Phase Stability in Mechanically Alloyed Mn-30at.%Al

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Mechanical alloying of Mn-30at. % Al powder mixture resulted in the formation of an α-Mn solid solution in the early stage of milling with the subsequent formation of β-Mn phase after 30h milling. Thermal treatment at 1060^{0}C, confirmed the recently extension of the high temperature ε-phase. However, the presence of impurity atoms, mainly iron, impeded the expected ε→β transformation during quenching. Such transformation is obtained by annealing the metastable ε-phase at 400^{0}C and was found to be time dependent. Magnetic properties assessments of both as milled and annealed alloy are carried out.

1. Introduction:

Manganese has four allotropies α, β, γ, and δ all of which can dissolve aluminum. α-Mn is stable at room temperature with anti-ferromagnetic properties. Both α and β have complex cubic crystal structure with 58 and 20 atoms per body-centered, respectively [1,2].

The magnetic properties of Mn-Al alloys are due to the metastable ferromagnetic body-centered tetragonal τ phase, which can be obtained by various methods over a limited composition range either by controlled cooling from the high-temperature equilibrium hexagonal ε phase or by annealing the quenched ε phase. The ε → τ transformation occurs by different mechanisms depending on microstructure and initial composition of the ε phase. The ferromagnetic properties of τ phase strongly depend on the thermomechanical treatment and on the microstructure, which is very sensitive to treatment conditions [3,4].

McAlister and Murray [5] indicated that, the ε phase composition range was 53.16-59.56 at.%Mn. Liu *et al*. [6] showed that this range is 54.4-71.3 at.%Mn, and the ε phase transformation with composition less than 58 at.%Mn gives a ferromagnetic τ phase, while ε phase with composition more than 58 at.% Mn transformed massively to the β-Mn phase. Based on the DTA data, Müller *et al*. [4] found that the existence of ε-phase extended to lower temperature where the eutectoid temperature was 777^0C instead of 857^0C. Both the original binary Mn-Al diagram and the suggested modified one are shown in Fig. 1(a, b).

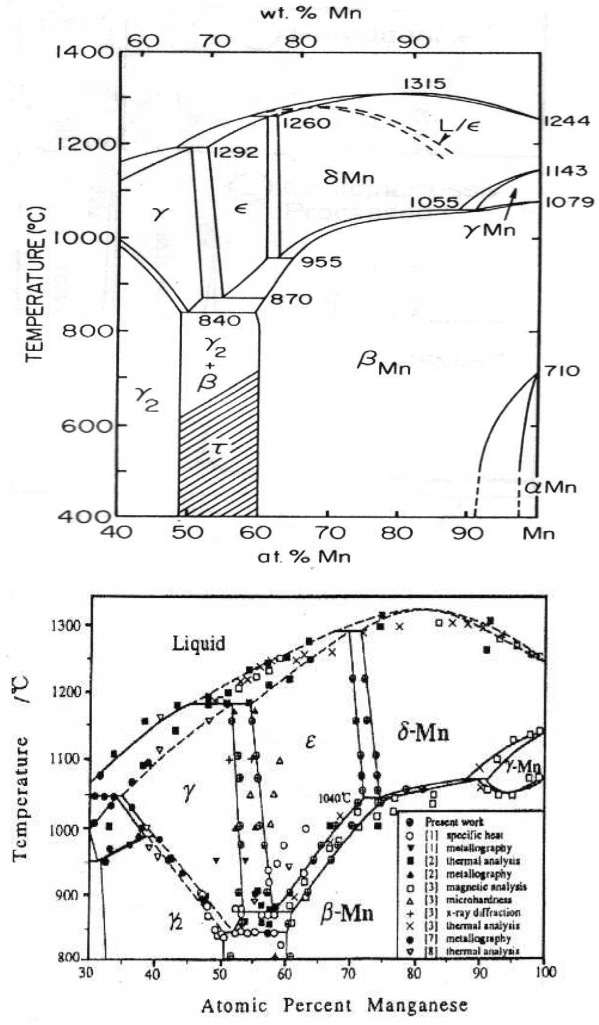

Fig. (1): Mn-rich portion of the Mn-Al phase diagram as assessed by; (a) McAlister and Murray. (b) Liu et al.

