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Gd Effect on Micro-Crystal Structure and Thermomagnetic Behavior of NiMnSn Magnetic Shape Memory Alloy

Ecem ÖZEN ÖNER[1*], Mediha KÖK[2]

[1,2] Department of Physics, Faculty of Science, Fırat University, Elazig, Turkey
[*1] e.ozenoner@firat.edu.tr, [2] msoglu@firat.edu.tr

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Abstract: In this study, the rare earth Gadolinium (Gd) element was added to the NiMnSn alloy, which is an alternative to the NiMnGa alloy group, with the increasing popularity of magnetic shape memory alloys. Since rare earth elements have strategic importance for our country in recent years, Gd element has been preferred in this study. X-rays and SEM-EDX analysis were performed to determine the morphological properties of the crystal structure and microstructure of the alloys. Magnetic measurements of the alloys were made with the physical property measuring device and it was determined that the magnetization values decreased with the addition of Gd.

Key words: Magnetic shape memory alloy, Smart materials, Rare earth element, Gadolinium

NiMnSn Manyetik Şekil Hatırlamalı Alaşımının Mikro Kristal Yapısı ve Termomanyetik Davranışı Üzerindeki Gd Etkisi

Öz: Bu çalışmada, manyetik şekil hatırlamalı alaşımlarının artan popülaritesi ile NiMnGa alaşım grubuna bir alternatif olan NiMnSn alaşımına nadir toprak gadolinyum (Gd) elemanı ilave edildi. Son yıllarda nadir toprak unsurları ülkemiz için stratejik bir öneme sahip olduğundan, bu çalışmada Gd element tercih edilmiştir. Kristal yapının morfolojik özelliklerini ve alaşımların mikro yapısını belirlemek için X-ışınları ve SEM-EDX analizi yapıldı. Alaşımların manyetik ölçümleri fiziksel özellik ölçüm cihazı ile yapılmıştır ve mıknatıslanma değerlerinin Gd ilavesiyle azaldığı belirlenmiştir.

Anahtar kelimeler: Manyetik şekil hatırlamalı alaşım, Akıllı malzemeler, Nadir toprak elementleri, Gadolinyum

1. Introduction

Smart materials; Materials whose structure can change significantly with external factors such as pressure, humidity, electric or magnetic field, light, temperature, acidity of the environment (pH) or chemical components are called materials [1-4]. Today, smart materials are classified into many subheadings. To give an example of smart materials; piezoelectric, thermoelectric etc., chromic materials (thermochromic, photochromic etc.), rheological materials (magneto-rheological, electro-rheological etc.) alloys can be given [3,5]. Magnetic shape memory alloys (MSMA) are smart materials that exhibit a magnetic field induced strain (MFIS). Compared to thermally activated shape memory alloys such as NiTi, MSHA's response is much faster (less than a millisecond compared to a few seconds), making them a good candidate material for use in actuator applications [6-10].

In this study, Gadolinium (Gd), which is one of the strategically important rare earth elements, was added to reduce the transformation temperature of the NiMnSn magnetic shape memory alloy. At temperatures above 20 °C, Gd is paramagnetic. Gadolinium was identified by Jean de Marignac in 1880 by spectroscopy of the mineral gadolinite, and he named this element Gadolinium after the mineral gadolinite [6,11,12]. This mineral is named after the Swedish/Finnish chemist Johan Gadolin, who discovered and characterized it in the 18th century. Gadolinium has been the benchmark magnetocaloric material for room temperature magnetic cooling since Brown's pioneering work in 1976. Gadolinium is readily available and has a relatively high magnetocaloric effect and a Curie temperature around room temperature [13-15]. The aim of this study, in order to see the effect of Gd element on NiMnSn magnetic shape memory alloy, various characterization analyzes were performed by preparing different ratios. X-ray (XRD) diffraction method analysis was performed to have information about the atomic arrangement of the material. SEM-EDX analysis was performed in order to see the changes in the surface of the alloys made by changing the amounts of the elements. Since it is a magnetic alloy, magnetization measurements were made.

