Microstructure and Magnetic Properties of Optimally Annealed Ni$_{43}$Mn$_{41}$Co$_{5}$Sn$_{11}$ Heusler Alloy

Nastiti Elwindari$^1$, Budhy Kurniawan$^1$, Candra Kurniawan$^2$, Azwar Manaf$^1$

$^1$Physics Department, Faculty of Science, Universitas Indonesia, Depok 16424, Indonesia.
$^2$ Research Center for Physics LIPI, Puspitek Office Area, Tangerang Selatan, Banten, Indonesia

E-mail : azwar@ui.ac.id

Abstract. In this work, synthesis and characterization of a polycrystalline Ni$_{43}$Mn$_{41}$Co$_{5}$Sn$_{11}$ (NMCS) alloy are reported. Alloy preparation was conducted by melting the constituent components of the designated alloy under an inert Argon (Ar) atmosphere in a vacuum mini arc-melting furnace. Microstructure observation to the as-cast and annealed ingots showing dendritic structure in the as-cast sample. Series of annealing treatment to the sample at 1173 K have changed dendrites progressively in the homogeneous structure after 24 hours annealing time. The annealed sample consisted of a NiMnCoSn main phase with 99.3% volume fraction. Hence, the 24 hours annealed ingot is a single phase alloy. The curie temperature of the annealed NMCS alloys was found in the range 348–351 K. Loop hysteresis evaluation of the annealed ingots showed that ingot which annealed for 12 hours showed the largest magnetization value of 57.96 emu/g.

1. Introduction

Heusler alloy is one of rare-earth-free material based Ni-Mn-X (X=Sn, In, Sb) which have been attracting serious attention among researchers, especially Heusler alloys of low temperature magnetic transition and those of good intrinsic property. In addition to the intrinsic properties like Curie temperature, total magnetization, entropy change ($\Delta S_M$) are the primarily important factor, the preparation process which strongly determine the microstructure of alloys and magnetic ordering[1] also important to obtain the large value of refrigeration capacity (RC) and entropy change at the same time.

The arc-melting furnace is one of the established tools from which alloys can be made through melting process and successive solidification. Despite arc melting furnace is a more straightforward tool for the production of alloys; however, an additional treatment like a long time annealing the as-cast ingot at a sufficiently high temperature is still required in order promote grain homogenization toward homogeneous single phase alloys. The arc-melting technique in many cases has proven useful, in alloys fabrication including that of Heusler alloys, with improved Magneto caloric effect (MCE) properties [2,3] despite more modern technique like rapid solidification by melt-spinning technique, which effectively substantially shortened annealing stage is readily available.

It is mostly accepted that ingots which obtained from arc melting method contained inhomogeneous grains. Thus, the solidified ingot needs to be annealed for a long period of time to
facilitate the atomic diffusion in order to obtain a uniform phase. Ghosh and Aksoy et al.[4,5] have studied the influence of annealing time on MCE of Ni-Mn-Sn bulk samples at 1173 K from 0 h to 24 h and a maximum magnetic entropy change could be found when annealing time is close to 24 h. In this research work, we studied the effect of annealing treatments to the microstructure and magnetic properties of Ni$_{43}$Mn$_{41}$Co$_5$Sn$_{11}$ alloy. The magnetic properties of the annealed ingots were evaluated to determine the total magnetization and Curie temperature.

2. Experiment Method
We used Ni, Mn, Co, and Sn powders with nominal purity better than 99.9%. All the starting powders with were mixed, as the feedstock for the preparation of alloy with a designated Ni$_{43}$Mn$_{41}$Co$_5$Sn$_{11}$ composition. The mixed powders were blended, hand grinded in a mortar and then poured into a cylindrical die. The green compact was obtained after pressured by an uniaxial pressure and sintered at 1173 K for 1 hour for densification. The dense sample was then melted using a mini vacuum arc melting furnace for several times to ensure a homogeneous element distribution throughout the sample. The cast alloy was inserted into a quartz tube under a flowing argon gas during annealing treatment at 1173 K for annealing times 0, 6, 12, and 24 hours to obtain more homogenous samples. The microstructure changes of as-cast NMCS and the effects annealing timeware obtained by scanning electron microscopy (SEM) using a JEOL JSM-6510LA microscope equipped with energy dispersive spectrometry (EDS).