Several attempts have been carried out in order to explore the possibility of obtaining the τ-phase using mechanical alloying technique (MA). However, the initial composition used was mainly in the range 50-60 at.%Mn.[7] The aim of the present work is to examine the composition of Al-70at.%Mn to identify the type of phases which can be obtained by (MA) and thermal treatment. The magnetic properties of such phases are also examined in this work.

2. Experimental work

The starting materials are fine powders (≈325 mesh) of Mn (99.9%) and Al (99.97%) were mixed to prepare a sample of Mn-30at.%Al by mechanical alloying. This was carried out in a relatively high-energy ball mill using hardened steel ball, with the ball to weigh ratio as 10:1. Ten grams of starting powder were charged into sealed vial with rotating speed of 500 rpm under argon atmosphere.

The mechanical alloyed and heat treated green compacted (600 MPa) powders are characterized by x-ray diffraction (XRD), Siemens D5000 powder diffractometer with Cu-K_α radiation (λ = 1.5406 Å). Annealing treatment of the mechanical alloyed specimens was carried out for different temperatures and times and the sample had been immersed in Al_2O_3 powder in order to prevent oxidation. The magnetic properties of the specimen were measured by a vibrating sample magnetometer (VSM). The Fe contamination in the specimens after 5h and 30h was 0.13 and 0.36 wt.%Fe, respectively as determined by using Unicam atomic absorption spectrometer.

3. Results and discussion:

3.1. X-Ray Diffraction

The nominal composition of the Mn-30at.%Al powders was milled for various setting times up to 50h. The diffraction results after different stages of milling are shown in Fig. (2). In the early stages of milling a continuous decrease of Al-lines intensity suggests solid solution formation of the α-Mn type structure. The Al lines completely disappeared at 50h milling, while the crystalline structures persist. The Mn-rich side of the Mn-Al binary diagram, Fig. 1(a), indicates that at relatively low-temperature and with Al-content up to 30at.% two solid solutions α and β can be obtained and both have a complex cubic structure.[1,2]. The pure α-Mn is been limited to ≈ 2.01 at.%Al and β-phase has a maximum Al-solubility of 40.42 at.%. However, some of the reported results on the system with Al up to 45at% indicates that α-Mn rather is formed after mechanical alloying [7]. Confusion could arise between α and

β-Mn phases indexing, since they have a very close d-values, e.g. their main peak have d-values of 0.2010 and 0.2014 nm, respectively. On the other hand, mechanical alloying technique is known to produce supersaturated phases. However, in the present work, it might be that the α-Mn supersaturated phase which was formed in the early stage of milling gradually transformed to β-Mn. The X-ray diffraction lines broadening with milling process are commonly related to particles refinement.

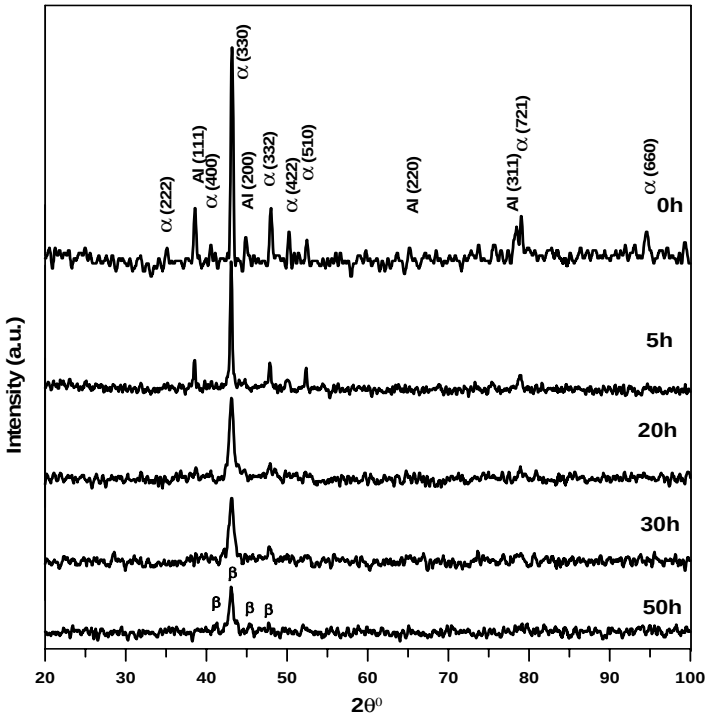

Fig. (2): XRD patterns of MA Mn-30 at.% Al for different milling time.