* Corresponding author: e.ozenoner@firat.edu.tr. ORCID Number of authors: [1] 0000-0001-8784-8044, [2] 0000-0001-7404-4311

2. Experimental

In this study, high purity powdered (99.9%) Ni, Mn, Sn and Gd elements were used. For alloy production, each alloy is designed to be 10 g. Alloys codes; $Ni_{50}Mn_{38}Sn_{12}$ (Gd0), $Ni_{50}Mn_{34}Sn_{12}Gd_4$ (Gd4), $Ni_{50}Mn_{32}Sn_{12}Gd_6$ (Gd6), $Ni_{46}Mn_{38}Sn_{12}Gd_4$ (Gd44), $Ni_{44}Mn_{38}Sn_{12}Gd_6$ (Gd66). The production of pelletized NiMnSn-Gd magnetic shape memory alloys was made by arc melting method. The melting process was carried out several times while the samples were in the system, thus homogenizing the alloys in the system. Post-production alloys have become bulk. In bulk alloys, a second homogenization process was carried out by keeping the alloys in an ash furnace at 900 °C for 24 hours. In this study, the crystal structures of the produced NiMnSn-Gd alloys were determined at room temperature using a Bruker D8 X-ray diffractometer at room temperature. For this study, the samples were mechanically polished and chemically etched in 20 ml of HCl + 5 g FeC_3-H_2O + 96 mL methanol solution, then the microstructures and chemical compositions of all alloys were determined using a Hitachi brand scanning electron microscope. Magnetic measurement is important to analyze the properties of magnetic shape memory alloys rather than traditional shape memory alloys. Transitions and changes between phases in the structure of the sample can be thoroughly analyzed and evaluated. The magnetization measurements of the Gd0, Gd4, Gd44, Gd6, Gd66 alloy samples were precisely measured with the Quantum Design PPMS 7 (Physical Properties Measurement System) device at room temperature between -6 Tesla and 6 Tesla.

3. Result and Discussion

Figure 1 shows the results obtained from the x-ray diffractogram of Gd undoped and doped NiMnSn alloy at room temperature. The results obtained are supported by the literature [16-18]. In the Gd0 alloy, precipitate phases were also observed together with peaks belonging to the martensite phase. Here, the martensite phase exhibits the characteristic 10 M modified orthorhombic martensite crystal structure [16]. The precipitate phases are thought to be due to insufficient homogenization during the production of the alloy. In the x-ray diffractograms of Gd4 and Gd44 alloys, the number and intensity of peaks belonging to martensite phases increased unlike the main alloy. This may be due to the contribution of Gd element to NiMnSn alloy. Along with the martensite phase, precipitate phases were also observed. In the x-ray diffractograms of Gd6 and Gd66 alloys, unlike other alloys, peaks belonging to the austenite (A) L21 phase were observed. In Gd66 alloy, unlike Gd6 alloy, there are also peaks belonging to the martensite phase with low intensity. The other result extracted from the XRD curve is the crystal size (D) of the alloys obtained using (1), Scherrer's equation, which depends on some parameters including width at half maximum (FWHM), Bragg angle (θ), wavelength [19]:

$$D = K\,\lambda/(B\cos\theta) \tag{1}$$

where, B indicates the Full width at half maximum FWHM of the sharpest x-ray curve, K is the shape factor (K = 0.9) and the wavelength of the beam λKα(Cu) applied in the measurement was taken as 1.5406 Å. Figure 2 shows the average crystal size comparison of Gd doped NiMnSn alloy. It was observed that the crystal size of Gd-doped NiMnSn alloys increased compared to the Gd0 main sample.

