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RESEARCH ARTICLE

Ni-Mn-Al Heusler Alloy Samples Preparation by Mechanical Alloying Method and Study of their Investigated Properties

Shailendra V Dhanal[1]*, **Husainkhan Devadi**[1], **V G Akkimardi**[2], **S A Kori**[3]

1 Sanjay Ghodawat University, Kolhapur, Maharashtra, India
2 Basaveshwar Engineering College, Bagalkot Karnataka, India
3 Central University of Andhra Pradesh, Anantapur, Andhra Pradesh, India

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* **Corresponding author**.

shailendra.dhanal@sanjayghodawatuniversity.ac.in

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Abstract

Objective: In this work, ternary Ni-Mn-Al Heusler alloy powder samples were fabricated using mechanical alloying technique to study its alloy formation mechanism and the effects of mechanical alloying on the investigated properties. **Methods:** The samples were prepared using high energy planetary ball mill under argon conditions. The milling time of 0 h (hour/hours), 5 h, 10 h and 15 h were selected to see the progress of alloy formation. The microstructural, compositional, thermal and magnetic studies of ball milled powder samples were conducted. **Findings:** Compositional study reveals stoichiometric Heusler composition (X_2YZ) of Ni-Mn-Al alloy with no contamination. The optimum milling time required for the formation of alloy by mechanical alloying resulted through the proper selection of milling parameters. The average crystallite size obtained reveals that nanocrystalline structure of Ni-Mn-Al alloy was achieved during the ball milling operation. The successive heating of powder particles in differential scanning calorimetry showed crystallization and alloy formation. **Novelty/Applications:** The magnetic study indicated soft ferromagnetic nature of the selected ball milled powder sample suggesting the alloy can be developed for possible ferromagnetic shape memory alloy applications.

Keywords: Ni-Mn-Al; Heusler alloy; Mechanical alloying; Ball milling; Structural properties

1 Introduction

Heusler alloys are important intermetallics with fixed stoichiometric composition 2:1:1 (X_2YZ) called full Heusler alloys and 1:1:1 (XYZ) called half or semi Heusler alloys, where X and Y are transition metals and Z is in column 13-18 from periodic table[1]. In recent years Ni-Mn based Heusler alloys with general formula Ni-Mn-Z where Z can be gallium (Ga), tin (Sn), antimony (Sb) and indium (In) in stoichiometric composition (2:1:1 and 1:1:1) have generated interest in research for the actuators, sensors and refrigerators applications[2]. These are ternary alloys promising materials in many modern research applications such as magneto-mechanical and magneto-electronics [3]. Even though Ni-Mn-Ga alloy systems are well-known Heusler alloys, their highly brittle nature, low martensitic transformation temperature, high cost of gallium have put constraints to use these alloys practically. From the preparatory studies, authors indeed found the presence of some unique properties in Ni-Mn-Al ternary alloy and motivated to investigate this alloy experimentally. Ni-Mn-Al alloys are investigated theoretically and experimentally by some researchers as potential Heusler alloys and shape memory alloys. Initially they were considered to enhance the brittleness of binary Ni-Al alloys [4]. Also, the understanding of large magneto strains in Ni-Mn-Ga Heusler alloy activated an interest in the various properties of Ni-Mn-Al alloys [4,5]. Unlike Ni-Mn-Ga alloy systems, the structural and magnetic properties of mechanically alloyed ball milled Ni-Mn-Al Heusler alloys have not been investigated clearly so far. Still, arc melting is most employed method for the synthesis of Ni-Mn based Heusler alloys [6].

Recently, mechanical alloying technique using powder metallurgy route has been recognized as an effective method for the synthesis of smart materials for industrial applications because this offers feasibility in producing mass-scale production at nanoscale range using devices such as high energy planetary ball mills, attrition ball mills and also practically it is important and possible to mold fine powders into desired shape by consolidation easily [7–11]. According to the available literature, very few attempts have been made to synthesize Ni-Mn-Sn Heusler alloys by mechanical alloying [7,8] to determine structural and magnetic properties. In this work, ternary Ni-Mn-Al Heusler alloy was synthesized by mechanical alloying technique and studied its formation mechanism. Then, the effects of mechanical alloying on the investigated structural and magnetic properties were studied.