According to Hall-Williamson relation [8] the crystallite size (L) and the strain in the lattice can be determined using the full width at half maximum (β) of the X-ray diffraction peaks as follow;

$$\beta \cos\theta = k\lambda / L + 2A\sqrt{(\varepsilon^2)}\sin\theta$$

where θ is the Bragg angle, λ is the wavelength, $\sqrt{(\varepsilon^2)}$ is the root mean strain, k is constant which taken to be ≈ 1 and the coefficient A depends on the distribution of strain and near to unity for random distribution of dislocations. The particle size after 30h of milling was found to be ≈ 25 nm. These

nanoparticles sizes are expected to increase interface area with a subsequent effect of enhancing the solid-state diffusivity during milling and the formation of β-Mn solid solution.

Thermal behaviour of the β-Mn phase obtained by milling could further prove to exact phase transformation nature. For the green compacted powder after 30h MA and heating at 1060^0C for 1h then water quenching, the x-ray diffraction pattern is shown in Fig. (3). The expected high temperature ε-phase is retained by quenching process in addition to only two peaks of β-phase. The existence of such small quantities of β-Mn phase is thought to be related to local inhomogeneity in the material composition which is inherited from the milling process. However, the obtained ε-phase after quenching for this composition is not in agreement with many commonly known phase diagrams [5,6]. The divergence exists mainly on the rich Mn-side of the diagram and concerns the extent of the high temperature ε-phase [6]. Furthermore, it is also reported by the same author[6] that retaining ε-phase through quenching to room-temperature in fact depends on Mn-content in the original β-Mn phase. The ε-phase which contains more than 58 at.%Mn will be transformed by quenching to β-Mn, while material with lower Mn-content will retain the high temperature ε-phase. It should be indicated that the $\varepsilon \rightarrow \beta$ transformation is a massive type transformation, best called a short migration reaction by rapid movement of incoherent interface and not impeded by these boundaries. Such type of transformation is therefore likely sensitive to alloy composition even more, the presence of impurity atoms may provide a resistance to the rapid propagation of incoherent boundaries. Contamination by Fe atoms from the steel ball during milling process was identified by atomic absorption analysis which showed a maximum content of 0.36 wt.% Fe after 30h milling. It is therefore, possible to contribute the small volume fraction of the β-phase observed after quenching to an $\varepsilon \rightarrow \beta$ type transformation, which may occur in an impurity-free small area, while in the major part of the interface movement such transformation will be impeded by iron contamination and this leads to retaining of the high temperature ε-phase induced by quenching, unchanged.

3.2 Structure Stability

ε-phase is known to be unstable at room temperature and it is expected to transform either to the metastable τ-phase before it is finally transformed to β-Mn, or it will directly transform to β-Mn, depending mainly on Al-content in the alloy. In the present work, the obtained structure following quenching treatment which is mainly ε-phase, Fig. (3), is annealed for different times at 400^0C to examine this structure stability. XRD results, Fig. (3), for various annealing times confirmed the $\varepsilon \rightarrow \beta$ phase transition where the β-phase increased by increasing annealing time, i.e., it is a rather diffusion type of

transformation. Also, the absence of the metastable τ-phase indicates a rather ε-phase homogenous composition following high temperature treatment. It is thought that with a short time annealing for the as quenched specimen could lead to the formation of metastable phase, either τ or ε`. However, for a few minutes 1-5 min annealing, also indicated no metastable phase formation.

