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Determination Some Physical Properties of Ground NiMnCoSn Magnetic Shape Memory Alloy Powders

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Abstract: In this study, NiMnCoSn alloy was produced in the arc melting furnace and then grounded into small powder particles. After this procedure, particles of alloys were pelletized and heat treatment was applied to pellet alloys for 3 different temperatures (500 °C,700 °C and 900 °C). Differential scanning calorimetry (DSC), X-ray diffraction (XRD) and physical property measuring system (PMMS) were used for determining physical properties of samples. The biggest feature of NiMn-based shape memory alloys is that they are magnetically based. The feature that distinguishes magnetic shape memory alloys from traditional ones is that the shape memory effect is magnetic. For this reason, studies of NiMn-based alloys are becoming very popular. It was observed that, grounding procedure is effected all physical properties of NiMnSnCo shape memory alloys, seriously.

Key words: NiMnCoSn, magnetic shape memory alloy, thermal characteristics, XRD, microstructure

Öğütülmüş NiMnCoSn Manyetik Şekil Hatırlamalı Alaşım Tozlarının Bazı Fiziksel Özelliklerinin Belirlenmesi

Öz: Bu çalışmada, ark ergitme fırınında NiMnCoSn alaşımı üretilmiş ve daha sonra küçük toz parçacıklarına öğütülmüştür. Bu işlemden sonra alaşım parçacıkları pelet haline getirilmiş ve pelet alaşımlara 3 farklı sıcaklıkta (500 °C, 700 °C ve 900 °C) ısıl işlem uygulanmıştır. Numunelerin fiziksel özelliklerinin belirlenmesi için diferansiyel taramalı kalorimetri (DSC), X-ışını kırınımı (XRD) ve fiziksel özellik ölçüm sistemi (PMMS) kullanılmıştır. NiMn bazlı şekil hafızalı alaşımların en büyük özelliği manyetik bazlı olmalarıdır. Manyetik şekil hafızalı alaşımları geleneksel olanlardan ayıran özellik, şekil hafıza etkisinin manyetik olmasıdır. Bu nedenle NiMn esaslı alaşımlarla ilgili çalışmalar oldukça popüler hale gelmektedir. Öğütme işleminin NiMnSnCo şekil hatırlamalı alaşımların tüm fiziksel özelliklerini ciddi şekilde etkilediği görülmüştür.

Anahtar kelimeler: NiMnCoSn, manyetik şekil hafızalı alaşım, termal özellikler, XRD, mikro yapı

1. Introduction

The smart or sensitive materials can change their shape and respond with stress, moisture, electric or magnetic field, light, pH or chemical compounds [1, 2]. Shape memory alloys (SMAs) change their shape when exposed to a certain external force while in martensitic structure, and take their original shape when heated to austenite phase temperature [3-5]. SMAs frequently used in many fields such as automotive, textile, bioengineering, aviation, composites and micro electromagnetic system [6-9]. Magnetic shape memory alloys, which are developed as an alternative to traditional shape memory alloys, are materials that also show shape change with applying magnetic field [10, 11].

Magnetic shape memory alloys have a high magnetocaloric effect. When a magnetic field is applied, the entropy value of the material decreases, so the heat is dissipated from the magnetic cooling system into the environment. When the magnetic field is removed, it is observed that the magnetic entropy increases and therefore the material absorbs the heat energy from the environment [12-15]. magnetic shape memory alloy group are used as a coolant in the industry due to their magnetocaloric effect.

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Nowadays, NiMnSn-based Heusler type magnetic shape memory alloys are being developed [16, 17]. Because when this type of magnetic alloys are compared with traditional magnetic alloys such as NiMnGa, it is seen that the magnetization value between the transformation phases is high. This is thought to be due to the Manganese ratio in alloy [18-20].

Haluk E. Karaca et al. observed that as the applied magnetic field effects on NiMnCoIn shape memory alloy. In their study, when the magnetic field increased from 0.05 to 5 T, the martensite start (Ms) value decreased from 230 to 165 K [21]. Han et al. investigated that the magnetization difference between the transformation phases of $Ni_{50-x}Mn_{39+x}Sn_{11}$ by increasing amount of Mn ratio. They found that magnetic entropy change to below 1 T, and because of this feature, they reported that this alloy group is used in magnetic cooling applications [22].