2 Experimental Details

2.1 Materials

To synthesis Ni_2MnAl Heusler alloy, high purity (more than 99.5 %) Ni, Mn and Al elemental powders were used as initial constituents. The process was carried out using a high energy planetary ball mill (Fritch Pulverisette 5) in an argon atmosphere. The elemental powders were weighed and mixed in stoichiometric ratio of 2:1:1 by performing atomic weight calculations. The important parameters in ball milling operations (milling time, milling speed and ball to powder weight ratio) were selected [7]. Tungsten carbide (WC) balls of 10 mm diameter, milling vials of volume 250 ml were employed as grinding medias. Milling speed of 300 rpm and ball to powder weight ratio (BPWR) of 15:1 was kept constant throughout the milling process. Toluene was used as a surfactant agent to avoid agglomeration and to keep a steady condition between cold welding and fracturing of powder particles during milling. Work cycle of 30 min and 60 min of rest were performed to prevent overheating. The milling process was executed up to 15 h and the powder samples were taken out after 0 h, 5h, 10 h and 15 h to observe the growth of the alloy formation.

2.2 Methods

The microstructures of as-synthesized powder samples were analyzed by using X-ray Powder Diffractometer (XRD) at scan rate 2^0 per min with Cu-Kα radiation. The lattice strain and crystallite size of ball milled powder samples were determined using Williamson and Hall (W-H) method. For morphological and chemical analysis of samples Field Emission Scanning Electron Microscopy equipped with standard Energy Dispersive X-ray Spectroscopy (FESEM-EDX) instrument was used. Thermal stability and reaction kinetics of the ball milled powder samples were examined performing Differential Scanning Calorimetry (DSC) measurements at a constant heating rate of 10^0C/min under nitrogen gas flow. The magnetic properties of selected 15 hr ball milled Ni-Mn-Al Heusler alloy sample were measured by Vibrating Sample Magnetometer (VSM) at room temperature. The magnetic hysteresis curve and important magnetic parameters were obtained in terms of magnetization (M) versus applied magnetic field (H) at applied field up to 17 kOe. Also, to observe the effect of heat treatment on the magnetic properties, these samples were annealed using split type quartz tube furnace by vacuum sealed in the quartz tubes and subjected to heating at 800^0C (15, 18) with heating rate of 5^0/min for 12 hours followed by cooling in the furnace itself.

3 Results and Discussion

3.1 Microstructural studies

Figure 1 shows diffraction patterns of Ni-Mn-Al Heusler alloy as a function of milling time synthesized by planetary ball milling. Powder sample of 0 h (un-milled initial mixture) was prepared by mixing the elemental powders (Ni, Mn and Al) and identified according to JCPDS card no: 004-850 (Ni), 030637 (Mn) and 001-1176 (Al). Several different peaks and their corresponding planes at diffraction angle 2θ can be seen for selected milling hours suggesting reactions amongst them. Increase in milling time up to 10 h observed formation of new peaks of dissimilar intensities indicating new phase of Ni_2MnAl alloy identified by JCPDS card No: 98-060-8488 with cubic structure (lattice parameters equal to $6.060A^0$). When further milling proceeds up to 15 h, cubic $L2_1$ Heusler structure was identified according to JCPDS (98-060-8487) with lattice parameters equal to 5.824 $A^0$and space group as Fm-3m (number 225). Thus, as presented in Figure 1 the results show that the required ball milling time for the formation of Ni-Mn-Al Heusler alloy is 10-15 hours with BPWR 15 :1 and milling speed of 300 rpm.

