Süleyman Demirel Üniversitesi
Fen Bilimleri Enstitüsü Dergisi
Cilt 27, Sayı 1, 27-32, 2023

Süleyman Demirel University
Journal of Natural and Applied Sciences
Volume 27, Issue 1, 27-32, 2023

DOI: 10.19113/sdufenbed.1094481

Investigation of Martensitic Phase Transformation and Magnetic Properties of Fe-30%Ni-2.6wt%Mo-X%Co Alloys

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(Alınış / Received: 31.03.2022, Kabul / Accepted: 28.10.2022, Online Yayınlanma / Published Online: 25.04.2023)

Keywords
Thermally induced martensite,
Crystallographic properties,
Magnetic properties,
TEM,
SEM,
Mössbauer spectroscopy

Abstract: In this study, the microstructure of thermal effective martensitic phase transformation observed in the Fe-30wt.%Ni-2.6wt.%Mo-Xwt.%Co (X = 0.8, 1.8) alloy was investigated morphologically and crystallographically by using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). In SEM studies, it was observed that the morphology of the martensite phase changed from lath and lenticular structure to massive structure with the addition of Co to the alloy. In addition to this, nano martensite formation was also observed as another effect of Co addition (figure 2c, d). Properties of lenticular martensite, electron diffraction pattern of austenite and martensite structures were given by TEM studies. According to the Differential Scanning Calorimetry (DSC) analysis, it was determined that the martensitic transformation temperature (M_s) significantly increased with the increase of the Co amount in the alloys. Also, by using Mössbauer spectroscopy, it was shown that the amount of martensite increased with the increase of Co amount and the magnetic order of the alloy changed accordingly.

Fe-30%Ni-%2.6Mo-X%Co Alaşımlarının Martensitik Faz Dönüşümünün ve Manyetik Özelliklerinin Araştırılması

Anahtar Kelimeler
Termal etkili martensit,
Kristalografik özellikler,
Manyetik özellikler,
TEM,
SEM,
Mössbauer spektroskopisi

Öz: Bu çalışmada, Fe-30%Ni-2.6%Mo-X%Co (X = 0.8, 1.8) alaşımında gözlenen termal etkili martensitik faz dönüşümünün mikro yapısı, taramalı elektron mikroskobu (SEM) ve geçirmeli elektron mikroskobu (TEM) kullanılarak morfolojik ve kristalografik olarak incelenmiştir. SEM çalışmalarında, alaşıma Co eklenmesiyle martensit fazın morfolojisinin iğnemsi ve merceksi yapıdan masif yapıya dönüştüğü gözlenmiştir. Bununla birlikte Co ilavesinin diğer bir etkisi olarak nano martensit oluşumu da görülmüştür (figure 2c, d). Lentiküler martensitin özellikleri, östenit ve martensit yapılarının elektron kırınım modeli TEM incelemeleri ile verilmiştir. Diferansiyel Taramalı Kalorimetre (DSC) analizlerine göre, alaşımlardaki Co miktarının artmasıyla martensitik dönüşüm sıcaklığının (M_s) önemli ölçüde arttığı belirlenmiştir. Ayrıca Mössbauer spektroskopisi kullanılarak Co miktarının artmasıyla martensit miktarının arttığı ve alaşımın manyetik düzeninin buna bağlı olarak değiştiği gösterilmiştir.

1. Introduction

The morphology and substructure of martensite formed by thermal and deformation effects were extensively studied in Fe-Ni based alloys. When Ti, Mo, Si are added as the third element to Fe-Ni based alloys, the physical and mechanical properties of these alloys change. Martensitic transformations in particular (f.c.c $\rightarrow$ b.c.c or f.c.c. $\rightarrow$ h.c.p.) and change of magnetic properties (paramagnetic to ferromagnetic) increase the use of these alloys in industry [1-5]. In a study by Tanata et al. [6], the change in the morphology of the martensite phase formed by the addition of Co to the Fe-Ni-Si alloy was examined. The addition of Co is the reason for the increase in the austenite phase and the easier formation of the martensite phase (thin plate shaped). Shibata et al. [7] examined different martensite morphologies and martensite starting temperatures in Fe-Ni based alloys. In Fe-30wt.%Ni-Xwt.%Mo (X = 0.8, 1.8, 2.6) alloys, the M_s decreased as the Mo ratio increased, the percentage of martensite formation decreased, and the Mo element austenite

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was a stabilized element [8]. Yasar et al. [4] investigated the effect of Ti on the morphological and crystallographic properties of diffusionless phase transformations in Fe-30wt.%Ni-Xwt.%Ti alloys. Although many studies have examined the characteristics of thermally effective martensitic transformations (kinetic, crystallographic, and morphological) by adding the third element to Fe-Ni alloys, the effects of the fourth element in these alloys have not been fully revealed. In the present study, austenite grain size, martensite morphology, M_s, and magnetic properties of Fe-30wt.%Ni-2.6wt.%Mo-Xwt.%Co (X = 0.8, 1.8) alloys were examined with different physical methods.

