

# Nanostructured Anisotropic Permanent Mn-Al and Mn-Al-C Magnets

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## Introduction:

In the 1950s, K. J. Kono and A. J. Koch discovered that the Mn-Al alloy has ferromagnetic properties when it is in the metastable,  $L1_0$ -structured  $\tau$ -phase, which is face-centered tetragonal (f.c.t.) [1]. It was later discovered that the addition of small amounts of C in the Mn-Al alloy improves the stability of the  $\tau$ -phase [2]. It has been shown that mechanically milled (MM) samples of the Mn-Al permanent magnet have better coercivities than bulk samples, but lower Curie temperatures ( $T_C$ ) and magnetization values ( $M_S$ ) [2].

The Mn-Al permanent magnet can have many practical and commercial uses that may surpass the performance of conventional hard ferrites and still prove to be more cost effective than rare-earth magnets. Mn-Al magnets are relatively cheap to produce due to the availability of both Mn and Al [1]. They also are easily machined, don't corrode easily, have a high specific strength, a high modulus of elasticity, a high energy per unit weight, and high coercivities as compared to conventional ferrites [2].

In this paper, one process of creating MM powders in the magnetic  $\tau$ -phase is explained, and the results of an attempt to follow that procedure are discussed.

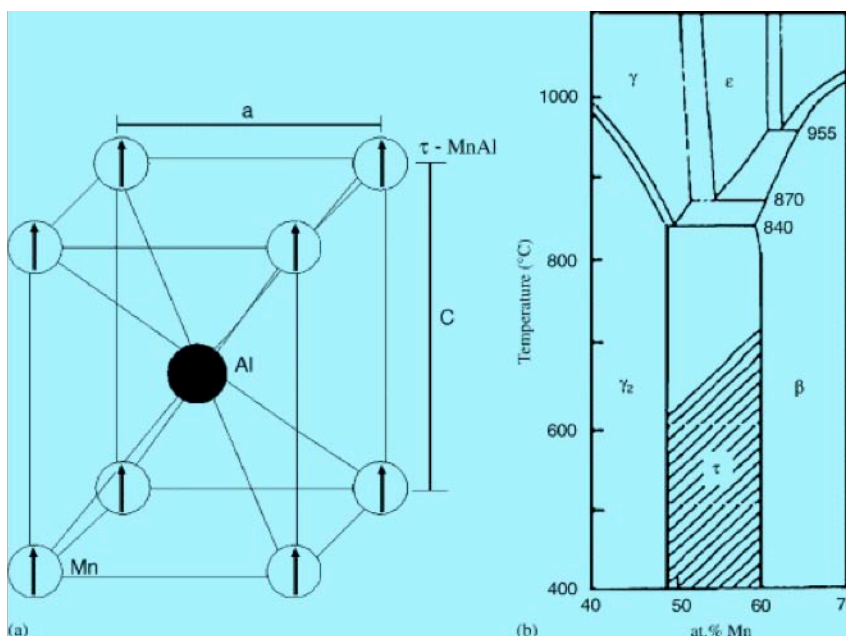


Figure 1: (a) Schematic diagram of  $\tau$ -Mn-Al structure, the magnetic moments of the Mn atoms are parallel to the c-axis of the Mn-Al, (b) part of the Mn-Al phase diagram showing the  $\gamma$ ,  $\gamma_2$ ,  $\tau$ ,  $\beta$  and  $\epsilon$ -phases. (The Diagram is taken from [2])

## Experiment:

The  $\tau$ -phase is most commonly produced by transforming the Mn-Al alloy from the high-temperature, non-magnetic  $\epsilon$ -phase, which is hexagonal closed-packed (h.c.p.), into the  $\tau$ -phase by a rapid quench. In order to achieve the  $\epsilon$ -phase and optimal coercive properties, both  $\text{Mn}_{54}\text{Al}_{46}$  and  $\text{Mn}_{52.3}\text{Al}_{46}\text{C}_{1.7}$  (atomic %) ingots were cast in an Argon atmosphere. About 5 % weight of Mn was added in order to offset the Mn that vaporizes during the casting process [2].

Each cast ingot was then subjected to a 20 hr heat treatment at 1150 °C in a Lindberg furnace under Argon gas. Upon removal from the heat treatment, the ingots were immediately quenched in a cold water bath. A Simens D5000 Diffractometer with a Cu X-ray tube (XRD) was used to ensure that the heat treated ingots were in the  $\epsilon$ -phase. Results from the XRD were also compared with the results found in [2].

The ingots were then pulverized as much as possible using liquid nitrogen, a hammer, and a mortar and pestle. The pulverized ingots were placed into a Spex 8000 Mixer/Mill with 3 hardened steel balls. About 8-8.5 g of pulverized ingot was milled for 15 hrs at a time, which is about a 3:1 ball to charge ratio. The pulverized ingot was loaded into the mixing cylinder under Argon gas. Again, the XRD was used to ensure that the MM powder was still in the  $\epsilon$ -phase.

