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Heat Treatment Effect on Thermal, Micro-Crystal Structure and Magnetic Behavior of $Ni_{45}Mn_{40}Sn_{10}Cu_5$ Heusler Shape Memory Alloy

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ABSTRACT

Ni-Mn-Sn-based Heusler alloys are important materials with potential applications as environmentally friendly smart materials with beneficial properties besides being magnetic. Both magnetic field-induced reverse martensitic transformation and high operating temperature are crucial for the applications of Ni-Mn-Sn-based magnetic shape memory alloys. In this study, different heat treatments (700 °C, 900 °C, 1100 °C) were applied to Ni45Mn40Sn10Cu5 samples produced by arc melting method and martensite transformation temperatures were determined. According to the thermal measurement results, martensite reverse transformation was observed in the sample without heat treatment and with 700°C heat treatment, while no martensite reverse transformation was observed at 900°C and 1100°C. When X-ray diffractograms of all samples were analyzed, peaks belonging to martensite phase and γ phase were detected. Finally, when the magnetic hysteresis of the samples was examined, it was observed that the magnetic saturation value decreased with increasing heat treatment and accordingly, the magnetization effect decreased.

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Introduction

Shape memory alloys (SHA) are alloys that have the ability to return to their original shape from the deformed shape by temperature and superelastic effect. Superelasticity is the ability of an alloy subjected to deformation by an external force to return to its original shape when the force is removed. Shape memory effect and superplasticity are two important parameters related to thermoelastic martensite transformation. Martensitic transformation is a diffusionless phase transition[1]. The shape memory effect is of two types. In the one-way shape memory effect, the alloy returns to its original shape when heated, while in the two-way shape memory effect, it is a shape change that can be repeated without any external mechanical effect during heating and cooling [2, 3]. Shape memory alloys are NiTi based alloys NiTiCu, NiTiFe, Cu (Copper) based alloys CuAl, CuSn and CuZn and Fe (iron) based alloys FeMnSi and Fe-Pt. In addition, magnetic shape memory alloys have recently attracted attention. Examples of magnetic shape memory alloys include NiMn-based alloys such as NiMnGa, NiMnFe and NiMnSn[1].

Magnetic shape memory alloys (MSHA), which have similar properties to shape memory alloys, were first studied by Ullakko and Aoltio in 1995 when martensite twinning was observed in Fe-Ni-Co and Ni-Mn-Ga alloys [4]. The discovery of the magnetic stresses of NiMnGa alloys has broadened their potential uses in actuators and boosted their population in the ferromagnetic field [5]. However, due to the high brittleness of these alloys, their efficiency in applications is low and their brittleness has been tried to be overcome by increasing their ductility by adding Co and Fe metals. Recently, the importance of producing and investigating Ni-Mn-X (Sn,Sb) heusler alloys has emerged as an alternative to the brittle NiMnGa alloys. The reason for the increased research in magnetic shape memory alloys is that they have become popular materials in recent years due to their magnetic, magnetocaloric and different physical properties [6]. Magnetic shape memory alloys undergo shape change while in the martensite phase under the influence of an applied external magnetic field and work faster than SHAs [7]. In these alloys, the martensitic transformation is from the austenite phase to the martensite phase [8]. Martensite transformation is sensitive to parameters such as magnetic field and temperature [9]. MSHA is ferromagnetic in the austenite phase and antiferromagnetic in the martensite phase. While ferromagnetic shape memory alloys show shape memory effect when temperature, mechanical force and magnetic field are applied, paramagnetic shape memory alloys return to their original state when temperature and mechanical force are applied. Magnetic and shape memory alloys have applications in the healthcare industry, sensors and actuators, textile industry, robot control systems, automotive industry.[10, 11]. Materials that show magnetic shape memory effect and whose physical properties are still being determined today are Fe-Pd-X (X=Cu, Rh) [12], , Ni2XGa (X=Mn, Fe, Co) [13], Co-Ni-X (X= Al, Ga) [14], Ni-Mn-Ga [15] alloys. Heusler NiMn-based Heusler alloys have become the center of interest in technical applications due to their physical properties and high magnetization value between the transformation phases. In this type of alloys, the Mn content is a critical value for magnetic properties. Since martensite transformation is affected by factors such as magnetic field and temperature, alloys with high Mn content have been investigated. For example, in 2006, Kainuma et al [16] demonstrated martensite transformation in Ni-Co-Mn-In single crystal and Ni-Co-Mn-Sn polycrystalline alloys and observed the shape memory effect [4]. In this study, NiMnSn based magnetic shape memory alloy was heat treated at different temperatures and the effect of heat treatment on phase transformation, microcrystalline structure and magnetic properties of the alloy was investigated.