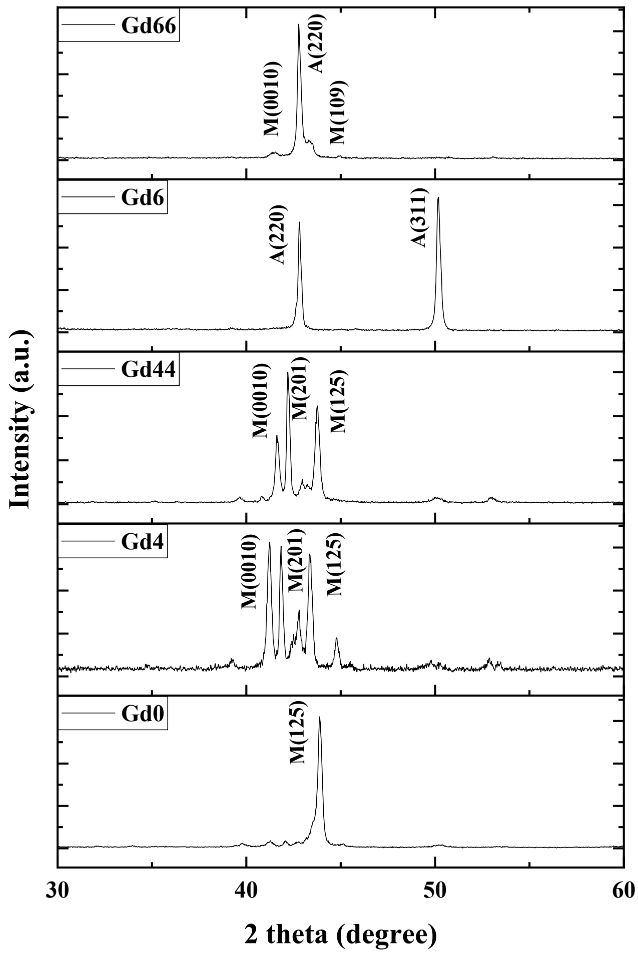


Figure 1. XRD results of Gd0, Gd4, Gd44, Gd6 and Gd66 samples

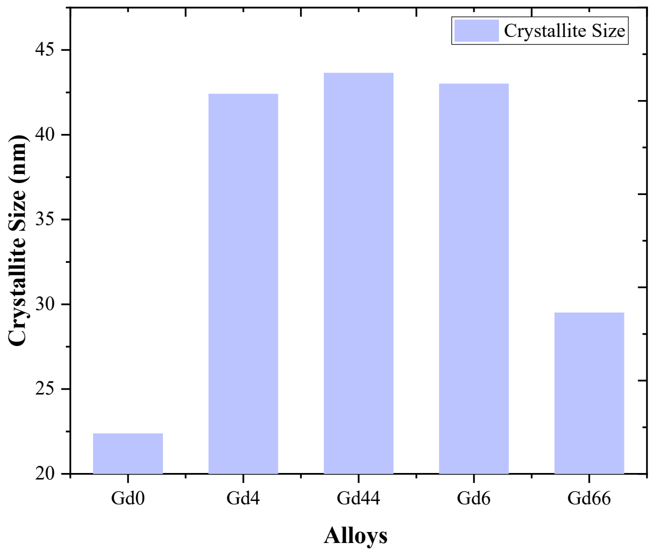


Figure 2. Comparison of crystal size of NiMnSn-Gd alloy

Scanning Electron Microscopy (SEM) technique was used to analyse the effect on the microstructure of NiMnSn-Gd shape-memory alloy and measurements were made at room temperature. The results are shown in Figures 3-4. Figure 3 shows the SEM image of the Gd0 master sample. According to the SEM image, needle type and parallel martensite plates are seen in the main NiMnSn alloy [20]. In addition, bump-shaped precipitate phases were occasionally observed. The reason for the formation of precipitate phases is that the full martensite phase (M) could not be obtained during and after the heat treatment during and after production. In addition, the regions marked in yellow show the voids formed. The reason for these voids may be the air bubbles formed during the melting of the alloying elements melted during production. Figure 4. a-b shows the SEM images of gadolinium doped Gd4 and Gd44 alloys taken at room temperature. In Gd4 alloy, nickel element ratio is higher, manganese element ratio is lower and Gd ratio is equal compared to Gd44 alloy. Considering these results, if we compare the images of the two alloys, the precipitate phase is observed in high density in Gd4 alloy, while the precipitate phase is very rare in Gd44 alloy and the size of the precipitate phases is enlarged. According to these results, the increase in nickel content increased the precipitate phases. Apart from precipitate phases, martensite plates and voids were observed in both alloys. Since the transformation temperatures of these alloys are almost close to room temperature, it is natural to see martensite plates. Figure 5. a-b shows the SEM images of two types of NiMnSnGd alloys doped with 6% Gd. In the alloys given with the codes Gd6 and Gd66, while the Gd ratio is constant at 6%, the nickel ratio is higher and the manganese ratio is lower in Gd6 alloy compared to Gd66 alloy. Similar to Gd4 and Gd44 alloys, the amount of precipitate phase increased depending on the nickel content. With the effect of Gd element, the flatness of the precipitate phases increased. It was also observed that the volume and number of voids increased. Another important result is the reduction of martensite plates. Since the austenite→ martensite transformation temperature of these alloys is below room temperature, it is normal that the appearance of martensite plates decreases. SEM analysis shows images of both martensite and austenite phases (A) of the alloys. In addition, the austenite phase contains more Mn compared to the martensite phase (M). Saini et al. [21] obtained similar results for a $Ni_{46}Cu_4Mn_{45}Sn_5$ shape memory alloy and found that the SEM image is a mixture of martensite and austenite phases. They also stated that the needle-like component in the images represents the martensite phase, which is characteristic of martensitic transformation.