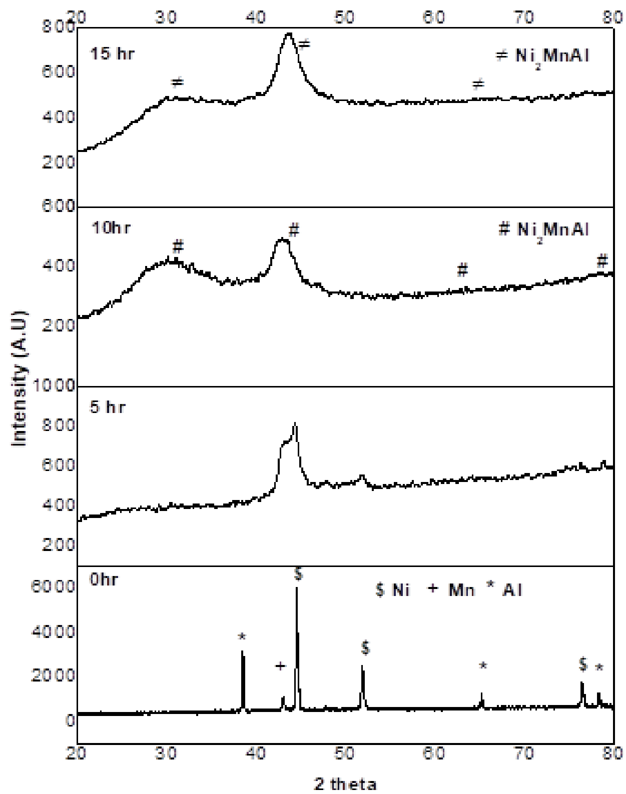

Fig 1. X-ray diffraction pattern of Ni-Mn-Al powder samples up to 15 h

Figure 2 presents the graph of average crystallite size (D) and lattice strain as a function of milling hours determined by Williamson and Hall equation[12,13]. The crystallite sizes were determined using Scherrer equation, D= $K\lambda/B\cos\theta$. It can be observed that crystallite size reduces rapidly up to 5 h but then very slowly up to 15 h suggesting dominance of fracture of powder particles over cold welding during initial hours[13,14]. Also, increase in lattice strain can be seen as ball milling operation progresses. The results are summarized in Table 1. From which, average crystallite size obtained reveals that nanocrystalline structure was achieved during the ball milling operation.

From FESEM microanalysis (Figure 3) initial mixture of 0 h presents cauliflower-like shape and irregular granularity with an average particle size of 10-12 μm. Upon further processing, reduction in particle size in the range of 3-4 μm was found after 5 h milling due to intensive force of grinding balls. After 10 h milling due to severe plastic deformation particle union takes place increasing average particle size from 4 to 7 μm. For this stage, it can be concluded that due to ductile nature of aluminum, these particles stuck to the grinding media and other element surfaces which forms larger particles promoting cold wedding. The particle size of 1-2 μm was achieved after 15 h mechanical alloying suggesting that 15 h milling time is adequate to achieve uniform distribution of elements. For Chemical composition and contamination identification, prepared 15 h as-milled powder sample of Ni-Mn-Al alloy was chosen. Typical EDX spectrum (refer Figure 4) shows that alloy sample do not contain an impurity. The EDX analysis results for selected sample as shown in Table 2 confirms Heusler phase having composition $Ni_{52}Mn_{25}Al_{23}$ (at %).

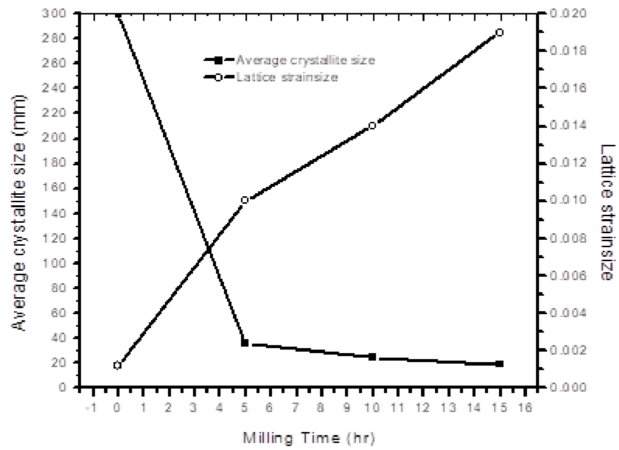

Fig 2. Average crystallite size and milling time as a function of milling time

Table 1. Lattice strain and crystallite size for ball milled samples for different milling hours

Milling hours (h)	Bcosθ (rad)	sinθ	Lattice strain (ε)	Crystallite size (D)
0	0.00484	0.378	0.0012	299
5	0.0402	0.373	0.010	36
10	0.0575	0.370	0.014	25
15	0.0778	0.74	0.019	19