Experimental

The NiMnSnCu alloy was prepared by using 99.9% pure Ni, 99.9% pure Mn, 99.9% pure Sn and 99.9% pure Cu powders according to the mass ratio for 10 g given in Table 1 and then these powder mixtures were pelletized under 1 ton pressure. These pelletized powder mixtures were melted in an arc furnace to obtain ingots, thus producing Ni45Mn40Sn10Cu5 (at. %) magnetic shape memory alloy. To improve the homogeneity of this alloy, it was heat treated at 700°C, 900°C and 1100°C for 1 hour and then subjected to flash cooling in saline ice water. The alloys were coded as T2, T2-700, T2-900 and T2-1100, respectively. Then, to study the effect of heat treatment on NiMnSnCu alloy, differential scanning calorimetry (DSC) measurements and x-ray measurements of the heat-treated alloys were taken, followed by magnetization hysteresis and SEM investigations.

Table 1. Atomic percent and weight percent ratios of the alloy.

T2 (no heat treatment alloy)	Ni	Mn	Sn	Cu
At. %	45	40	10	5
wt. in 10 gr	4.164	3.464	1.871	0.501

Results and discussion

Heat flux versus temperature curves of NiMnSnCu alloys without heat treatment and NiMnSnCu alloys heat treated at 700 ºC, 900 ºC and 1100 ºC for one hour were measured at heating-cooling rates of 10 ºC/min. in a pure nitrogen gas atmosphere with a flow rate of 100 ml/min. The results of these measurements are shown in Figure 1 and summarized in Table 2. Table 2 shows A_s austenite start temperature, A_f austenite finish temperature, A_p austenite peak temperature, M_s martensite start temperature, M_p martensite peak temperature, M_f martensite finish temperature. While examining the data in Table 2, it is required to compare the non-heat-treated sample and the alloy sample heat treated at 700 ^{o}C together. Whenever the transformation temperatures of these alloys are compared, it is noted that although A_s temperature values remain constant, A_f temperature values increase in T2-700 alloy while M_s temperature values drop. When heat treated alloys at 900 and 1100 ^{o}C are compared to non-heated alloys, austenite phase transformation temperatures are detected, but martensite phase transformation temperatures are not determined. Najan ul Hasan et al. reported that an important factor affecting the transformation temperature is the change in matrix composition within the alloy. They considered that substitution of atoms with different sizes from the parent atoms causes expansion or contraction of the unit cell and hence lattice distortion [17]. It can be said that when the heat treatment temperature is at 900 C and 1100 C, the lattice structure of NiMnSnCu alloy is deformed due to shrinkage and expansion of atoms and therefore the martensite transformation temperature cannot be observed.

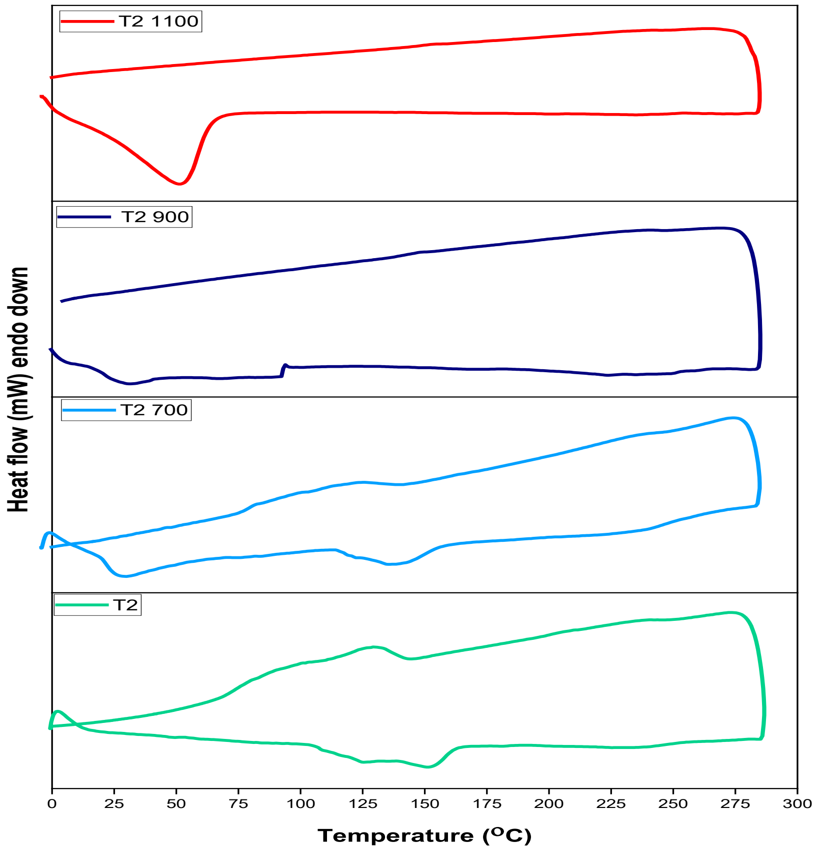


Figure 1. DSC curves of unheat treated and heat treated NiMnSnCu shape memory alloy

