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Development of Rare-Earth Free Mn-Al Permanent Magnet Employing Powder Metallurgy Route

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Abstract

Most widely used high-performance permanent magnets are currently based on intermetallics of rare-earths in combination with Fe and Co. Rare-earth elements required for these magnets are getting expensive by the day. Consequently, there is a thrust worldwide to develop economical rare-earth free permanent magnets. It is acknowledged that the τ phase in Mn–Al alloys possesses magnetic properties without the presence of ferromagnetic elements such as Fe, Co, and Ni. In the present study, we report the synthesis of magnetic τ phase of $Mn_{54}Al_{46}$ alloy synthesized using mechanical alloying followed by solutionizing and annealing to obtain the desired magnetic phase.

It is well known that Al dissolves partially in Mn matrix hence supersaturated solid solution of $Mn_{54}Al_{46}$ alloy powder was obtained by mechanical alloying using a planetary high-energy ball mill. For this purpose elemental Mn and Al powders were ball-milled in Argon atmosphere at 400 rpm using stainless steel bowl with ball to powder ratio of 15:1. These mechanically alloyed $Mn_{54}Al_{46}$ powders were then consolidated using spark plasma sintering at 550°C for 20 min. followed by solution treatment at 1050°C for 5 hrs and then water quenched to retain high temperature ε phase. Subsequently, the ε $Mn_{54}Al_{46}$ samples were annealed in the temperature range 450°C-650°C to obtain the magnetic τ phase. These samples were characterized by XRD and SEM and the magnetic properties were measured using a vibrating sample magnetometer (VSM). It was observed that the magnetization and coercivity of MnAl magnets exhibited strong dependence on annealing temperature and annealing time.

Introduction

MnAl based magnets possess hard magnetic properties without ferromagnetic elements (3d transition metals) and rare-earth metals [1]. The low costs and availabilities of the Mn and Al, good machinability, high specific strength, high modulus of elasticity, as well as the excellent corrosion resistance, make this material particularly attractive. Mn metal is in general antiferromagnetic. By increasing the atomic distance between Mn atoms to 2.96 Å or more, the element becomes ferromagnetic [2]. The hard magnetic properties of MnAl magnets originate from the magnetic τ phase which is a metastable phase that can be obtained either by quenching the high-temperature phase followed by isothermal annealing at temperatures between 400 and 700°C or at a controlled cooling rate from high-temperature non-magnetic

ε–phase (h.c.p.) which transforms into a non-magnetic ε_0-phase (orthorhombic) by an ordering reaction, and then transforms into a ferromagnetic τ-phase (f.c.t.) by a martensitic phase transition, i.e. $\varepsilon - \varepsilon_0 - \tau$ Typical properties are saturation magnetization (σ_s) of 88-96 emu/g [1,3] and coercieve force of 1.5 kOe [4]. Prolonged annealing and elevated temperatures result in decomposition of the τ-phase into the equilibrium cubic γ_2- and β-phases.
Mechanical milling have been used to synthesize a number of rare earth permanent magnet alloys, including $Nd_2Fe_{14}B$ [5], $Nd(Fe,Mo)_{12}N_x$ [6] and $SmCo_5$ [7]. In the present study we have done preliminary investigation on the microstructure and magnetic properties of mechanically milled and spark plasma sintered MnAl alloys.

Experimental

Pure Mn and A1 powders were weighed in stochiometric ratio to give compositions of $Mn_{54}Al_{46}$. The powders along with 2% process control agent were then sealed in stainless steel bowl together with 10 mm balls and filled with pure Ar gas. The ball to powder weight ratio was about 15:1. Mechanical alloying of the as-mixed powders was carried out at 400 rpm. Mechanically alloyed Mn & Al powders were sintered employing spark plasma sintering technique followed by two-step heating. The homogenization was carried out at 1050 for 5hrs followed by water quenching to retain the high temperature ε phase. These pellets were annealed in the temperature range 450°C-650^{o}C for the synthesis of metastable magnetic τ phase. As milled, solutionized and annealed specimens were characterized by X-ray diffraction (XRD) measurements. Their magnetic properties were studied using a vibrating sample magnetometer (VSM) at room temperature.

Results and Discussion

Figure 1 shows change in XRD pattern of the MnAl powder with respect to milling time. The XRD pattern of the blended elemental powders shows clear diffraction peaks from α-Mn and Al phases. The intensity of the diffraction peaks from Al phase diminishes with increasing milling time. This indicates diffusion of Al into the α-Mn matrix during mechanical alloying and finally forming α-Mn solid solution.

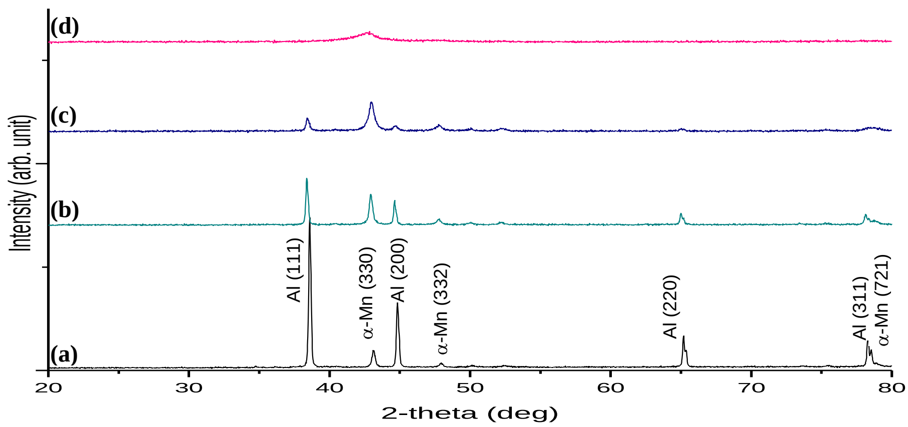

Fig. 1 XRD patterns of (a) the blended elemental powders and milled for (b) 20h (c) 70h, (d) 150h