3. Result and Discussion
Plot of the x-ray diffraction (XRD) traces of series annealed NMCS alloy samples compared with that of as-cast sample is shown in Figure 1. Phase analysis based on diffraction peaks revealed the presence of crystalline Ni$_{43}$Mn$_{41}$Co$_5$Sn$_{11}$ phase as the main phase in the alloys which is in accordance with database in Inorganic Crystal Structure Database (ICSD). Some additional phases were also identified. Intensity increment of three primary peaks after annealed treatment were observed at diffracted positions around 40°-45°, 60°-65°, and 75°-80° arise from crystal with the orientation hkl index [220], [400] and [422]. It happened because the main phase NMCS alloy before anneal has not been present in the phase of fully crystalline, but yet still presence in the form of dendrites, so further treatment was needed in order to reach a proportion of optimal concentration diffusion. This was demonstrated by plot of 24 hours annealed sample showing almost single phase alloy.

![Figure 1](image-url)  
Figure 1. Plot of diffraction trace for annealed Ni$_{43}$Mn$_{41}$Co$_5$Sn$_{11}$ samples compared with that of as-cast.
Table 1. Volume fraction of as-cast and annealed Ni_{43}Mn_{41}Co_{5}Sn_{11} alloy.

| Phase         | Volume Fraction (%) | As-cast | Annealed 6 h | Annealed 12 h | Annealed 24 h |
|---------------|---------------------|---------|---------------|---------------|---------------|
| NiMnCoSn      | 68.7                | 48.6    | 45.3          | 99.3          |               |
| Ni_{2}MnSn    | -                   | 49.4    | 52.6          | -             |               |
| Ni_{3}Mn      | 3.0                 | 2.0     | 2.2           | 0.7           |               |
| Ni_{3}Sn      | 16.9                | -       | -             | -             |               |
| Mn_{2}Sn      | 11.4                | -       | -             | -             |               |
| Total         | 100                 | 100     | 100           | 100           |               |

The peaks indicated that alloy phase are growing during the annealing time. In the peak plane [220] shows the crystal structure of austenite with cubic L2_1 Heusler structure. The peaks of annealed sample are mixed with a small amount of some extra phases, most likely Mn-rich phase around 25~35 and 60~65 degree. This result indicates that material peaks were eliminated for further process. Longer annealing time, obtain a uniform phase. Because of the longer atom diffusion distance in a bulk sample is need longer annealing time to obtain the sample homogeneous [1,6]. As the increase annealing time, the stress can gradually release and at the same time, the grain growth can also reduce friction.

Table 1 summarizes result of volume fraction of phases in alloys which determined by quantitative XRD analysis of XRD data in Figure 1. It indicates a successful annealing treatment at 1173 K for 24 hours to transform as-cast sample of multi-phase dendrite structure to almost single phase alloy with NiMnCoSn phase as the main phase.

Table 2. The composition of grain semi-quantitatively analyzed at 3 different points by EDS.

| Analysis at | Composition of element (wt.%) | Predicted phase |
|-------------|-------------------------------|-----------------|
|             | Ni  | Mn  | Co  | Sn  |               |
| α           | 44.76 | 19.16 | 2.20 | 33.87 | Ni-Mn-Co-Sn   |
| β           | 41.04 | 36.82 | 2.12 | 20.02 | Ni-Mn-Co-Sn   |
| γ           | 8.60  | 85.97 | -   | 5.43  | Mn- Rich      |
In order to find out how the microstructure develop towards a single phase structure, SEM observation of the fracture surface of the bulk sample was then carried out for as cast and annealed alloys. SEM micrographs of annealed and as-cast samples are shown in Figure 2. Obviously, as-cast sample showing dendrite structure of in-complete grains which is significantly different with that for the annealed alloys. The grain size and grain morphology of annealed samples progressed with annealing time from which it was observed that the alloy phase began to form small crystallites with a diameter of about 1.5 μm-2.5 μm. The annealed sample has smaller crystallite size compared with that of as cast alloy.