2. Material and Method

The alloy used for this study is Fe–30%Ni–3.6% Mo-XCo (wt.%) (X=0.8 and 1.8). This alloy was prepared using the technique vacuum induction melting under argon atmosphere. Samples were prepared with a thickness of 150 μm and placed in silica capsules (evacuated). The samples in the silica capsules were heat treated in the heat treatment furnace at 1100 °C for 12 hours and then cooled by throwing them into room temperature water. These samples were then stored in liquid nitrogen at -196 °C for 10 seconds and thrown into the water at room temperature. For SEM studies, these heat-treated samples were thinned up to 50 μm. Finally, a mechanical polishing treatment was applied to these samples. The SEM and TEM samples were polished at Jet-polishing using a solution consisting of 90ml Perchloric acid ($HClO_4$), and 10 ml Methanol (CH_3OH). Microstructural characteristics of the surfaces of the samples were examined with JEOL JSM5600 SEM with a power of 30 kV. For TEM studies, a JEOL 3010 type device was used. With this device, it was worked at 300 kv operating voltage.

70 μm thick samples with a diameter of 3 mm were prepared from room temperature austenite phase samples for DSC measurements. For the thermal analysis of these alloys, a PerkinElmer Sapphire model thermal analyzer (DSC) was used. Measurements were made between 20 °C and -120 °C under a cooling rate of 5 °C/min.

Samples with austenite and martensite phases at room temperature were prepared for the Mössbauer spectrometer using mechanical and chemical thinning processes. The magnetic properties and volume quantities of the parent and product phases were determined using Mössbauer spectrometer. A spectrometer with a 50 mCi ^{57}Co radioactive source (diffused in Rh) was used for the study. The normous-90 computer program was used for the obtained data.

3. Results and Discussion

SEM observation revealed that the austenite grain and austenite matrix in the examined Fe–30wt.%Ni–2.6wt.%Mo-Xwt.%Co alloys transform to α'-martensite. Figure 1 shows the formation morphology of austenite grains in these alloys depending on the amount of Co.

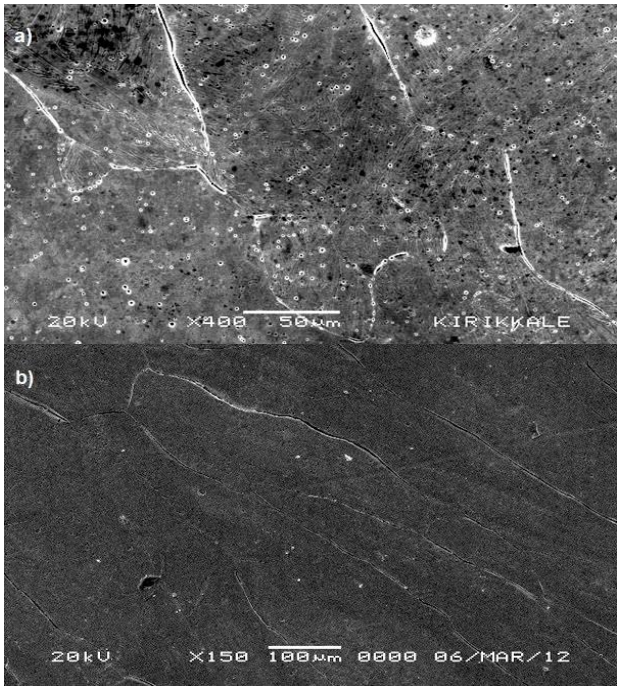

Figure 1. Austenite grains formed in samples cooled by being thrown into room temperature water after 12 hours of heat treatment at 1100 °C (a) Fe-30wt.%Ni-2.6wt.%Mo-0.8wt.%Co, (b) Fe-30wt.%Ni-2.6wt.%Mo-1.8wt.%Co.

In many studies, it has been revealed that elements added to Fe-Ni based alloys (Ti, Mo) affect grain sizes [4, 8, 9]. It is understood from figure 1 that the grain size has grown with the increase of the amount of Co.