Among these magnetic shape memory alloys, NiCoMnIn alloys have been most extensively studied. Ni-Mn-Ga is one of the most studied MSMAs. Substitution of Ga with Sn is an economical alternative for Ni-Mn-Ga alloys. In NiMn-based magnetic shape memory alloys, the magnetic moments are strongly dependent on the distance between Mn-Mn atoms. The bonding mechanism between Ni and Mn leads to a martensite transition. In these materials, especially alloys with high Mn content, the martensite transition should be affected by factors such as magnetic field, composition, temperature and should be developed for practical applications [16, 23-25]. NiCoMnSn alloys are also very promising for practical applications as they do not contain expensive elements [26]. In this study, thermal and crystal structure of grounded NiMnCoSn MSMA bulk were investigated. The aim of this study is to examine all physical properties of powdered NiMnSn alloy by heat treatment. Powdered NiMnCoSn alloy is rare.

2. Experimental Procedure

After determining the mass ratio of the $Ni_{50}Mn_{36}Sn_{12}Co_{2}$ (%at.) quaternary magnetic shape memory alloy, 50 g of powder mixture was prepared by using pure element powder and pelleted using a hydraulic press. The atomic and weight ratios of the alloy are given in Table 1.

Table 1. Atomic percentage ratio of NiMnSnCo alloy produced

	Ni	Mn	Sn	Co
Atomic (%)	50	36	12	2
Mass ratio in 50 g	22,73	15,32	11,035	0,913

The alloys' mixture, which became a pellet, was melted in a vacuum atmosphere using arc melter device. The alloy was homogenized on the first level by repeating the melting process several times. After that, the alloy in bulk form was kept at 900 ºC for 24 hours and the second-level homogenization process was performed, and thus the production part was completed. After production it was seen that high volume of porosity was determined into bulk NiMnCoSn magnetic shape memory alloy. Alloy samples were ground in agate mortar.

For this reason, NiMnCoSn alloy was grinded into shape and macro powders of alloys were obtained as seen in Figure 1a. The alloys' powder, which was then pulverized with coarse grains, were turned into pellets (In order to see the properties of the NiMnSnCo alloy more easily, the macro powdered alloys were turned into pellets) and were kept at three different temperatures (500 ºC, 700 ºC, and 900 ºC) for 8 hours, after these treatments aging process was carried out under both pressure and temperature (Fig. 1b).

Fig. 1. a. Powder form of NiMnCoSn alloy, **b.** Pellet form of NiMnCoSn alloys' powders

The phase transformation of all samples were measured with a heating-cooling rate of 10 ºC/ min. using a Perkin Elmer differential scanning calorimeter (DSC) in a nitrogen gas atmosphere. The crystal structure of main and heat treated powder alloys were determined by XRD diffractometer at room temperature. Finally, room temperature magnetization measurement was made to investigate magnetic properties of the NiMnSnCo alloy by using Quantum PPMS (physical property measurement system) device in the magnetic field range of -8T to 8T.

1. Results and Discussions

Differential scanning calorimetry (DSC) is often used to determine the phase transformation temperature of shape memory alloys. The most used and important shape memory alloy characterization device is DSC, and the transformation temperatures are found by measuring the heat absorbed or emitted by the heating and cooling of very small samples taken from the materials [27]. DSC measurements were taken in nitrogen gas atmosphere with a heating rate of 10 ºC/min. to determine the transformation temperatures of non-heat treated and heat treated pelletized alloys at 500 ºC, 700 ºC and 900 ºC for 8 hours. Figure 2 displays complete heating and cooling DSC curves of the main and heat-treated samples taken between -40 ºC and 200 ºC. According to the DSC measurement results, multiple peaks were observed during heating in the main ground alloys (particle alloy), and transformation was not observed during cooling procedure. As a result of the aging of the pelleted powdered NiMnCoSn alloy at 500 °C and 700 °C, phase transformation peak disappeared on the heating or cooling. However, a significant peak was observed during heating in the alloy, which was aged at 900 °C for 8 hours. This peaks that martesite→austenite transformation was occurred by heating. Austenit→martensite transformation sign did not seen for all of ageing alloys and nonageing alloys. It can be said that force which use for ground alloys effect to destroy arranging of atoms in the crystal structure.