Table 2 summarizes EDS evaluation results on three different spots as indicated by α, β, γ shown in Figure 2b. The chemical composition based on microanalyses by EDS showing in some extent different with designated composition of synthesized alloy. It could be due to the change of weight for the synthesized alloys because of mass reduction during the alloy preparation process. Even though, it indicates that the chemical composition at points α and β may be of the main phase evolves during the crystal growth. Generally it is accepted that the characteristic transition temperature can be determined by the electron concentration principle\[7\]. In this case, it can be referred to the valence electron per atoms are respectively 10 \((3d^84s^2)\) for Ni, 7 \((3d^54s^2)\) for Mn, and 4 \((5s^25p^2)\) for Sn. In connection with the volume fraction Ni\(_{43}\)Mn\(_{41}\)Co\(_5\)Sn\(_{11}\) alloy, the phase of NiMnCoSn as the main phase is the largest among other phases\[8,9\]. In this regards, the existence of NMCS main phase in the alloy can be confirmed that the sintered alloys were formed which have a main phase of NiMnCoSn composition.

![Hysteresis Loop](image1)

**Figure 3.** (a) Magnetic hysteresis (b) Magnetic saturation and coercivity of Ni\(_{43}\)Mn\(_{41}\)CoSn\(_{11}\) as a function of annealing time.

| Anneal Time | \(M_s\) (emu/g) | \(M_r\) (emu/g) | \(H_c\) (Oe) | \(T_c\) |
|-------------|-----------------|-----------------|--------------|--------|
| 0 h         | 35.29           | 2.28            | 75.33        | 348 K  |
| 6 h         | 55.19           | 2.47            | 65.10        | 348 K  |
| 12 h        | 57.96           | 3.85            | 45.60        | 350 K  |
| 24 h        | 47.28           | 6.53            | 38.78        | 351 K  |

Figure 3 shows the hysteresis loop of annealed samples compared with the as-cast. All samples are showing soft magnetic characteristic which different value of total magnetization at a fixed maximum applied magnetic field in the magnetization process. The values were plotted in Figure 2b along with their respective coercivity values. It indicates that total magnetization value increases until 57.96 emu/g in the sample annealed for 12 hours and decreases again at 24 h annealing times, whereas the coercivity value shows a continuous decrease with annealing time. Values of total magnetization and
coercivity for all samples are summarized in Table 3 which representing the magnetic characteristics of these samples. The Curie temperature value was around at 348 K~351 K. Obviously, the Tc of NiMnCoSn phase is not affected by the microstructure. The largest value of total magnetization was obtained in a sample after 12 hours annealing time (see Table 3) in which there are two major magnetic phases in the sample respectively NiMnCoSn with volume fraction of 45.3% and Ni2MnSn with 52.6% in volume fractions. Whereas in the 24 hours annealed sample, there was only 1 major phase with 99.3% in volume fraction of NiMnCoSn. Although the 24 hours annealed sample showed a single phase system, the total value of magnetization is lower than that of 12 hours. In line with previous research, Ma and Dan [10,11] indicate that the total value of magnetization of Ni2MnSn phase larger than NiMnCoSn phase. In this case, the total magnetization 'Js' of the sample may be calculated through the rule of mixture according to equation (3.1) [12].

\[ J_{s\text{alloy}} = \sum_{i=1}^{n} V_{i} J_{s_{i}} \]

where \( J_{s_{\text{alloy}}} \) is the saturated magnetic field of alloys, \( V_{i} \) is volume fraction of phases in alloys to \( i \), and \( J_{s_{i}} \) is saturated magnetic field of phases to \( i \). This should result in total value of magnetization of the 12 hours annealed sample is higher than that of the 24 hours annealed sample.

4. Summary
The microstructure and magnetic properties of Ni_{14}Mn_{14}Co_{8}Sn_{11} alloy have been investigated. The as-cast alloy consisted of dendrite structure which progressively transformed into a fully crystalline grain structure. Annealed temperature at 1173 K for 24 hours is necessary to homogenize the microstructure towards a single phase alloy. However, the largest total magnetization value could be obtained in a sample that annealed for 12 hours resulted in a value about 57.96 emu/g with the corresponding coercivity of 45.60 Oe.

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