Magnetic Field Processing of Ferromagnetic MnAlC Alloys

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$Mn_{54}Al_{44}C_2$ forms the metastable $L1_0$ intermetallic compound, and exhibits ferromagnetic behavior after appropriate heat treatment. This material offers a low-cost, lightweight alternative to rare earth, alnico and ferrite magnets currently in use. Characterization techniques include vibrating sample magnetometry (VSM), X-Ray diffraction (XRD), optical microscopy and transmission electron microscopy (TEM), while mechanical milling, melt spinning and vacuum induction melting are routinely employed for alloy formation. Finally, we explore heat treatments under magnetic fields as a potential technique to tailor and enhance magnetic properties of interest.

The materials scientist uses a variety of techniques to enhance physical properties for engineering applications. Traditionally, a metallurgist varies the compositions of alloys in conjunction with heat treatment and work hardening to improve performance. The use of magnetic field processing to modify the phase equilibria and transformation kinetics of ferromagnets is a novel extension to these well-established techniques. Here we describe efforts to synthesize and process the ferromagnetic phase of manganese aluminum using both traditional and recently developed techniques. Several alloy synthesis methods are evaluated including traditional casting, arc melting in argon, melt spinning, and mechanical alloying followed by sintering. The study also requires microstructural analysis of the alloys prior to and following isothermal processing in both the presence and in the absence of applied magnetic fields. Our microstructural analysis techniques will include XRD, VSM, Optical Microscopy, SEM, TEM, and AFM.

In MnAlC, the $L1_0$ intermetallic compound is ferromagnetic. This may surprise the reader given that aluminum is paramagnetic and manganese is anti-ferromagnetic in their pure forms. The binary phase diagram of manganese-aluminum is shown in figure 1 (Okamoto 1997). Near equiatomic composition, MnAl alloys may form the metastable $L1_0$ phase upon aging from the as quenched ε phase (Yanar et al. 2002). The ε phase is a randomly ordered solid solution of manganese and aluminum in a hexagonal close packed lattice structure. The system can reduce its free energy by ordering itself, with alternating (002) planes of manganese and aluminum atoms. In this arrangement, known as the $L1_0$ microstructure, the hexagonal close packed lattice has distorted to a tetragonal one, with a c/a ratio of 0.95. Figure 2 illustrates the crystal structure of these phases, including the intermediate phase ε'. In the $L1_0$ configuration the spins on the manganese sites are exchange coupled to be parallel and exhibit ferromagnetic behavior.

The metastable $L1_0$ phase will decompose into solid solution of the equilibrium phases γ (bcc) and β-Mn (20-atoms per cell) after long times at ambient conditions. Carbon is added to stabilize the $L1_0$ structure by inhibiting formation of the equilibrium phases. Carbon has the additional affects of reducing the Currie temperature from 370°C to 300°C, increasing the saturation magnetization, and improving the workability of the alloy (Zeng et al. 2007). Numerous techniques exist to form the initial alloy including arc melting, spin melting, ball milling followed by sintering, and traditional casting. In direct arc melting, the alloy is heated by passing an electric arc through it to a grounded electrode, under vacuum or inert gas environment. When melt spinning is employed, the molten alloy is drizzled through an orifice on to the edge of a rapidly rotating, water-cooled, copper wheel. This facilitates rapid crystallization, thereby retaining the ε phase, which is stable at high temperature. Ball milling, or mechanical milling involves placing granules of the pure components into a steel vessel with hardened steel balls, and shaking the vessel vigorously for many hours. Mechanical impacts fracture the pieces into fine-grained particles and blend them until the desired homogeneity is obtained. The final alloy is formed by heating under compression, or sintering. Traditional casting was done in a zirconia-coated graphite crucible, after heating to 1250°C. The slow cooling rate for the cast alloys results in the formation of the equilibrium phases γ and β.