In Figure 2a-b, the SEM image of the sample, which was thrown into liquid nitrogen and then removed (waited for 10 seconds), is given. Athermal martensite crystal was formed by this heat treatment applied to the austenite phase and subsequent cooling in liquid nitrogen. The morphology of lenticular martensite formed by thermal effect is shown in Figure 2a with arrows. In addition, the lath and lenticular structures are shown in Figure 2b with arrows 1 and 2 in order. In many previous studies on ferrous alloys subjected to heat treatment, it has been observed that the product phase (martensite structure) formed can be in the form of laths or plates [8, 10, 11].

The midrib and twinned regions are recognized by suitable etching and the Martensite/Austenite (M/A) interface is marked on the figure. According to the information obtained on the basis of previous studies, lenticular martensites have regional internal twinning in their structures, while thin-plate martensites contain complete internal twinning (fig 2a, b). The relationship between the thin plate and lenticular martensite morphologies has been studied in detail and has shown variation in these morphologies with deformation effect [12-14].

Figure 2. Thermally induced b.c.c. (α′) martensite structures; (a-b) lath and lenticular martensite in Fe-30wt.%Ni-2.6wt.%Mo-0.8wt.%Co, (c-d) massive and lenticular martensite in Fe-30wt.%Ni-2.6wt.%Mo-1.8wt.%Co.

Nano martensite formation was observed with the addition of Co (figure 2c, d). The change in morphology with the increase of Co in the alloy is seen in Figure 2c, d. This change is noticeable as the lenticular and lath decrease in martensite morphology but increase in the amount of massive martensite as well. In addition to the decrease in lenticular martensite in particular, the midrib structures formed in small size arep noteworthy (the regions marked with arrows in Figure 2d). In addition, the twinnings that occur within these midrib structures are noteworthy.

Crystallographic analysis of α' martensite occurring with thermal effect in Fe-Ni-Mo-Co alloys produced similar results. In TEM investigations, the formation of partially lenticular plates was observed after heat treatment in the parent phase (austenite) of the Fe-30wt.%Ni-2.6wt.%Mo-0.8wt.%Co alloy. The diffraction pattern and key diagram are taken from the region marked with the bright-field and dark-field TEM images belonging to the lenticular martensite plates are given in Figure 3. In the diffraction pattern here, the zone from the parent phase corresponds to $[310]_{\gamma}$, while the zone of the product phase corresponds to $[131]_{\alpha'}$.

Thanks to DSC analysis, M_s, which is the transformation start temperature of the product phase, was found as -91 °C and -94 °C for the X=0.8, 1.8 respectively in the Fe-30wt.%Ni-2.6wt.%Mo-Xwt.%Co alloy (Figure 4). For Fe-30wt.%Ni alloy, the martensite transformation temperature at -42 °C significantly decreased with the addition of Mo and Ti elements to this alloy [15]. The effects of Ti and Mo added to Fe-Ni based alloys on martensite transformation temperature were discussed. Both elements were shown to decrease the temperature by increasing the % amount in the alloy [4, 8]. Supplement of Co into Fe-Ni-Mo alloy has raised the transformation temperature considerably (See Table 1).