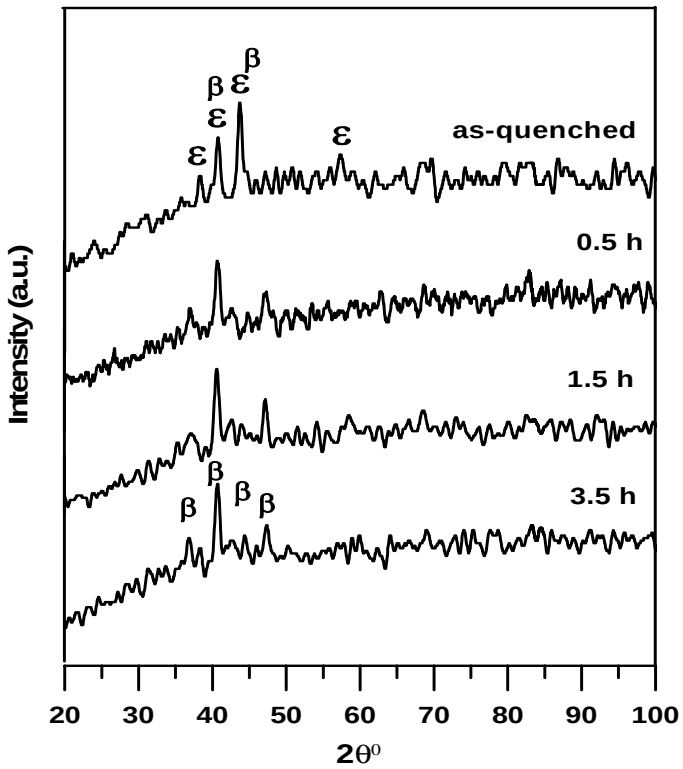

Fig. (3): XRD patterns of water quenched 30h MA Mn-30 at.%Al then annealed at 400oC, for various time.

Following a certain milling times 5h, another series of heat treatment are carried for the same powder composition at 450^0C and 600^0C. X-ray diffraction results, Fig. (4), indicated that, the starting milling structure is α-Mn in addition to a few lines of Al. The transformation to β-Mn which occurs is temperature dependent, i.e., of diffusion type. For the 600^0C-treatment, a higher rate of transformation can be deduced, where a relatively higher intensity of β-lines are observed compared to one after 450^0C, Fig. (4). In addition a small starting particle size is likely to enhance the diffusion process [9].

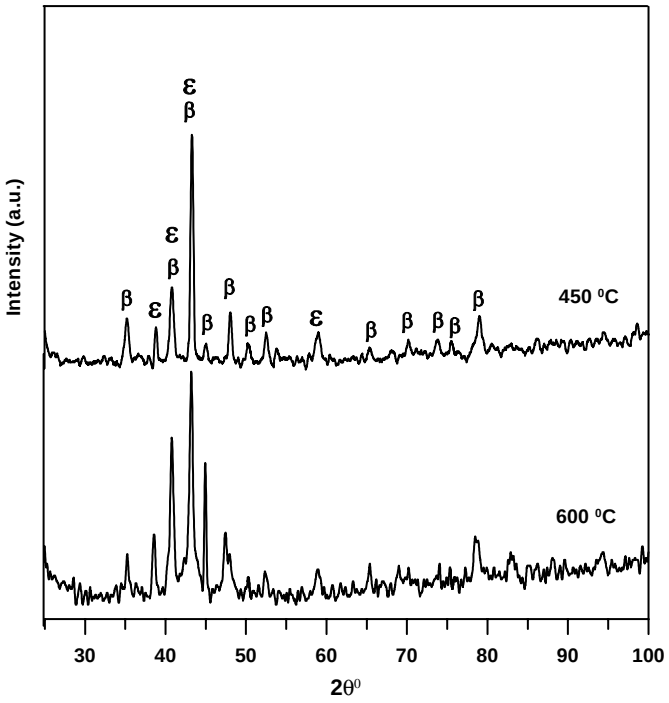

Fig. (4): XRD patterns of 4h milling of Mn-30 at.%Al and that annealed for 2h at 450°C and 600°C.

3.3 Magnetic measurements

The 5h milled specimen, show a ferromagnetic behaviour, Fig. (5). Similar results have been reported by Kim *et al*. [7] for Mn-45at.%Al produced by milling, where they suggested that the substitution of Al atoms in the α-Mn matrix partially destroys the antiferromagnetic arrangement and forms ferromagnetic clusters. Fig. (6), show the saturation magnetization B_S and coercivity H_C with milling time, where the B_S decreased while H_C slightly varies.