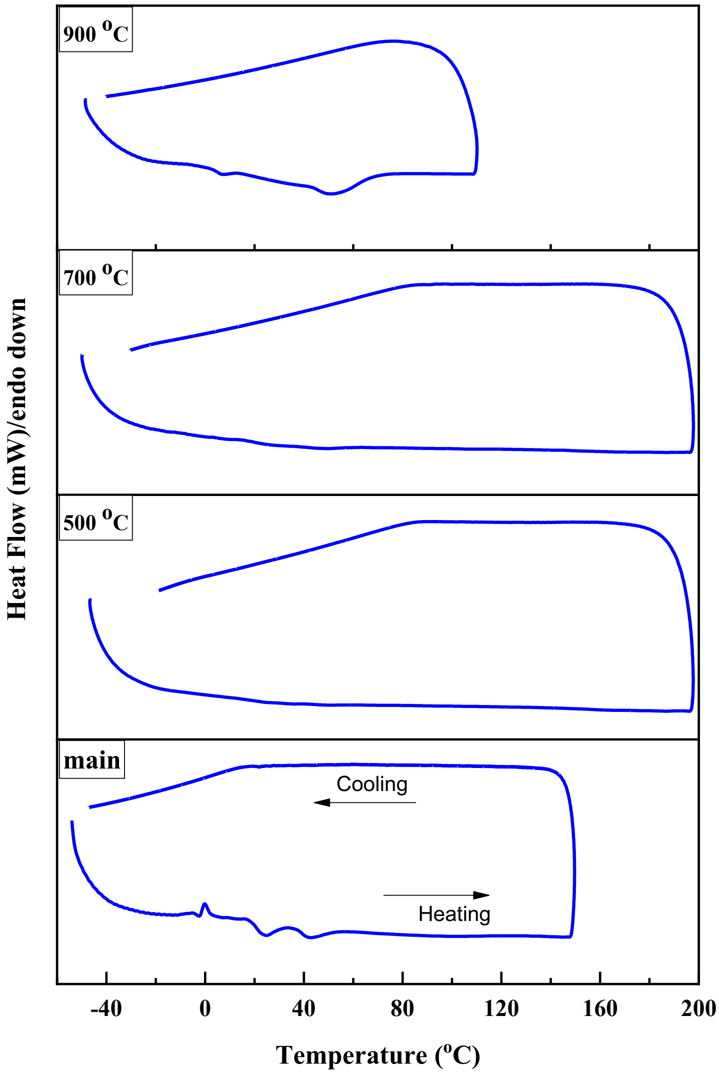