Figure 2 shows XRD patterns of the solution treated and annealed MnAl pellets exhibiting the high temperature ε phase, metastable τ phase along with stable β and γ_2 phase. It can be clearly seen from fig.2a that solution treatment at 1050°C for 5h and water quenching results in single phase which is high temperature ε phase. As it is well known that the ε phase transform to magnetic metastable τ phase by isothermal annealing at temperatures between 450 and 650°C. To achieve this transformation annealing of water quenched sample was done in this temperature range for varying length of time (10 min. to 40 min.). Present result is from preliminary study and detailed characterization is underway. Annealing treatment given at 550°C for 30 min. results in distinct peaks from magnetic phase τ. Further, magnetic property characterization was done using VSM for all these samples.

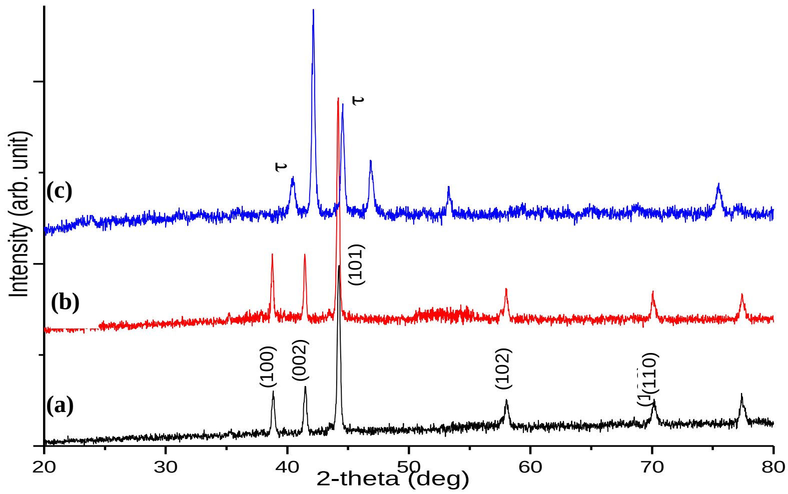

Fig. 2 XRD patterns of mechanically milled and spark plasma sintered MnAl pellet solution treated at 1050°C for 5h (a) Water quenched (WQ) (b) WQ-annealed at 600°C for 10 min. air cooled (c) WQ-annealed at 550°C for 30 min. air cooled

Figure 3 (a - d) shows the hysteresis loop of samples annealed between 550°C and 650°C for 20/30 min. Sample annealed at 550°C for 30 min. exhibits higher coercivity as well as remanence in accordance with the XRD result. The saturation magnetization is strongly dependent on the composition i.e. the amount of τ phase in the present system. Further, transformation of ε phase into τ phase depends on appropriate combination of annealing temperature and time. Optimization of annealing conditions which in turn manipulate the amount of τ phase could lead to further enhancement of magnetic properties.

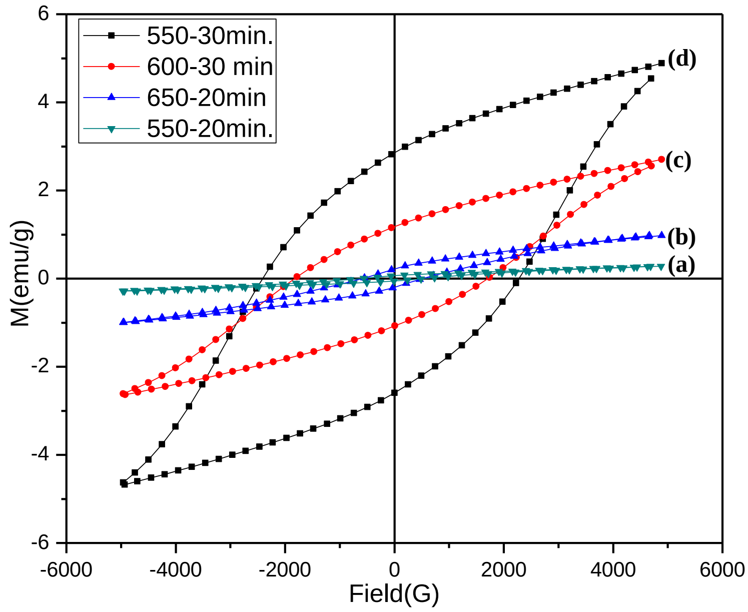

Fig 3 Hysteresis curves of MnAl pellets **(a)** 1050-5h-WQ/550-20min.-AC **(b)** 1050-5h-WQ/650-20min.-AC **(c)** 1050-5h-WQ/600-30min.-AC **(d)** 1050-5h-WQ/550-30min.-AC

Conclusions

Magnetism in rare-earth free Mn-Al system has been demonstrated by the M-H curves, by obtaining the τ phase in $Mn_{54}Al_{46}$ by suitable heat treatments.

- High energy ball milling for extended duration results in complete solid solution of α-Mn.
- High temperature homogenization for 5h followed by water quenching results in ε phase which is required for magnetic phase formation.
- Annealing treatment resulted in transformation of ε phase into magnetic τ phase.

The optimization of annealing process parameters is currently underway for transformation of ε phase of MnAl into magnetic τ phase which would lead to significantly higher magnetic properties.

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