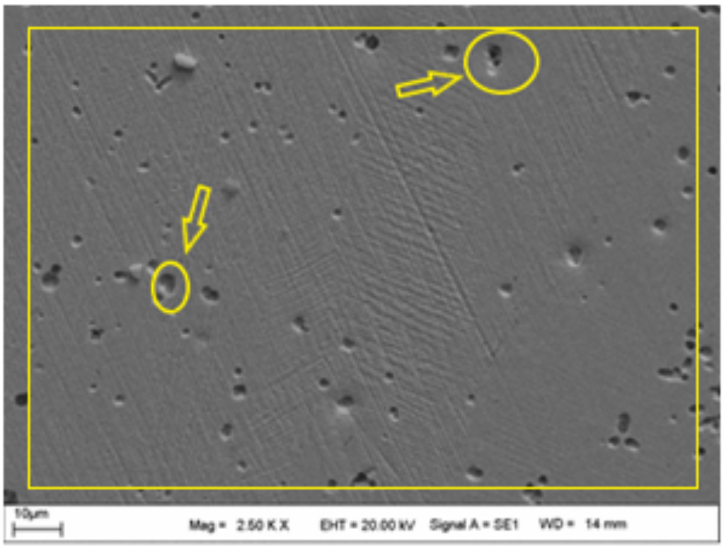
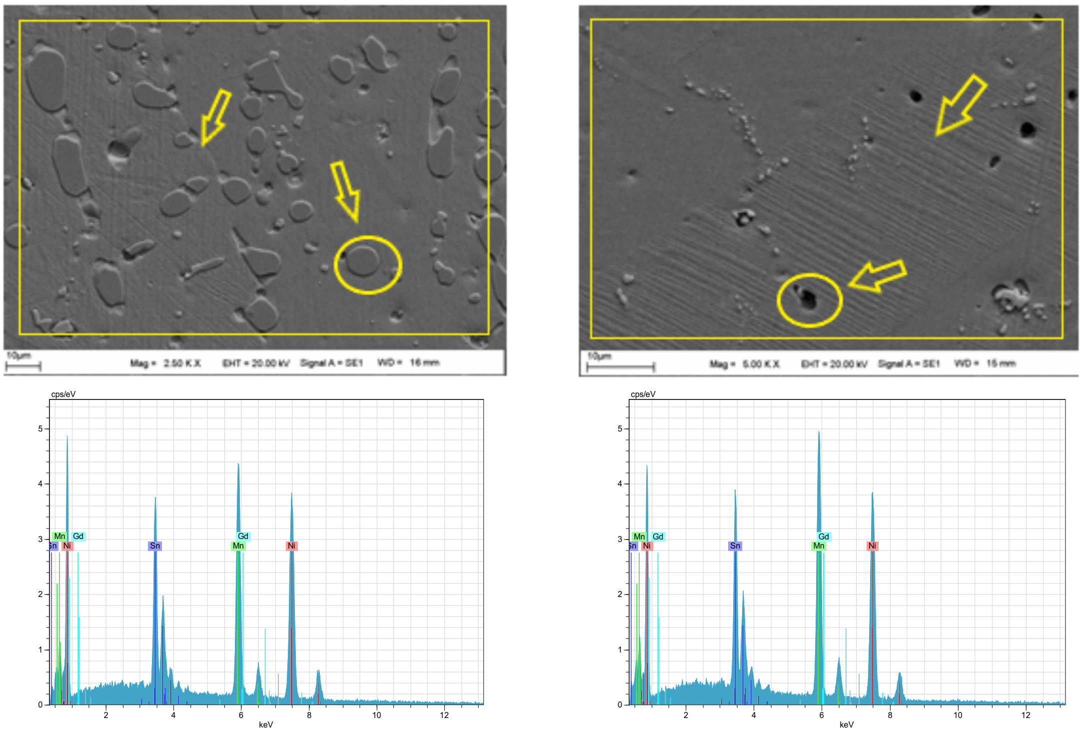