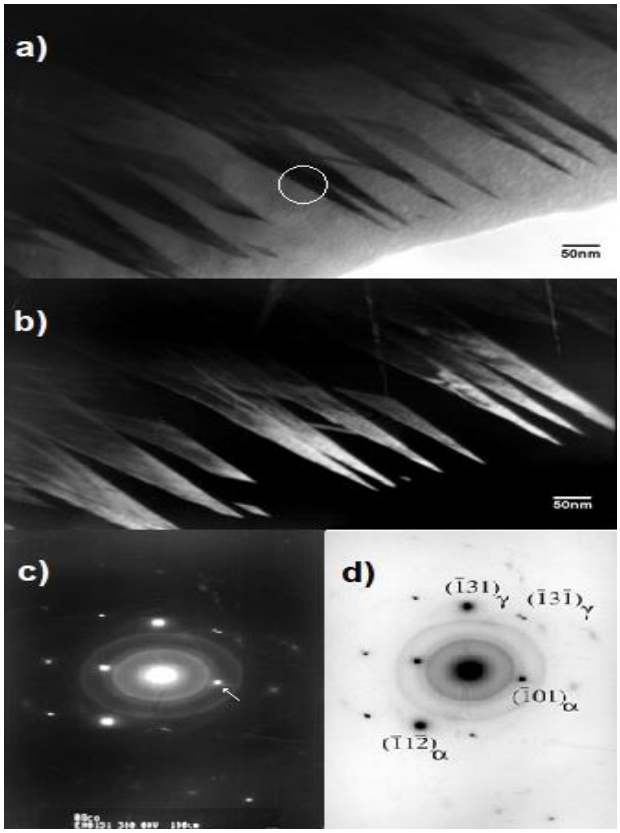

Figure 3. Lenticular martensite structure formed in Fe-30wt.%Ni-2.6wt.%Mo-0.8wt.%Co alloy; (a) Bright field electron micrograph of lenticular martensite, (b) Dark field images taken from $(\bar{1}01)_{\alpha'}$ superlattice reflection, (c) Selected area diffraction pattern of observed, (d) the indexed key diagram.

The magnetic properties of the parent and product phases have been examined by using the Mössbauer spectroscopy in Fe-Ni-Mo-Co alloys. Mössbauer spectra obtained for the examined alloys at room temperature are shown in Figure 5.

Mössbauer singlet spectrum of Fe-30wt.%Ni-2.6wt.% Mo-0.8wt.%Co alloy found in austenite phase at room temperature after homogenizing at 1100 °C was given in Figure 5a. According to Mössbauer spectrometry analysis, ferromagnetic (antiferromagnetic) property of alloys shows a six-line spectrum, while paramagnetic property displays a singlet spectrum (Figure 5b, c). As can be seen from the results, there is also a transition between magnetic characters thanks to the martensitic phase transformation ($\gamma \rightarrow \alpha'$). That is, there has been a transition from paramagnetic character to ferromagnetic character. The Mössbauer parameters such as isomer shifts (Austenite δ_A, Martensite δ_M), and hyperfine magnetic fields (internal magnetic field H (T)) with the calculated % volume fractions of phases are given in Table 1. According to Mössbauer results, the volume fractions of α' phase change with Co content in the alloys. The internal magnetic field is reduced by the addition of Si and Mo to Fe-based alloys [20].

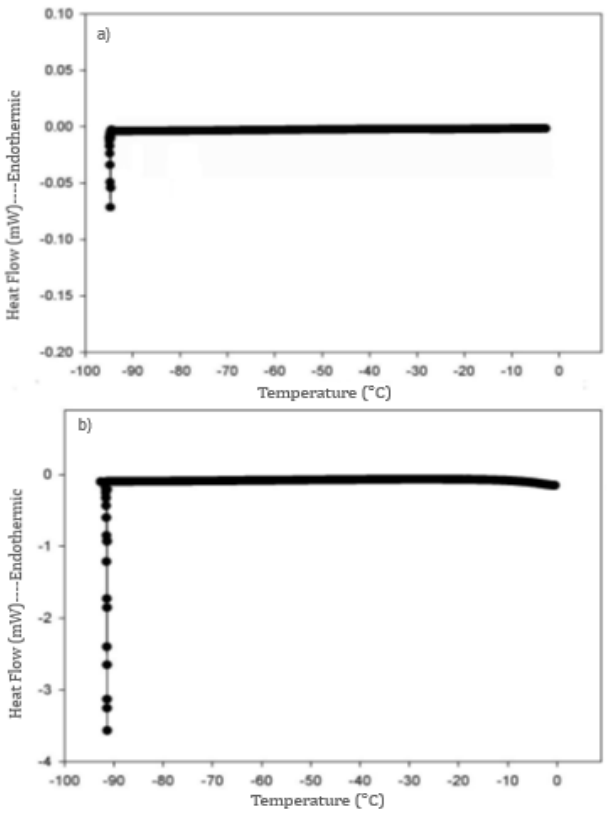

Figure 4. Heat flow change observed in the Fe-30wt.%Ni-2.6wt.%Mo-Xwt.%Co alloy, which was heat treated at 1100 °C for 12 hours, (a) X=0.8, (b) X=1.8

On the other hand, internal magnetic field increases with increasing Ni density in the nearest Fe region. Furthermore, the reduction in the internal magnetic field can be addressed as the result of the reduction in magnetic moments caused by electron transfer to the unfilled 3d bands [20-22]. With the addition of Co to these alloys, the decreasing internal magnetic field increased again. The change of M_s and austenite grain size according to Co amount is given in Table 1. In many previous studies, the relationship between austenite grain size and M_s has been revealed [9, 23]. In this study, it was confirmed by Mössbauer Spectrum analyses that increasing austenite grain size increased the amount of martensite phases.