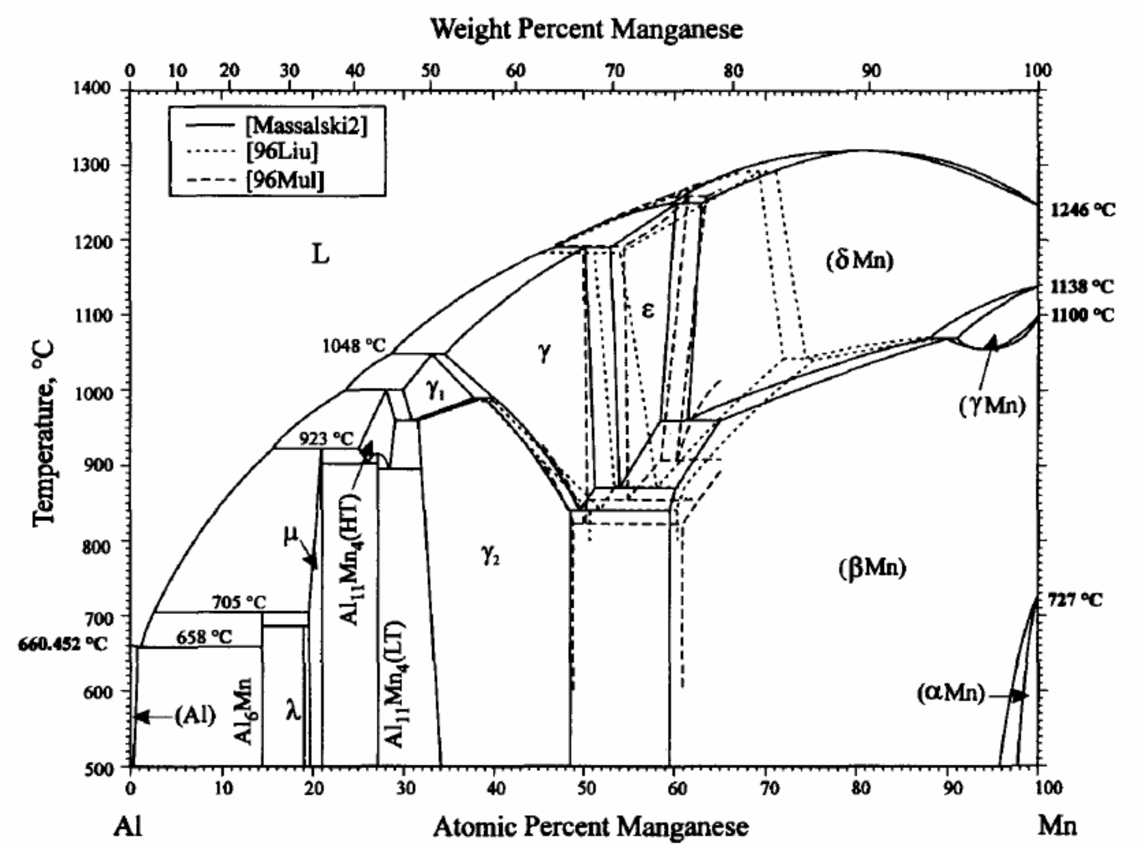

Figure 1: Manganese Aluminum binary phase diagram (Okamoto 1997). The ferromagnetic L10 phase is a metastable phase that forms in the two-phase region between γ2 and βMn.

To obtain the ε phase from an as cast alloy, we heat above 900°C and hold there for several hours to homogenize the solid solution. It is equally probable at this stage that an hcp lattice site is occupied by either manganese or aluminum. The hot ε phase is then cooled rapidly by submersion in water to retain the distribution of atoms. Subsequent heating of the ε phase allows some diffusion to occur and facilitates the formation of the $L1_0$ ordered intermetallic compound with its desirable ferromagnetic properties. In figure 3, we present x-ray diffraction spectra for melt spun MnAlC before and after aging at 500°C for one hour. In the spectra for no aging, all diffraction peaks have been identified as originating from the hexagonal close packed structure of the ε phase. After aging, the diffraction peaks for the ε phase are gone, and what remain are only signatures for the τ phase. Diffraction studies are an integral technique we use to determine microstructure rapidly and nondestructively.

The magnetic properties of the τ phase warrant further study, because they exhibit high performance metrics per unit mass, per unit volume, and per dollar of raw material, compared to rare earth magnets currently in use. We define properties of interest like coercivity, saturation magnetization, and remnant magnetization to characterize and compare the performance of magnetic materials. The coercivity is the field required to reverse the magnetization to zero from a saturated state. The coercivity is a measure of magnetic hardness, describing the resistance of a material to demagnetization. Permanent magnets like Alnico magnets exhibit high coercivity, whereas soft magnets such as ferrites exhibit a low coercivity. The saturation magnetization is the maximum induced magnetic moment that a material will develop in response to an applied magnetic field. Finally, the remnant magnetization is the magnetic moment retained by the material when the external field is reduced to zero following saturation.

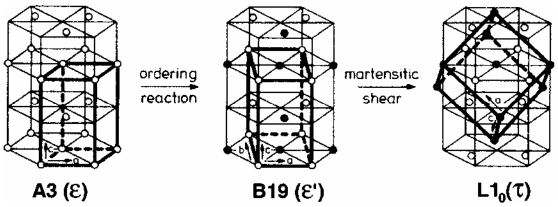

Figure 2: Proposed transformation sequence for the formation of τ-phase MnAl ferromagnetic structure from the hcp ε phase (Yanar et al. 2002).