Table 2. Transformation temperatures of T2 alloy before and after heat treatment

	A_s (°C)	A_p (°C)	A_f (°C)	M_s (°C)	M_p (°C)	M_f (°C)
T2	109.69	152	137	146.07	132.10	73.24
T2-700	109.03	143.06	158	138.21	122.40	97.57
T2-900	21.07	32.60	46.50	-	-	-
T2-1100	22.90	50.16	67.80	-	-	-

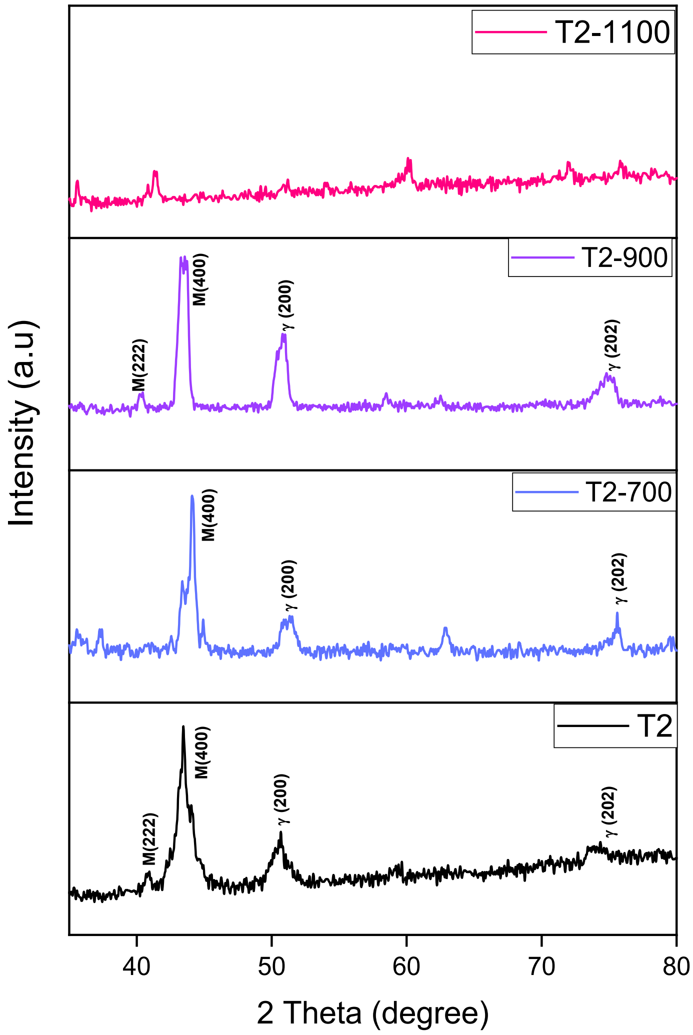


Figure 2. X-ray diffractograms of $Ni_{45}Mn_{40}Sn_{10}Cu_5$ sample obtained from non-heat-treated T2 and heat-treated samples

X-ray measurements are important for the determination of crystal structure information. The x-ray diffractograms of T2 alloy without heat treatment, heat treated at 700^{o}C, 900^{o}C and 1100^{o}C are given in Figure 2. The obtained x-ray diffractograms were indexed according to the literature [17]. As seen in the diffractograms of the alloys heat treated at 700^{o}C and 900^{o}C, more cleavage occurred and the peaks became more pronounced compared to the diffractogram at 1100^{o}C. It was observed that most of the peaks disappeared at 1100^{o}C. When the peaks formed as a result of heat treatment were indexed, peaks belonging to two phases were found. These phases were determined as martensite phase and the second one as γ phase. When the X-ray results are analyzed, the decrease in the vagueness of the crystal structure in the alloy heat treated at 1100 ^{o}C is in agreement with the DSC measurement results.

