Influence of intermetallic Fe and Co on crystal structure disorder and magnetic property of Ni$_{50}$Mn$_{32}$Al$_{18}$ Heusler alloy

H. A. Notonegoro$^{1,2}$, B. Kurniawan$^{1*}$, J. Setiawan$^3$, D. Nanto$^4$ and A. Manaf$^{1*}$

$^1$PPS Materials Science, FMIPA-Universitas Indonesia, Depok 16424, Indonesia.
$^2$Mechanical Engineering Dept., FT-Universitas Sultan Ageng Tirtayasa, Cilegon 42435, Indonesia.
$^3$Center for Nuclear Fuel Tecnology-Badan Tenaga Nuklir Nasional, Tangerang Selatan 15310, Indonesia.
$^4$Dept. of Physics Education, UIN Syarif Hidayatullah, Jakarta, 15412, Indonesia

*E-mail: Azwar@ui.ac.id

Abstract. This work reports a study on structure and magnetic properties influenced by both Fe and Co on Ni$_{50}$Mn$_{32}$Al$_{18}$ Heusler alloy as a candidate of magnetocaloric effect (MCE) materials. The Ni-Fe-Mn-Co-Al sample was prepared by arc melting furnace (AMF) in high purity argon atmosphere. X-ray diffraction investigation and magnetic hysteresis were conducted to characterize the synthesized sample. X-ray diffraction using Cu-K$_\alpha$ pattern shows that both Fe and Co introduce a tungsten type disorder of Ni$_{50}$Mn$_{32}$Al$_{18}$ Heusler alloy which partially replace the site position of Ni and Mn respectively. However, in this tungsten type disorder, it is difficult to distinguish the exact position of each constituent atom. Therefore, we believe it may allow any exchange interaction of each electron possessed the atom. Interestingly, it produced a significant increase in the value of the hysteresis magnetic saturation.

1. Introduction

The needs of magnetic refrigerator (MR) operated near room temperature have stimulated much research interest in magnetocaloric effect (MCE) alloy base. To establish main relation between magnetocaloric and magnetic values in MCE mechanisms is studying magnetic properties materials with sharp change of lattice parameters and structure type [1]. Various candidates for magnetocaloric alloys have been studied, including Ni-Mn-Sn-Ga, Ni-Fe-Mn-Ga, Ni-Co-Mn-Al, Ni-Mn-Sn and Ni-Mn-Al system [2–6]. Widespread research has been carried out with the focus on developing Ni-Mn-Al as an MCE alloy base [4]. Liu et al. reported potential application of high-temperature magnetocaloric Heusler alloy (HA) in previous studies [7]. Kainuma et al. found that various compound of Ni-Mn-Al alloy had affected martensitic transformation temperature and magnetic properties [8]. Moreover, Webster et al. found that Ni$_{50}$Mn$_{32}$Al$_{18}$ shows antiferromagnetic properties (AFM) in structure B2 (Wyckoff) [9,10]. However, Notonegoro et al. reported the similar Ni$_{50}$Mn$_{32}$Al$_{18}$ showed diamagnetic (DM) phase in structure B2 (Wyckoff). Furthermore, partial replacement of Al with Mn atoms to obtain Ni$_{50}$Mn$_{32}$Al$_{18}$ compound shows a ferromagnetic (FM) phase with B2 structure [11]. In other hand, Xuan et al. found substitution of Co atom to Ni site in Ni$_{50-}$xCo$_{x}$Mn$_{32}$Al$_{18}$ (x= 3, 4, 5, 6, 7, and 8) had shifts the temperature of martensitic transformation into a lower value and Co concentration play important rule as a tuning of a ferromagnetic austenite-weak-magnetic martensite[12]. Meanwhile, Graf et al. describe the properties of Heusler materials are strongly...
dependent on the atomic arrangement of the atoms. Eventually that the size of the band gap decreases with increasing amount of atomic disorder[13].

In this work, we report the study of crystallite structure and hysteresis magnetic properties (Ms) of Ni\textsubscript{50}Mn\textsubscript{32}Al\textsubscript{18} which some Ni atoms replaced by Fe and Mn atoms replaced by Co, respectively to make a Ni\textsubscript{44}Fe\textsubscript{6}Mn\textsubscript{24}Co\textsubscript{8}Al\textsubscript{18} HA system.