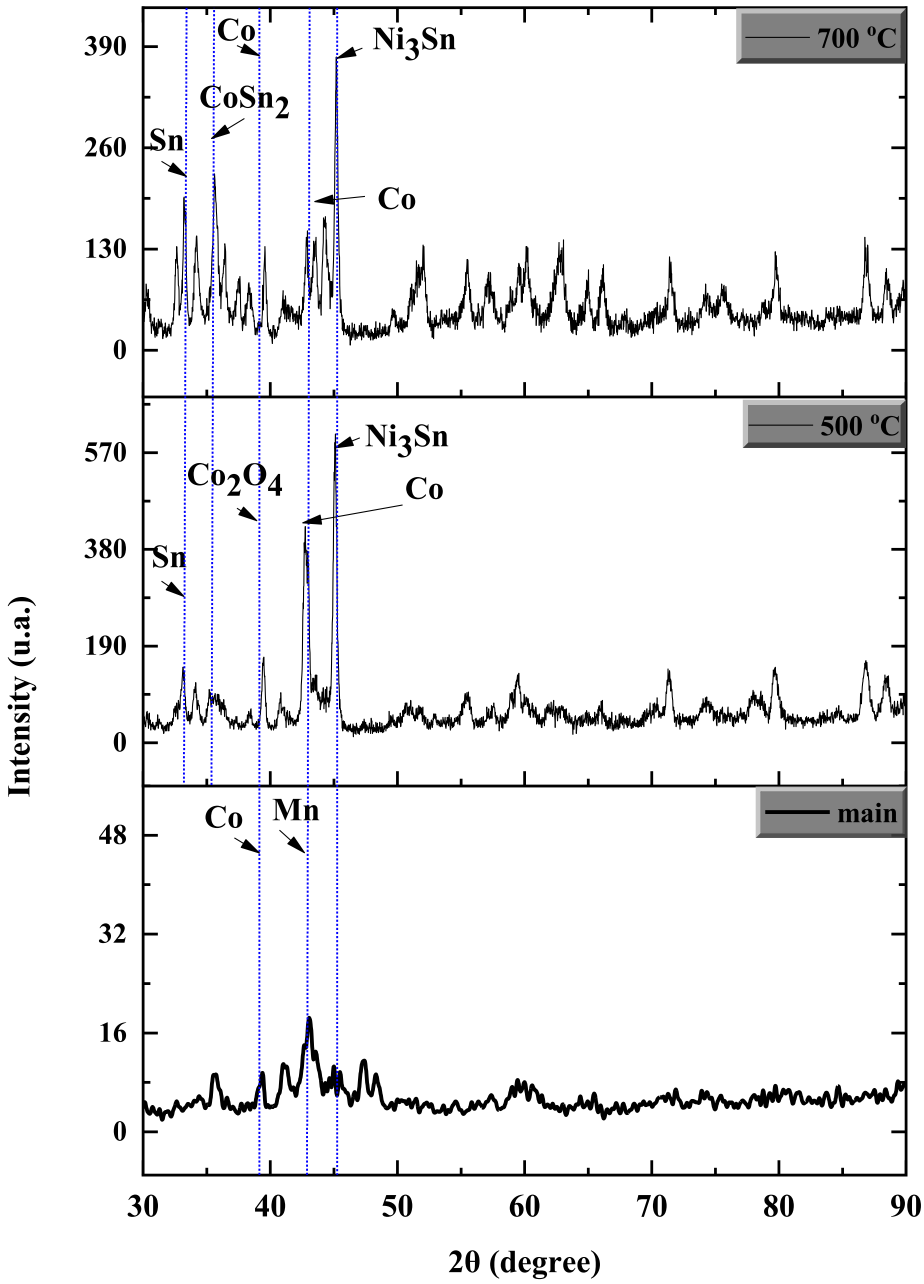