We measure the magnetic properties of our alloys with a Lakeshore 7400 vibrating sample magnetometer or VSM. This instrument applies a uniform magnetic field to the sample, and measures the magnetization of the sample in response to the field. A Hall probe mounted in the gap of the two solenoids senses the applied field. Electromagnetic pick-up coils detect the magnetization of a vibrating sample. The vibration frequency of the sample is locked-in to the pick-up coil measurement circuit such that only signals emanating from the vibrating sample are recorded. In this way we can reduce the noise level and exclude the contribution of Earth's magnetic field from our measurements. In figure 4 we present representative hysteresis data obtained in our laboratory for melt spun MnAlC. The coercivity for this sample was 1250G. The saturated condition is characterized by a zero or nearly zero

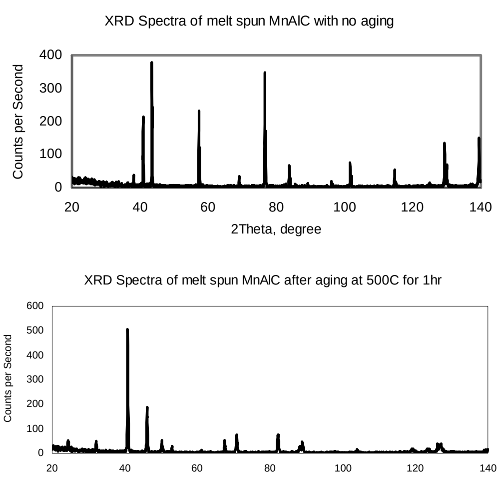

Figure 3: X-ray Diffraction spectra of melt spun $Mn_{54}Al_{44}C_2$ collected with Cu Kαx-rays on a Scintag XDS 2000 Powder diffractometer. The sample with no aging is primarily composed of the hcp ε-phase, while the same sample that was aged at 500°C for one hour has developed the L10 structure of the τ phase.

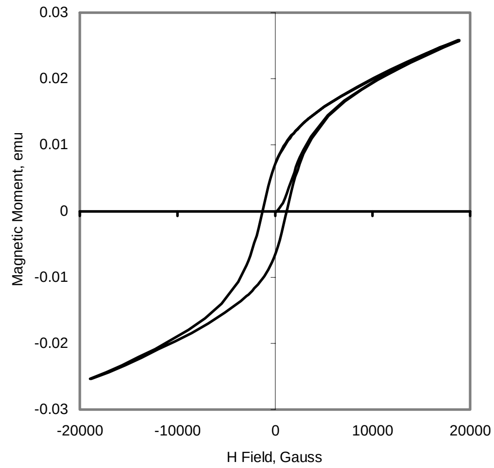

Figure 4: Hysteresis loop of melt spun $Mn_{54}Al_{44}C_2$ exhibiting a coercivity of 1250G.

slope at the extremities of the first and third quadrants. The non-zero slope indicates that the material is not saturated; therefore, neither the saturation magnetization nor the remnant magnetization could be determined from this run. Fortunately, we have in our arsenal yet another tool for magnetic measurements. The pulse magnetizer applies a very intense magnetic field (~100,000G) in order to saturate the sample permitting us to measure the saturation magnetization and the remnant magnetization.

The magnetic field response of a ferromagnetic material contributes to the free energy of the crystal, and can thereby influence the phase diagram, altering the transformation temperatures and solid solubility of the system (Ludtka et al. 2004). With this new tool, we metallurgists gain access to previously unavailable compositions and microstructures. The main requirement for magnetic fields to have influence on a transformation is that there exist differing magnetization responses between the parent and product phases. Clearly this condition exists for MnAl, as the ε phase is paramagnetic while the τ phase is ferromagnetic. In the $L1_0$ phase MnAlC, the saturation magnetization is inversely dependent on grain size. If the addition of a magnetic field accelerates nucleation of the τ phase, the resulting microstructure would have a smaller average grain size and could potentially exhibit an improvement in properties. Magnetic fields have already been shown capable of driving all of the austenite in steel to transform to martensite at temperatures above those normally required to complete the transformation (Ludtka et al. 2004). The martensite start temperature was also raised by 80K by the application of a 40T magnetic field during cooling. Magnetic field processing can yield unique and novel microstructures with enhanced performance for a broad spectrum of materials. Magnetic fields enable us to define a new set of thermodynamic equilibria, in the M-H-T phase space.

Magnetic materials play a critical role in human technology. Improvements in magnetic material properties lead to improved performance, lighter weight components, and greater scientific capabilities for society and space exploration. MnAlC alloys may offer a new alternative permanent magnetic material. Novel microstructures with significant performance enhancement gained through magnetic field processing could result in a significant weight reduction of components containing ferromagnetic materials. This would enabling the design and construction of lighter weight instrumentation for space exploration. Future plans for this study include data analysis from experiments performed at the National High Magnetic Field Laboratory (FSU), optical and transmission electron microscopy studies, and the synthesis of new alloys for additional experiments. We aim to improve magnetic properties of MnAlC permanent magnet alloys through conventional and magnetic field processing.

References

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