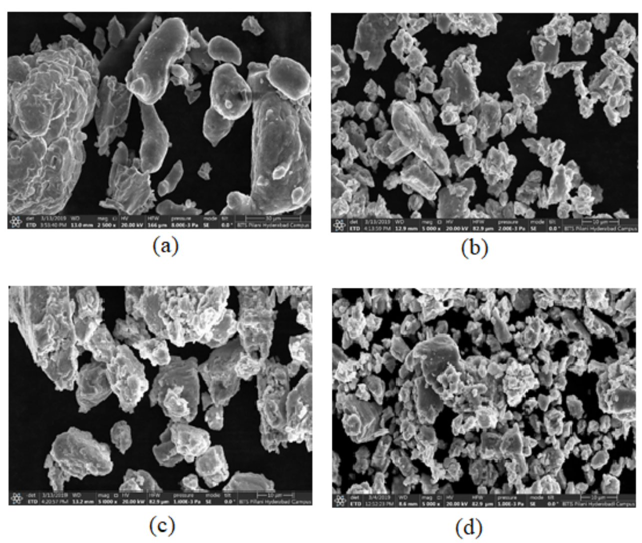

Fig 3. SEM images of ball milled Ni-Mn-Al powder samples for (a) 0 h (b) 5 h (c) 10 h and (d) 15 h

Table 2. Elemental composition of Ni-Mn-Al Heusler alloy

Element	Weight %	Atomic %
Al	60.54	52.13
Mn	27.34	25.16
Ni	12.12	22.71

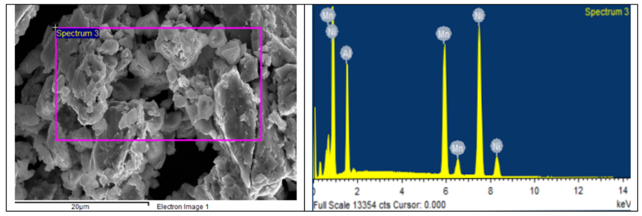

Fig 4. EDX spectrum of selected 15 h ball milled Ni-Mn-Al sample

3.2 Thermal studies

During thermal stability study, DSC shows the subsequent heating of powder samples of 0 h, 5 h and 15 h (Figure 5 a-c). It can be observed that 0 h alloy sample shows an endothermic reaction at peak temperature of 662^0C indicating melting point of Al. The parallel feature is absent in 5 h DSC graph suggesting reaction of Al with Ni and Mn. Here, broadening of curve shows consistency with the XRD results of 5 h milling (refer Figure 1). DSC of 15 h displays broad exothermic reactions in the range of 400^0C to 600^0C suggest alloying process of Ni-Mn-Al due to the release of strain energy generated in powder particles.

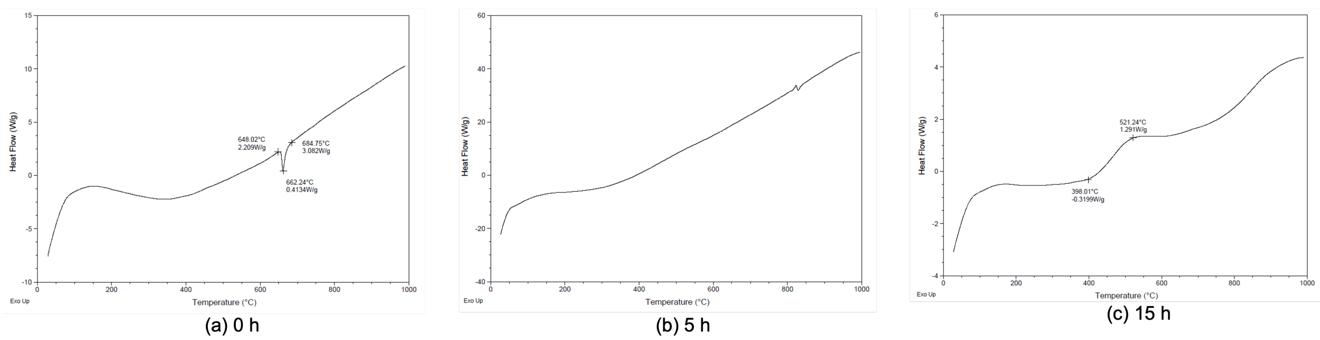

Fig 5. DSC heating for ball milled Ni-Mn-Al samples of (a) 0 h, (b) 5 h and (c) 15 h