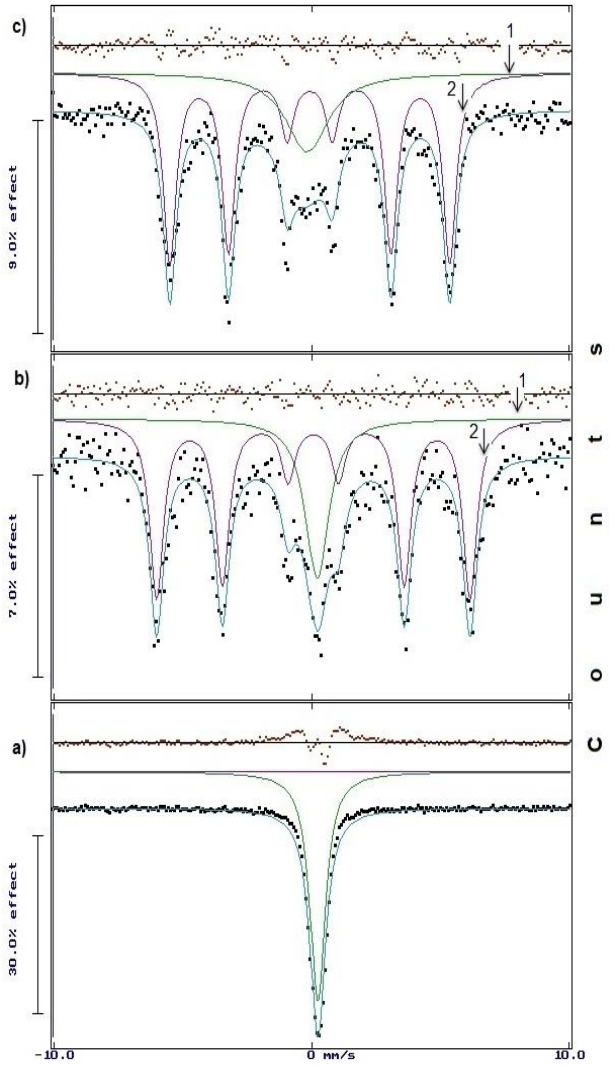

Figure 5. Mössbauer spectra; (a) Fe-30wt.%Ni-2.6wt.%Mo-0.8wt.%Co alloy (at room temperature), a single peak shows austenite phase, (b) Line 1 corresponds to austenite phase whereas line 2 belongs to martensite phase (Fe-30wt.%Ni-2.6wt.%Mo-0.8wt.%Co alloy), and (c) Line 1 corresponds to austenite phase whereas line 2 belongs to martensite phase (Fe-30wt.%Ni-2.6wt.%Mo-1.8wt.%Co alloy).

Table 1. Austenite grain size, M_s and some Mössbauer parameters

Sample (wt.%)	Grain size (μm)	M_s (°C)	M (%)	H (T)	δ_A (mm/s)	δ_M (mm/s)
Fe-30Ni-2.6Mo-0.8Co	83	-91	75.19	37.69	0.20±0.005	0.071±0.005
Fe-30Ni-2.6Mo-1.8Co	120	-94	76.98	33.66	0.16±0.004	0.067±0.005

4. Conclusion

In Fe-30wt.%Ni-2.6wt.%Mo-Xwt.%Co alloy, the morphology of thermally induced martensite structure, difference of martensite start temperature and magnetic properties of the alloys were studied depending on the amount of Co. As a result of these investigations, it was observed that austenite grain size increased with the increase of Co amount, and therefore the transformation temperature decreased. Morphologically, martensite formed by heat treatment reveals a lath, lenticular, and massive martensite structures in Fe-30wt.%Ni-2.6wt.%Mo-Xwt.%Co alloys. From the TEM investigations and electron diffraction pattern analysis in the Fe-30wt.%Ni-2.6wt.%Mo-0.8wt.%Co alloy, it was seen that the formation of with thermal effect α′ lenticular martensite crystal exhibited. Co element supplemented to Fe-Mn-Mo alloys changed the magnetic susceptibility. This situation was analyzed by Mössbauer spectrum. At the same time, as a result of Mössbauer spectrum analyses, it was calculated that the amount of Co and the amount of α′ martensite increased.

Acknowledgment

This study was carried out using the laboratories of Kırıkkale University Scientific and Technological Research Application and Research Center (KÜBTUAM).

Declaration of Ethical Code

In this study, we undertake that all the rules required to be followed within the scope of the "Higher Education Institutions Scientific Research and Publication Ethics Directive" are complied with, and that none of the actions stated under the heading "Actions Against Scientific Research and Publication Ethics" are not carried out.

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