2. Experimental procedures
Ni\textsubscript{44}Fe\textsubscript{6}Mn\textsubscript{24}Co\textsubscript{8}Al\textsubscript{18} alloy was prepared in an appropriate quantity of high purity Ni, Fe, Mn, and Al metal powder. The mixing compound compacted with 10 tons in a 12 mm cylinder die for 5 minutes and sealed in quartz cube 1.5 mm diameter. After flushing with high purity argon (HPA) three times, the compacted sample sintered in 900 °C for 1 hour under vacuum condition. This way was necessary to simplify sample preparation and in order to reduce mass lost during smelting process. The arc melting furnace (AMF) methods were smelting on vacuum condition after flushing five times with HPA. These samples were remelted four times to ensure composition homogeneity then followed by the annealing process for 72 hours in 900 °C in vacuum condition. This was a better annealing time then 48 hours in 900 °C as we reported before [14]. Crystallite structure and magnetic properties were examines using XRD with Cu-K\textalpha and PERMAGRAPH® L © MAGNET-PHYSIK Dr. Steingroever GmbH.

3. Results and discussion
3.1. Order and Disorder of Heusler Structure compound
Study of crystal structure is essential to understanding properties of Heusler compounds correlated with experimental results. Cu\textsubscript{2}MnAl-type structure of Heusler alloy identified by the occurrence of the fcc-typical on (111) and (200) plane reflections, and their relation to the (220) plane reflection [13]. XRD pattern in Figure 1 shows structure of Ni\textsubscript{44}Fe\textsubscript{6}Mn\textsubscript{24}Co\textsubscript{8}Al\textsubscript{18} compound. The type plane reflection shows of Cu\textsubscript{2}MnAl-type structure. Thus, as result of refinement base on JCCPDS - COD 98-063-2933, the structure of Ni\textsubscript{44}Fe\textsubscript{6}Mn\textsubscript{24}Co\textsubscript{8}Al\textsubscript{18} determined as tungsten-like structure whereas the X, Y, and the Z atoms become equivalent distributed in all positions. The value 4\textit{a}=4\textit{b}=4\textit{c} shows a cubic lattice and a reduced symmetry of \textit{Fm\textbar{3}m} also known as an A2-type disorder (Wyckoff) whereas remains only the cubic primary reflection [13].

![Figure 1. XRD pattern of Ni\textsubscript{44}Fe\textsubscript{6}Mn\textsubscript{24}Co\textsubscript{8}Al\textsubscript{18} compound at room temperature. Ni\textsubscript{44}Fe\textsubscript{6}Mn\textsubscript{24}Co\textsubscript{8}Al\textsubscript{18} correspond to tungsten-type disorder of HA compound.](image)

3.2. Microstructure and Morphology
Micrograph from optical microscope results depicted in Figure 2 shows the microstructure of Ni\textsubscript{44}Fe\textsubscript{6}Mn\textsubscript{24}Co\textsubscript{8}Al\textsubscript{18} HA compound after 72 hours annealed. The general microstructures consist of three type of grain. Grain established in three colors: black, gray and white. On red circle appears the white grain occupy a grain boundary, and grain beside of the white grain.
The microstructures define the effect of tungsten-type disorders onto grain shape. Whereas the atomic structure had initiated the overlapping structure between the grains, generate the proper solubility in Ni$_{44}$Fe$_6$Mn$_{24}$Co$_8$Al$_{18}$ HA compound.

3.3. Magnetic Properties of the compound
The hysteresis magnetic saturation of Ni$_{44}$Fe$_6$Mn$_{24}$Co$_8$Al$_{18}$ has shown in Figure 3. The magnetic polarization (J) reached 0.3 T when the magnetic field strength (H) below 250 kA/m. We suggest which the tungsten-type disorder had increased hysteresis magnetic saturation value reach more than 0.3 T contrast with magnetic hysteresis curve of Ni$_{50}$Mn$_{32}$Al$_{18}$ as a comparison. We believe the overlapping structure inside of the alloy had a correlation with exchange interaction between their electrons whereas aligned the magnetic moment and raised the magnetic saturation [10,15]. Therefore, doping intermetallic Fe and Co on Ni$_{50}$Mn$_{32}$Al$_{18}$ positively enhanced magnetic saturation significantly.