The MM powder underwent a final annealing for 10 min at 400 °C in the Lindberg furnace in an Argon gas atmosphere. The XRD was then used to see whether or not the annealed powder transformed into the  $\tau$ -phase.

In the end the powder was to be placed into an equal channel, 90° angled die and extruded into a bulk material.

## Results & Discussion:

Initially there were 5 ingots, which were already cast by one of Professor Baker's graduate students. After pulverizing those ingots and starting the mechanical milling process, it was discovered that the ingots were not in the  $\epsilon$ -phase. This signified that the ingots were never heat treated, and thus not ready to be mechanically milled.

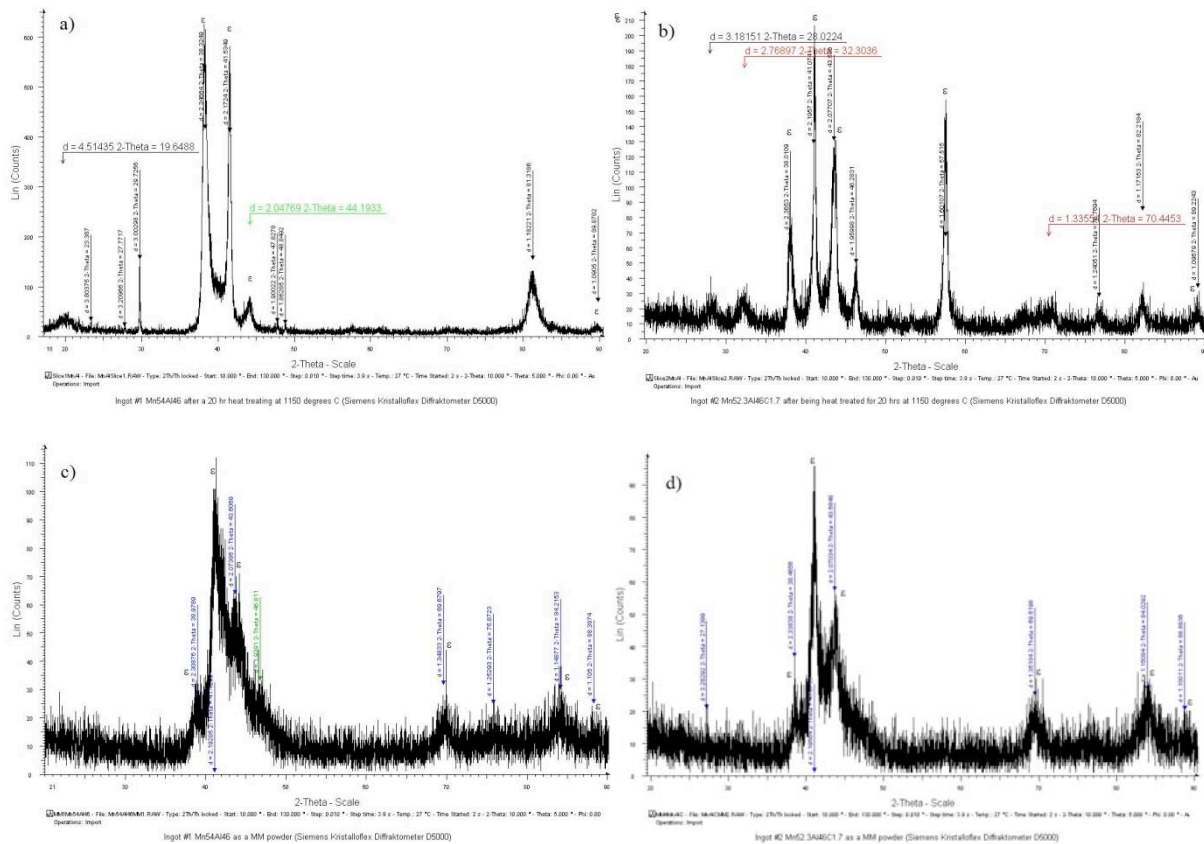
To correct this problem there were the 2 possible courses of action, 1. Trying to heat treat the pulverized ingots or 2. Re-casting all 5 ingots and starting over from the beginning. Due to a high probability of contamination by oxidation and due to the difficulty of quenching powder in water, it was decided to recast the ingots. An extra 5% weight manganese (Mn) was added to each ingot before re-casting.

In spite of having Qi Zeng's XRD results (Qi Zeng was able to produce the  $\tau$ -phase using this same method [1]), the PCPDFWIN database, and the CaRine Crystallography 3.1 program, it was still difficult to completely determine the origin of each peak in the XRD results. It is

difficult to get any accurate readings off of Qi Zeng's papers. The PCPDFWIN database doesn't contain any XRD results that were exact matches to this experiment, and therefore wasn't a very reliable source. The CaRine program only gives possible peak values if the lattice parameters are already known. In this experiment, the lattice parameters of the  $\epsilon$ -phase are not known. However, after the heat treating of all the ingots, it was determined that at least 3 of the ingots (#1, #2, & #4) were mostly in the  $\epsilon$ -phase.