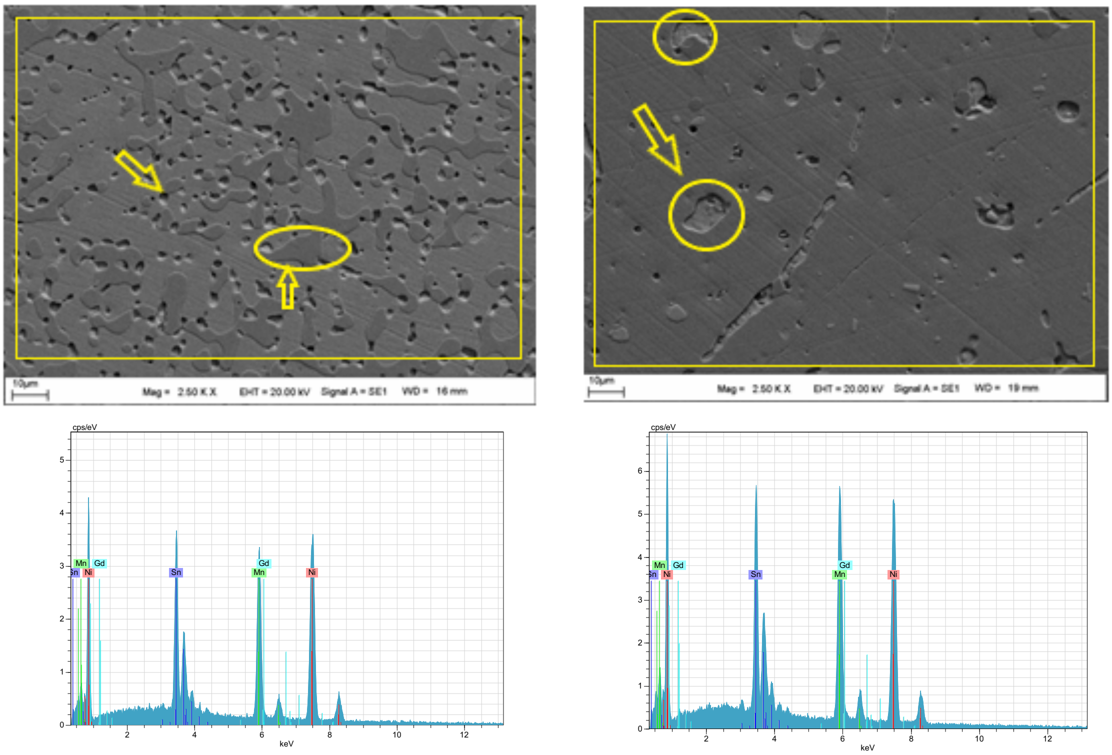