4. Conclusion
We successfully synthesized Ni$_{44}$Fe$_6$Mn$_{24}$Co$_8$Al$_{18}$ alloy by AMF method. The substitution of intermetallic both Fe and Co formed a Ni$_{44}$Fe$_6$Mn$_{24}$Co$_8$Al$_{18}$ alloy which Cu$_3$MnAl-type structure, have generated the tungsten-type disorder in Heusler alloy compound. In microstructure view, this type disorder allows the occurrence of the overlapping phases in grain system. These conditions had beneficial in raising significantly the value of magnetic saturation in the alloy.
5. Acknowledgement

The authors gratefully acknowledge the support of Department of Physics, Universitas Indonesia for the research facilities. The authors wish to thank Dr. Vivi Fauzia for support. This work was supported by the Universitas Indonesia under the research grant contract of Hibah Publikasi Internasional Terindeks untuk Tugas Akhir Mahasiswa UI 2016 under the research grant contract no. 1993/UN2.R12/HKP 05.00/2016. References

Reference

[1] Tishin AM, Spichkin YI Int J Refrig 2014;37:223–9. doi:10.1016/j.ijrefrig.2013.09.012.
[2] Chatterjee S, Giri S, De SK, Majumdar S J Alloys Compd 2010;503:273–6. doi:10.1016/j.jallcom.2010.05.026.
[3] Sokolovskyi VV, Fazulzul MR, Buchelnikov VD, Drobosyuk MO, Taskaev SV, Khovaylo VV J Magn Magn Mater 2013;343:6–12. doi:10.1016/j.jmmm.2013.04.069.
[4] Kim Y, Kim EJ, Choi K, Han WB, Kim HS, Shon Y, et al J Alloys Compd 2014;616:66–70. doi:10.1016/j.jallcom.2014.07.034.
[5] Dan NH, Duc NH, Yen NH, Thanh PT, Bau LV, An N, et al J Magn Magn Mater 2015;374:372–5. doi:10.1016/j.jmmm.2014.08.061.
[6] Ghosh A, Mandal K J Appl Phys 2015;117. doi:10.1063/1.4913951.
[7] Liu C, Zhang W, Qian Z, Hua Z, Zhao Q, Sui Y, et al J Alloys Compd 2007;433:37–40. doi:10.1016/j.jallcom.2006.06.070.
[8] Kainuma R, Gejima F, Sutou Y, Ohnuma I, Ishida K Mater Trans - JIM 2000;41:943–9.
[9] Webster JP, Ziebeck KRA Volume 19C: “Alloys and Compounds of d-Elements with Main Group Elements. Part 2” in SpringerMaterials (http://dx.doi.org/10.1007/103532 n.d. doi:10.1007/10353201_31.
[10] Ersoy H, Sandratskii L, Dederichs P, Eriksson O Exch Organ Behav Teach J 1975.
[11] Notonegoro HA, Kurniawan B, Setiawan J, Manaf A. Magnetic hysteresis evolution of Ni-Al alloy with Fe and Mn substitution by vacuum arc melting to produce the room temperature magnetocaloric effect material 2016;020019:020019. doi:10.1033/1.4953944.
[12] Xuan HC, Chen FH, Han PD, Wang DH, Du YW. Effect of Co addition on the martensitic transformation and magnetocaloric effect of Ni–Mn–Al ferromagnetic shape memory alloys. Intermetallics 2014;47:31–5. doi:10.1016/j.intermet.2013.12.007.
[13] Graf T, Felser C, Parkin SSP. Simple rules for the understanding of Heusler compounds. Prog Solid State Chem 2011;39:1–50. doi:10.1016/j.progsolidstchem.2011.02.001.
[14] Notonegoro HA, Ferdian D, Prasetyo Y, Manaf A. Microstructure analysis of synthesized iron substituted Ni44Fe6Mn32Al18 Heusler alloy 2016;1729. doi:10.1063/1.4946939.
[15] Mubarok N, Notonegoro HA, Thosin KAZ, Manaf A AIP Conf Proc 2016;020022:020022. doi:10.1063/1.4953947.