Fig. 2. The DSC curves of main and heat treated powder NiMnCoSn alloys

X-ray diffraction method is used to determine whether the materials are amorphous and crystalline structure. This method is based on Bragg's law. With X-ray diffraction methods, it is possible to measure the exact dimensions of the unit cell in any crystal and to determine the arrangement of the atoms in the crystalline form [28]. X-ray measurements were taken in the range of 30-90 with a scanning speed of 2 °/min for samples which nonheat treated and heat treated at 500, 700 °C. The X-ray diffractograms of the alloys are given in Fig. 3. The XRD peaks were indexed by the literature [29-31].

In this study, when the XRD diffractions are examined, the elements or compounds that the peaks belong to are shown in the Fig. 3. In particular, it is seen that the XRD diffraction is concentrated between 30 and 50 degrees. It is an expected result that the highest peaks belong to Ni and Mn elements.

The particle size was calculated with the Debye Scherrer equation ($D = K.\lambda / \beta.\cos\theta$) and the graph was drawn from the obtained nanometer (nm) unit. When the graph in Fig. 4 was examined, it was observed that the particle size increased with the increase of the heat treatment temperature. This can be explained that thermal expansion with heating important effect of the grain size of NiMnSnCo alloy.



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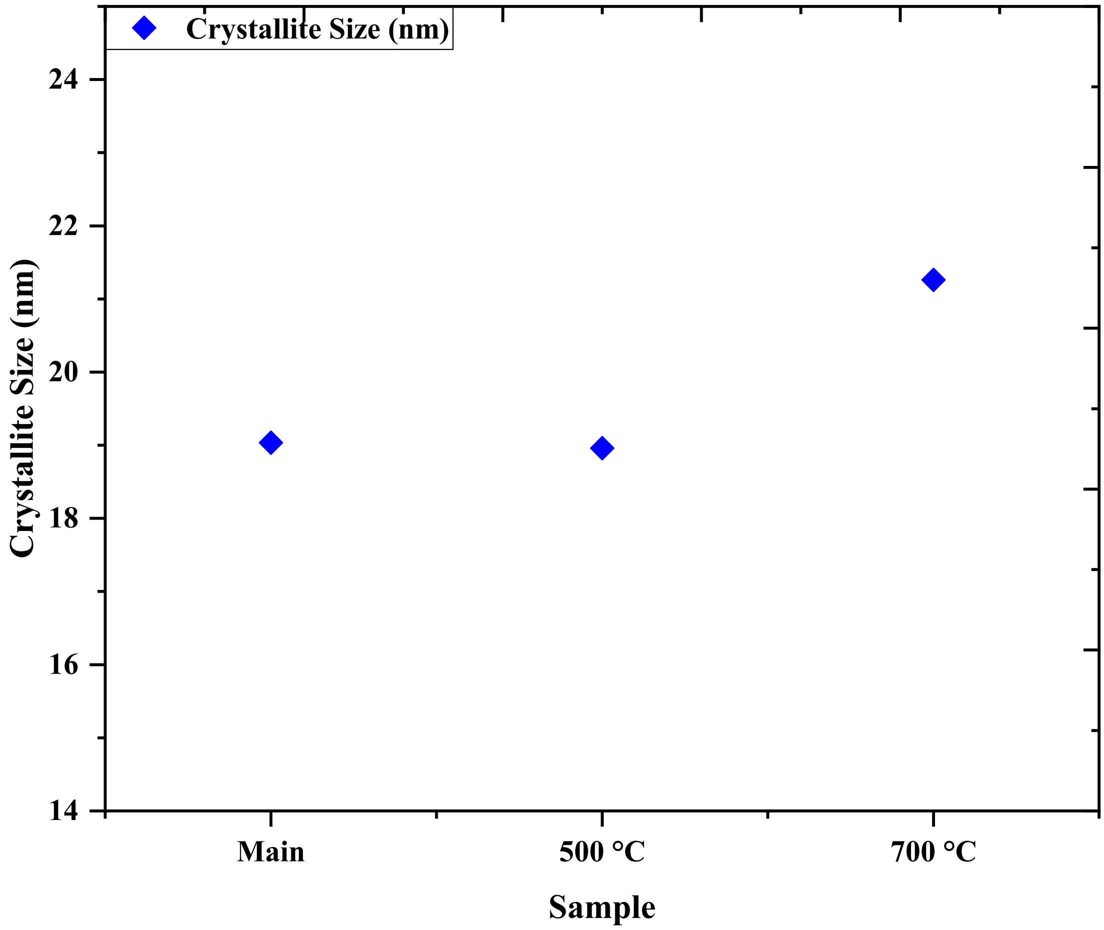

