According to Mössbauer results; The amount of martensite increases with addition and increasing of Co content in related Fe-25%Ni-5%Si alloy. At the same time the hyperfine magnetic field of martensite increases but the isomer shift decreases with increasing of Co content.
3. M_s increases with addition of Co in Fe-25%Ni-5%Si alloy but M_s decreases with increasing Co content in Fe-25%Ni-5%Si-x%Co alloys
4. Co is an effective element which can be used to control magnetic transition. Also AC susceptibility value increases with increasing of Co content.

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