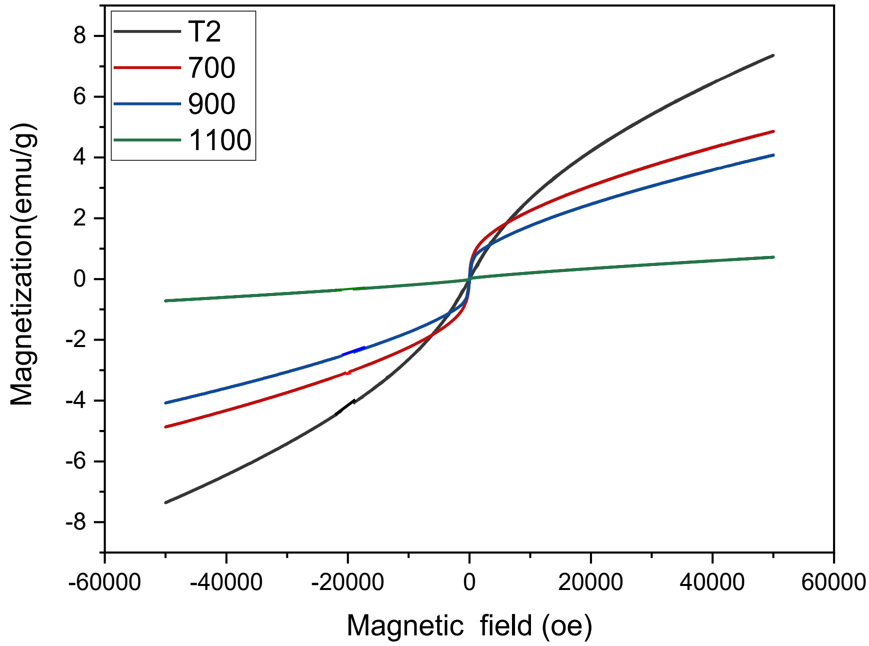


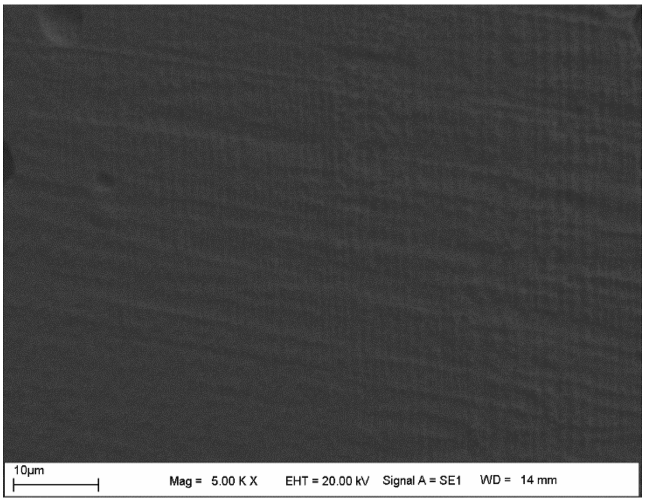
Figure 3. Magnetization hysteresis of untreated and heat treated T2 alloy at room temperature

The magnetic hysteresis of untreated T2 alloy samples heat treated at 700°C, 900°C and 1100°C for 1 hour are shown in Figure 3. These measurements were taken between -50000 Oe (-5T) and 50000 Oe (+5T) in the martensite state (room temperature). The saturation value of the T2 alloy without heat treatment is 7.10 emu/g, the saturation value of the alloy heat treated at 700°C is 4.71emu/g, and the saturation value of the alloy heat treated at 900°C is 3.98 emu/g. Unlike these, it can be said that the alloy heat treated at 1100°C did not reach saturation. The alloy with the highest magnetic saturation is the untreated T2 alloy. These values are summarized in Table 3. There is magnetic hysteresis in all four samples, but magnetic hysteresis is not observed in the alloy heat treated at 1100°C. It can be understood by analyzing the hysteresis curve whether the magnetic material has magnetic properties suitable for the areas in which it will be used. From the hysteresis curve, information about the saturation magnetization (saturation), coercivity and magnetic permeability of the magnetic material can be obtained [18]. While the area of the hysteresis curve is small in materials with soft magnetism, it is larger in materials with hard magnetism[19]. Materials with a coercive field less than 125 Oe are called soft magnetic materials, while materials with a large force field are called hard magnetic materials [20].