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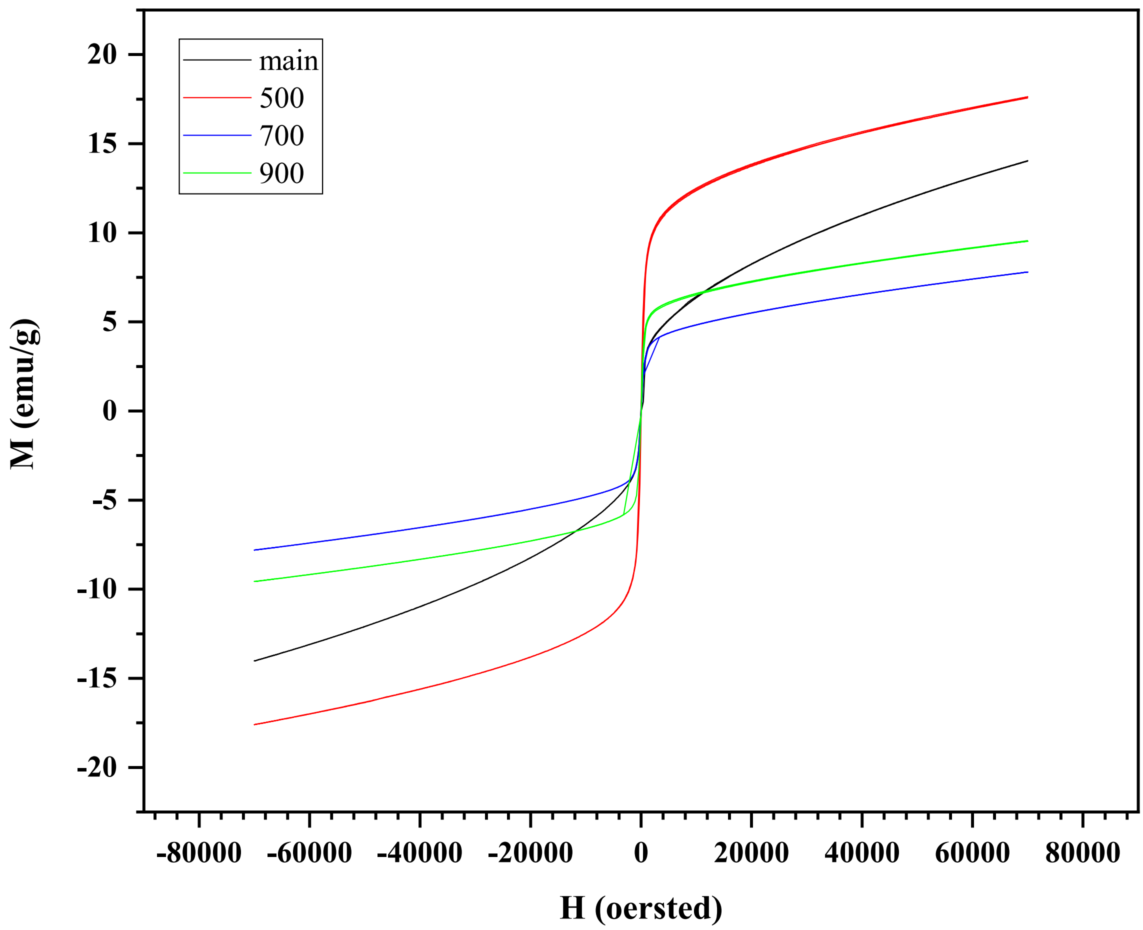
Magnetic measurements are very important in magnetic shape memory alloy analysis. Therefore, transition between phases or sudden changes in magnetic properties can be detected and evaluated. Magnetic measurements were taken with Quantum Design PPMS 7 (Physical Properties Measurement System) at room temperature, between -8 Tesla and 8 Tesla magnetic field before heat treatment and after heat treatment at 500 ºC, 700 ºC and 900 ºC. When Fig. 5 is examined, the internal magnetic properties of the NiMnSnCo alloys changed after 500 ºC heat treatment temperature. Magnetization of alloys value increased for 500 ºC temperature, after this temperature, magnetization of alloy decreased. Kök et al. explained that rising oxidation amount of alloys diminished the saturation values of alloys [32, 33].