Figure 3. SEM image of Gd0 alloy



(a) (b)

Figure 4. a) SEM image of Gd4 alloy **b)** SEM image of Gd44 alloy



(a) (b)

Figure 5. a) SEM image of Gd6 alloy **b)** SEM image of Gd66 alloy

Figure 6 shows the magnetization values of NiMnSn-Gd alloys at room temperature in 6T external magnetic field. According to these results, in general, there is a decrease in magnetization value with Gd doping for 6 Tesla external magnetic field. If Gd4, Gd44, G6 and Gd66 alloys prepared by changing the ratio of nickel and manganese are compared among themselves, it is concluded that decreasing the nickel ratio is more effective than manganese in decreasing the magnetization value for all of them.

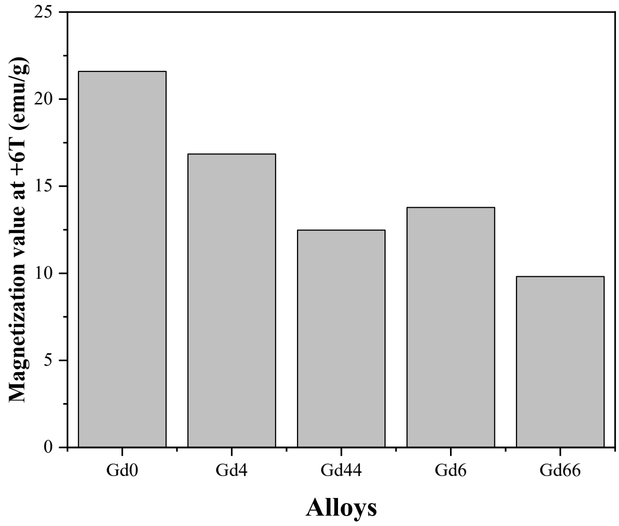


Figure 6. Comparison of saturation values of NiMnSGd alloys

Figure 7 a-e shows the magnetization measurements of the base NiMnSn alloy and Gd doped NiMnSn alloys in the temperature range of -120 °C to 100 °C under 1 Tesla magnetic field. These measurements were performed at a heating-cooling rate of 1 °C/min. The measurements made using the PPMS device could not be measured for higher temperatures, since the maximum temperature that the device can reach is 100 °C. It is known from previous study[14] that the transformation temperature of Gd0 alloy is between 84 and 120 °C. The thermomagnetic hysteresis formation in Figure 7.a. could not be completed because the system did not reach 120 °C, but the beginning of the hysteresis is seen. In Gd4, Gd44 and Gd66 alloys, hysteresis was found to occur at the points where austenite→martensite, martensite→austenite transformation occurred. In Gd6 alloy, as seen in our previous study[14], no transformation hysteresis is observed in the magnetization hysteresis since a low energy transformation occurs.