Ingot #1 ( $\text{Mn}_{54}\text{Al}_{46}$ ) & part of ingot #2 ( $\text{Mn}_{52.3}\text{Al}_{46}\text{C}_{1.7}$ ) were mechanically milled (MM) in the Spex Mill. Ingot #4 was MM in the Attritor, which didn't produce good results. About half of the recovered MM powder had escaped from the Attritor container and settled on the lid, potentially being contaminated by oxidation. Much of the pulverized ingot didn't even become milled and was left as large grains (about 1 mm in diameter). The XRD results showed that some of the  $\epsilon$ -phase was lost after mechanical milling in the Attritor.

After several attempts at annealing the MM powder, neither ingot #1 nor ingot #2 succeeded at achieving the ferromagnetic  $\tau$ -phase. The XRD results indicated that the MM powders were transforming from the  $\epsilon$ -phase to the  $\gamma_2$ -,  $\tau$ - &  $\beta$ -phases (mostly  $\beta$ -phase), instead of just (or mostly) to the  $\tau$ -phase.



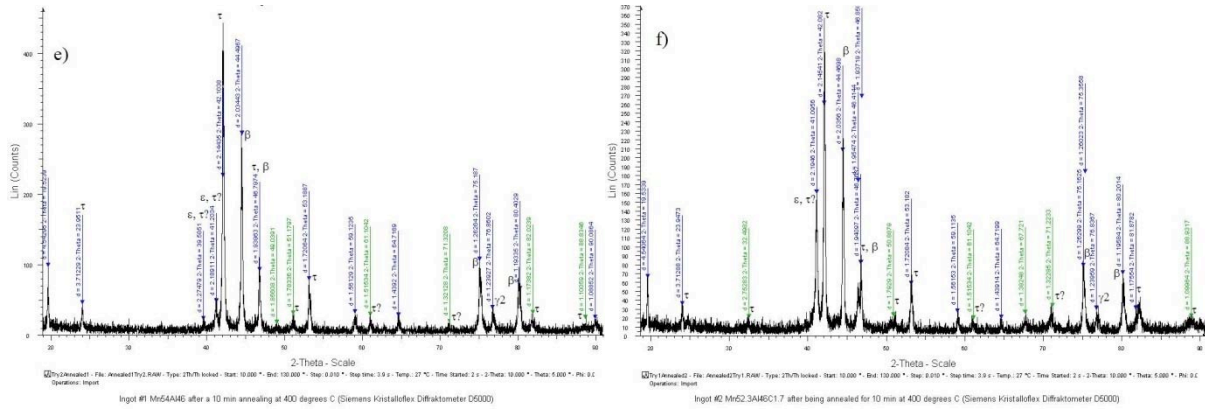


Figure 2: These are the XRD results for ingot # 1 ( $Mn_{54}Al_{46}$ ) & ingot #2 ( $Mn_{52.3}Al_{46}C_{1.7}$ ). (a) Ingot #1 after a heat treating of 1150 °C for 20 hrs followed by a rapid quench, (b) Ingot #2 after a heat treating of 1150 °C for 20 hrs followed by a rapid quench, (c) MM powder from ingot #1, (d) MM powder from ingot #2, (e) The powder from ingot #1 after the final annealing of 400 °C for 10 min, (f) The powder from ingot #2 after the final annealing of 400 °C for 10 min

$\beta$ -phase peaks are likely due to an excess of Mn. The extra 5% weight of Mn that was added to the ingots before being re-casted was probably where this excess was introduced. It could be that since the ingots were re-casted in a Bridgman furnace instead of an Arc-Melter, there wasn't as much vaporizing that occurred. The lower amount of exposed surface area and the lower temperatures of the Bridgman furnace could explain why the Mn didn't vaporize as much. The 5% weight increase was a suggestion that came from using the Arc-Melter.

Because of the lack of success in producing the ferromagnetic powder, the extrusion was never attempted.

Future attempts at creating a MM Mn-Al alloy should include testing that would determine how much Mn vaporizes in a Bridgman furnace so that the post-cast alloy is as close to  $Mn_{54}Al_{46}$  (or  $Mn_{52.3}Al_{46}C_{1.7}$ ) as possible. Also, it would very useful to obtain some very accurate XRD results of both oxidized and pure samples of the  $Mn_{54}Al_{46}$  and  $Mn_{52.3}Al_{46}C_{1.7}$  that are created using the same method as the experiment and that are in the  $\beta$ -,  $\epsilon$ -,  $\tau$ -, &  $\gamma_2$ -phases for comparison purposes.

## Acknowledgements:

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