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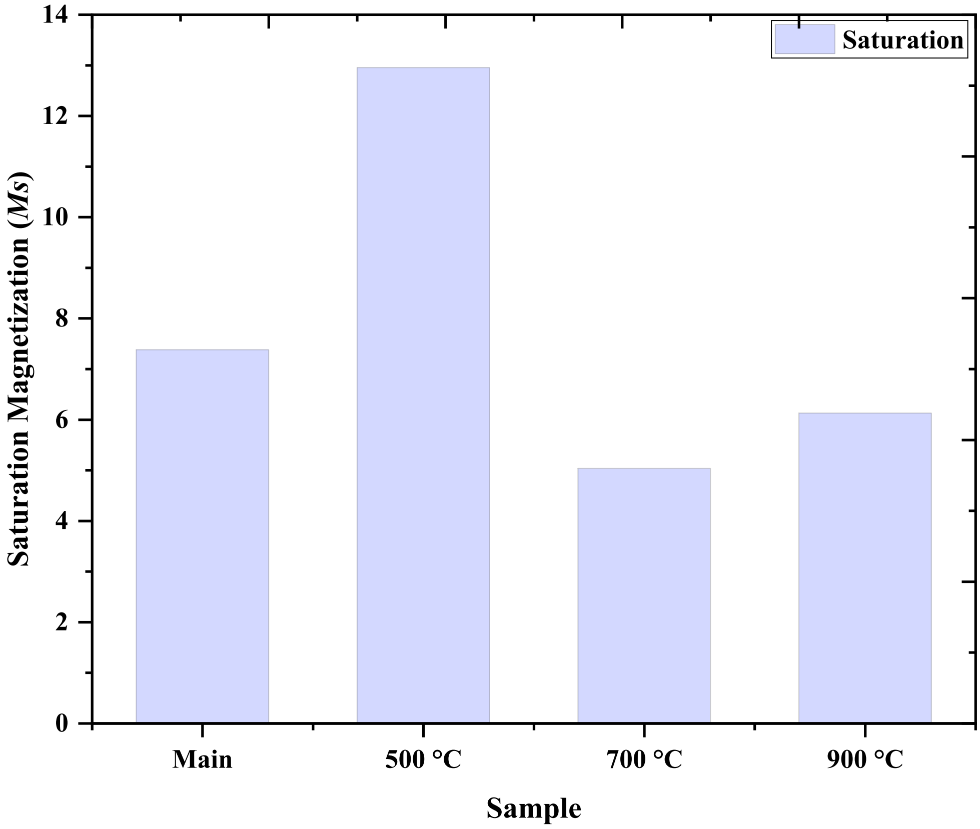
The difference between saturation magnetization and natural magnetization has to be made with magnetic domains. Saturation magnetization is a structural property independent of particle size but dependent on temperature. There is a big difference between paramagnetic and ferromagnetic susceptibility. Compared to paramagnetic materials, the magnetization of ferromagnetic materials reaches saturation at high temperatures and moderate magnetic fields. The flattening of the magnetization curve is interpreted as reaching saturation [34].

Fig. 6 in the magnetization graph, the slope of the fixed part of the curve gives the saturation magnetization. The difference between saturation magnetization and natural magnetization has to be made with magnetic domains. Saturation magnetization is a structural property independent of particle size but dependent on temperature. The results obtained are in agreement with the magnetization plot [34]. Kök et al. observed that the magnetic saturation decreased as a result of high temperature oxidation applied to the NiMnGa alloy and attributed the reason to the increase in the amount of oxide on the alloy [17]. While the highest magnetic saturation value is seen in the sample that is heat treated at 500 ºC, it is seen that the magnetic saturation values of the samples that are heat treated at 700 ºC and 900 ºC are close to each other.



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2. Conclusion

In this study, magnetocaloric, crystalline and scientific research of NiMnCoSn magnetic shape memory alloy was aimed.

- Three different temperatures were selected according to the DSC results. When the DSC analysis results are examined, it is seen that the samples do not give any transformation. It is thought that the reason is because the samples are melted first and then grinded. According to the DSC results, the absence of austenite or martensite phase means that the crystal structure of the sample did not change with temperature.
- When the XRD results were examined, a common peak was observed around 30 and 50 degrees, and it was determined that it was in agreement with the literature results [35].
- It can be seen that magnetization measurements, the most obvious result is seen in the sample, which is heat treated at 500 ºC. This is followed by the main sample, 900 ºC, 700 ºC.
- Saturation magnetization values were calculated from the slope, and then the results were graphed. When the particle size results are examined, it is seen that it is compatible with the magnetization values.

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