3.3 Magnetic studies

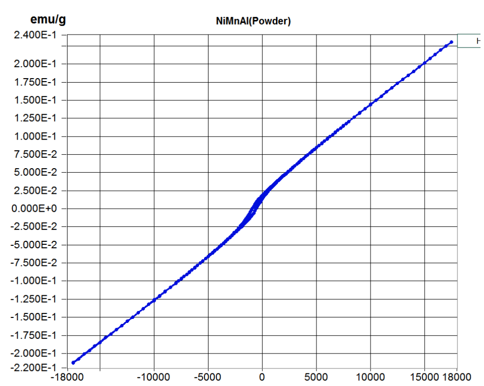

Fig 6. Magnetization curve of as-synthesized 15 hr ball milled Ni-Mn-Al sample

Figure 6 and Figure 7 shows magnetization (M-H) curves of as-milled and annealed (at 800^0C) samples respectively of selected 15 h ball milled Ni-Mn-Al sample. The coercivity (Hc) and saturation2 magnetization (M_{sat}) are important factors in magnetic measurements of materials. Magnetic parameters depend upon grain size, composition, heat treatment and interaction between atom element[14]. Generally, annealing causes to decrease the Hc of ball milled powder samples due to increase in grain size[15]. As seen from hysteresis curve of annealed Ni-Mn-Al alloy sample (Figure 7), value of Hc increases after performing annealing operation and M_{sat} slightly decreases. This ascertain behavior can be explained due to non-magnetic particles (Al) distribution. The sharp shape of hysteresis loop of as-milled sample shows antiferromagnetic nature, while upon annealing improvement in magnetic properties displays soft ferromagnetic nature of the alloy. Table 3 shows the magnetic parameters evaluated using VSM. Thus, the results showed that the prepared Ni-Mn-Al Heusler alloy seems to be useful for the development of gallium free ferromagnetic shape memory alloys.

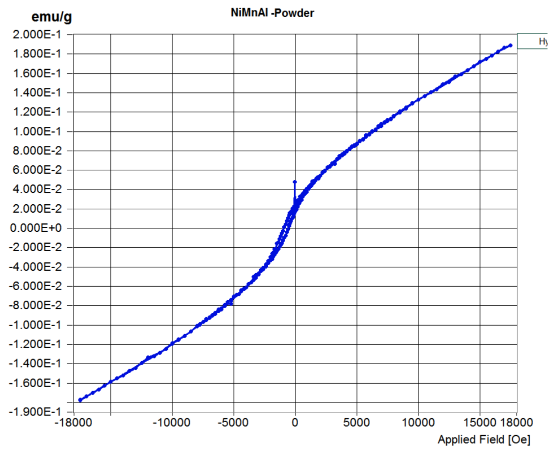

Fig 7. Effect of annealing on the magnetization of 15 hr ball milled Ni-Mn-Al sample

Table 3. Magnetic parameters of Ni-Mn-Al alloy

Sample	Coercivity Hc (Oe)	Saturation Magnetization M_{sat} (emu/g)	Remanence (M_R/M_{sat})
As-milled	167.53	0.24	0.0176
Annealed	182.43	0.20	0.0354

4 Conclusions

Nanocrystalline Ni-Mn-Al Heusler alloy was synthesized successfully by mechanical alloying technique using high energy planetary ball mill. Ball milling process was interrupted after every 5 h up to 15 h removing small volume of powder for the inspections. Through proper selection of milling parameters during mechanical alloying, optimum milling time of about of 15 h was obtained in the formation of Ni-Mn-Al Heusler alloy maintaining the balance between particle cold welding and fracture. By microstructural studies, prepared alloy was identified having cubic $L2_1$ Heusler structure with space group Fm-3m (number 225) according to corresponding JCPDS card. Large reduction in the crystallite size was observed during initial hours showing dominance of fracture over cold welding. Gradual rise in the lattice strain was observed as milling process progresses. The compositional analysis revealed that the synthesized alloy confirms the desired Heusler stoichiometric composition (X_2YZ) by atomic percent signifying that mechanical alloying is an effective technique to fabricate Ni-Mn based Heusler alloys. Also, during thermal stability observations, the subsequent heating of the ball milled powder particles at different milling time in DSC showed crystallization of Ni-Mn-Al Heusler alloy. The magnetic study observations suggest that the alloy has a potential for its use in the development of ferromagnetic shape memory alloys. Thus, this study shows the strong interest about Ni-Mn-Al ternary alloy prepared by mechanical alloying around Heusler composition for the use of shape memory alloys.

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