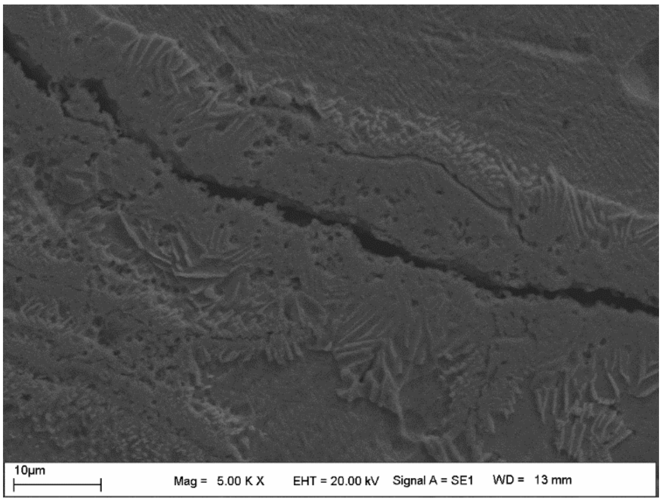
Table 3. Saturation values of untreated and heat treated T2 alloy.

	without heat treatment	**T2-700**	**T2-900**	**T2-1100**
saturation (emu/g) (at 5T magnetic field)	7.10	4.71	3.98	---

The surface examinations (SEM) obtained as a result of the heat treatments applied to the alloys are as shown in Figure 4. Shape memory alloys can show shape memory ability in different phases under temperature and stress conditions. All SEM measurements were taken at the same magnification for comparison. According to these results, thick plate and v-type martensite plates are observed in the NiMnSnCu alloy without heat treatment. In the 700 °C heat treated alloy, precipitate phases and cracks are seen along with martensite plates. At 900 °C, the surface morphology of the heat-treated alloy shows precipitate phases in the form of humps and pits between the martensite plates. Finally, in the alloy heat-treated at 1100 °C, the precipitate in the form of a rather large hump with martensite plates is noticeable.



(a)



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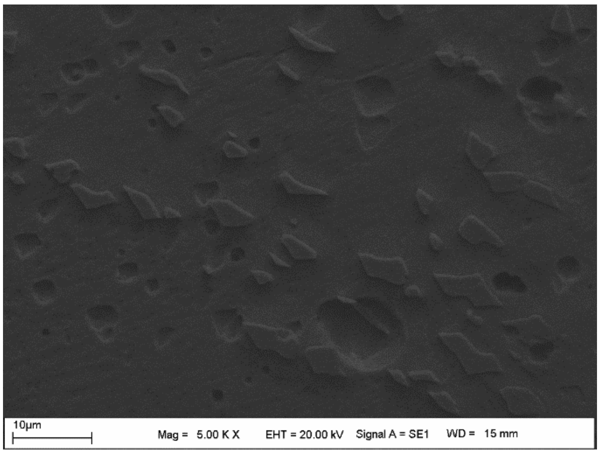
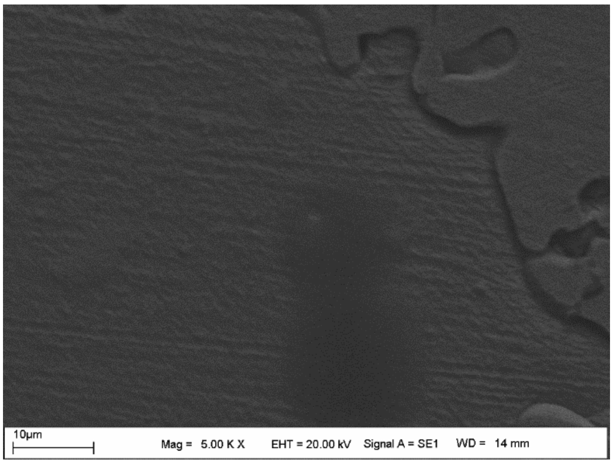


(c)



(d)

Figure 4. SEM images of (a) untreated, (b) 700^{o}C, (c) 900^{o}C and (d) 1000 ^{o}C heat treated $Ni_{45}Mn_{40}Sn_{10}Cu_5$ alloys for 1hour

Conclusions

The effects of heat treatment were investigated by applying different heat treatments (700°C, 900°C, 1100°C) to the $Ni_{45}Mn_{40}Sn_{10}Cu_5$ sample produced by arc melting method. The results of the heat treatment effects are as follows

- While martensite transformation was observed at T2 (no heat treatment) and 700°C heat treatment, no martensite transformation was observed at 900°C and 1100°C. It can be said that the change in the lattice structure due to interatomic expansion and contraction with heat treatment is effective.
- From the X-ray diffractograms, peaks belonging to the martensite phase and γ phase were detected in the alloy without heat treatment and heat treated at 700 and 900 ^{o}C. In the 1100 ^{o}C heat treated alloy, no phases were detected.
- When the magnetic hysteresis of the samples was examined, it was observed that the magnetic saturation decreased with increasing heat treatment and the alloy heat treated at 1100 ^{o}C exhibited paramagnetic properties.
- In the microstructure examination, it was observed that precipitate phases were formed with heat treatment.

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