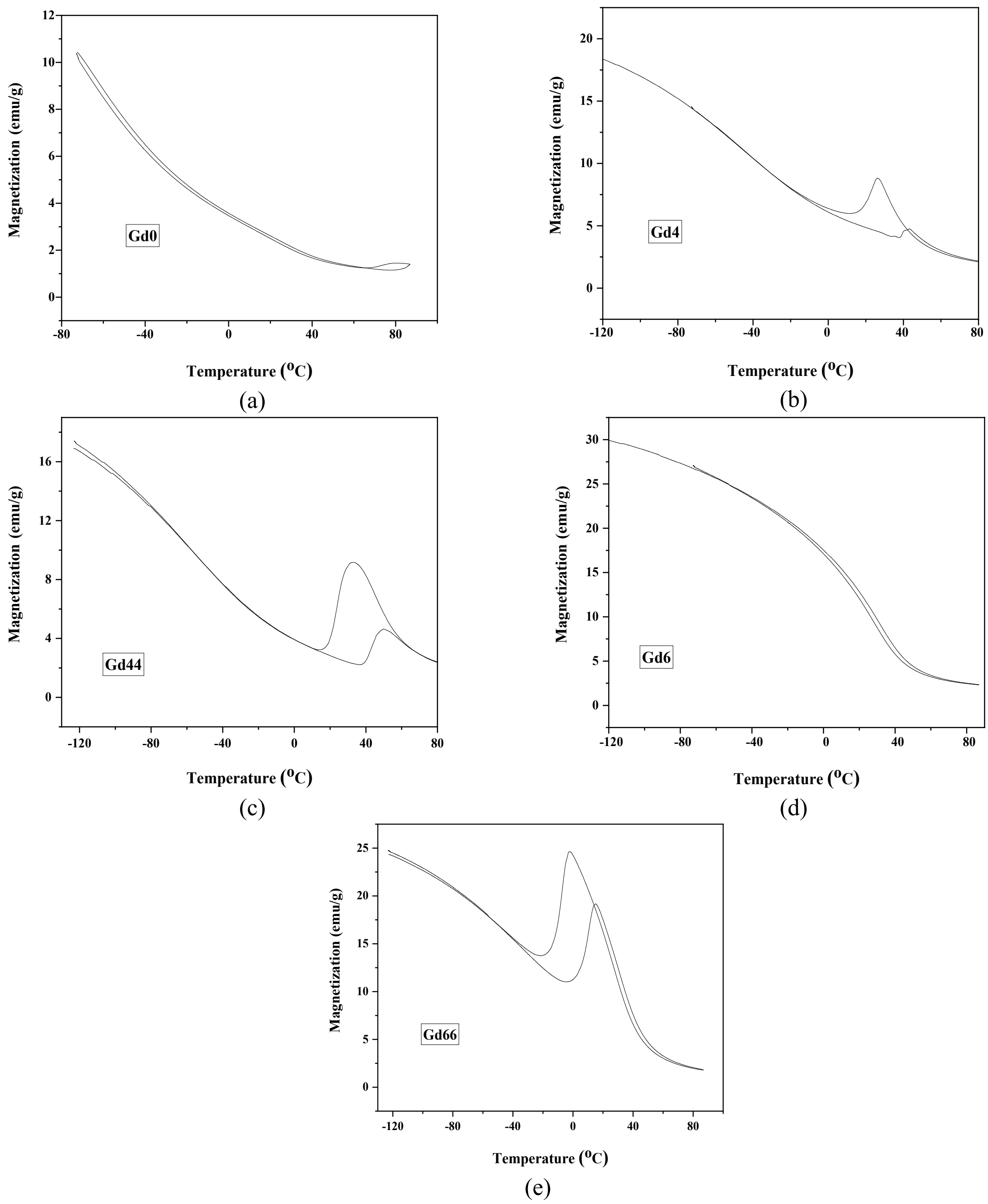


Figure 7. Variation of magnetization with temperature of alloys a) Gd0, b) Gd4, c) Gd44, d) Gd6, e) Gd66

Conclusions

In this study, the effect of Gd doping of NiMnSn magnetic shape-memory alloy on the microcrystalline structure and thermomagnetic hysteresis of the alloy was investigated. As a result of microstructure and crystal structure investigations, peaks belonging to the martensite phase of the NiMnSn alloy without Gd were found, while peaks belonging to the precipitate phases and austenite phase were found with Gd doping. Needle-type martensite plates and V-type martensite plates were observed in SEM images. After thermomagnetic measurements, a wide magnetic hysteresis was found in Gd4, Gd44 and Gd6 alloys. The starting and ending points of this hysteresis were found to coincide with austenite and martensite phase temperatures.

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