Based on the NMR results, [10] two inequivalent Mn sites are found in β-Mn; site I is believed to be non-magnetic, while site II is believed to be weakly magnetic. Non-transition metals impurities are thought to preferentially occupy site II, where they may bring about magnetic order due to moment localisation through lattice expansion. From the above results it is possible to indicate that Al atoms could partially occupy sites that bring magnetic order, of the supersaturation solid solution produced during milling.

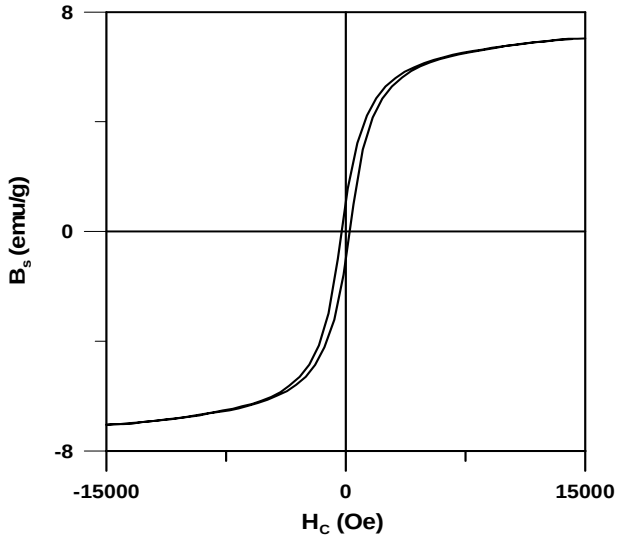

Fig. (5): Hysteresis curve of 5h MA Mn-30 at.%Al powder.

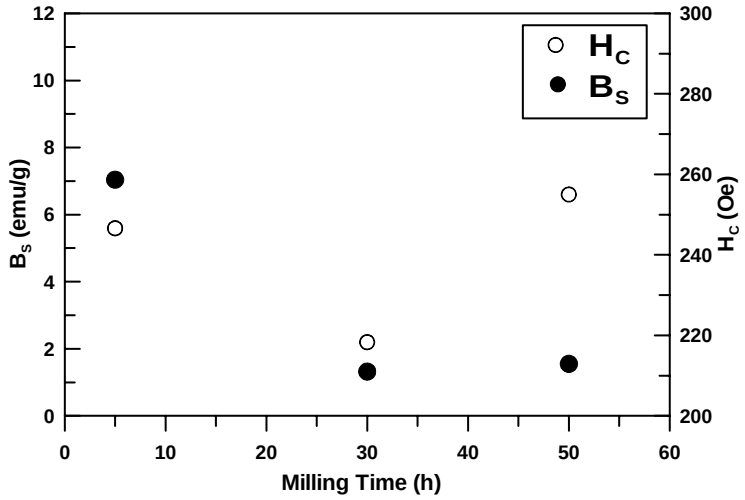

Fig. (6): Saturation Magnetization B_S and Coercivity H_C as a function of milling time for Mn-30at.%Al.

The magnetic properties of the heat-treated samples are shown in Table (1), where a slight change of magnetization with respect to mechanical alloying can be observed. It might be noted that, the observed values of saturation magnetization B_S and coercivity H_C is very small with respect to the values observed with τ-phase which was 3.57-6 kOe [11,12].

Table (1): The magnetic properties of Mn-30at.%Al alloys after various heat treatment.

	5h (MA)		As quenched 30h (MA) annealed at 400 ^{0}C for 3.5h
	450 ^{0}C, 2h	600 ^{0}C, 2h	
H_C (Oe)	155.3	253	530.9
B_S(emu/g)	6.61	0.85	3.8

4. Conclusion:

Using mechanical alloying technique it is possible to obtain the stable β-phase from the Mn-30at.%Al powder mixture. A wider range for the high temperature ε-phase is found which confirm early suggestion for the binary Mn-Al diagram modification. The high temperature $\varepsilon \rightarrow \beta$ phase transformation during quenching can be impeded by the existence of impurity atoms. The metastable ε-phase transformed to the equilibrium β-phase by annealing at 400^0C. Weak magnetic properties of both the as-milled and the annealed alloys are mainly related to disorder atoms coupling.

5. References:

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