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Alloying with a few atomic percent of Ga makes MnAl thermodynamically stable

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ABSTRACT

Ternary alloys of the form $Mn_{55}Al_{45-x}Ga_x$ have been produced in the range $0 < x < 45$. In alloys with $5 < x \leq 9$ after appropriate heat treatments, two different phases with the $L1_0$ structure can be made to coexist. One is thermodynamically stable, as is binary MnGa, and the other is metastable, as is binary MnAl, but in the ternary alloys, both phases contain only a few atomic percent of Ga. The magnetic properties of the ternary alloys are superior to those of the binary analogues. The resistance to thermal decomposition of the ternary metastable phase is greatly improved compared to binary MnAl and the thermodynamically stable $L1_0$ phase does not undergo a phase transformation at temperatures up to at least 700 °C. These results enable longer processing times at higher temperatures thus facilitating the development of rare earth free MnAl-based magnets which are capable of providing a sustainable alternative to certain types of Nd-Fe-B.

1. Introduction

An $L1_0$-structured, thermodynamically metastable phase can be produced in near-equiatomic Mn-Al alloys by undercooling the hexagonal, high temperature phase, ε [1]. The magnetic properties of this $L1_0$ phase combined with the fact that it contains no rare earth elements makes MnAl highly attractive as a sustainable alternative to rare earth permanent magnets like Nd-Fe-B. The barrier to the introduction of $L1_0$-MnAl as a permanent magnet is its metastable nature; the phase decomposes during the high temperature processing necessary to achieve optimum magnetic properties. The stability of $L1_0$-MnAl can be improved somewhat by C-doping [2], but the phase remains metastable, moreover the Curie temperature and magnetocrystalline anisotropy field are significantly degraded by the C addition [3]. In the Mn-Ga system, a thermodynamically stable, $L1_0$ phase with very good hard magnetic properties can be produced at near-equiatomic compositions [4–6], but the critical nature of global Ga supplies [7] means that commercial application of bulk materials with approximately 50 at % Ga is unviable [8]. The challenge is to produce a thermodynamically stable $L1_0$ phase with a low Ga content. Ternary Mn-Al-Ga alloys offer solutions to the above problems and here, we show that by substituting Al with Ga in $Mn_{55}Al_{45-x}Ga_x$ (at%), an $L1_0$ phase with excellent hard magnetic properties can be produced at all ternary compositions between the metastable and stable binary end members. In $Mn_{55}Al_{45-x}Ga_x$ with $5 < x \leq 9$, after appropriate heat treatments, both stable and metastable $L1_0$ phases can be made to coexist in the same ternary alloy. The two $L1_0$ phases differ in their lattice parameters, chemical compositions and magnetic properties. The thermodynamically stable Mn-Al-Ga $L1_0$ phase, produced by adding just a few at% Ga to MnAl, has the potential to revolutionize research on MnAl magnets, making it possible to process at elevated temperatures for longer times.

The phases known respectively as γ_2 and λ in the phase diagrams of Mn-Al and Mn-Ga have been reported to be isostructural (*R*3*m*, Al_8Cr_5 type [9]), although it should be noted that there is some discussion in the literature concerning whether the space group *R*-3*m* may be a more appropriate description for the phase in the Mn-Ga system [9]. As detailed experiments appear not to have been carried out on the phase in the Mn-Al system, we assume in the current work that the two phases are isostructural, and for simplicity, all phases with this structure will be referred here as γ_2. In the Mn-Al system, the metastable $L1_0$ phase is known as τ and it decomposes into the equilibrium phases, β-Mn ($P4_132$, Mn *cP*20

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type) and γ_2 at elevated temperatures [1]. In the binary Mn-Ga system, as-cast alloys of composition $Mn_{55}Ga_{45}$ consist of γ_2, which is retained to room temperature by relatively rapid cooling [4]. In stark contrast to the Mn-Al system, the γ_2 phase in Mn-Ga transforms into a thermodynamically stable $L1_0$ phase on heat treatment at intermediate temperatures [4].

2. Experimental

The compositions of the ternary alloys were in the range $Mn_{55}Al_{45-x}Ga_x$ where $0 \leq x \leq 45$ (at%) so that the binary end members of the series were $Mn_{55}Ga_{45}$ and $Mn_{55}Al_{45}$. Mn-Al-Ga ternary alloys were produced by arc melting appropriate quantities of elemental materials with purity 99.8% for Mn, 99.99% for Al and 99.999% for Ga. Annealing was carried out in quartz tubes backfilled with a 0.2 bar Ar, having firstly evacuated to 10^{-7} bar. The samples were annealed for 24 h at 600 °C and for 48 h at 1100 °C to investigate the formation of the $L1_0$ phase. Further annealing at 500 °C and 700 °C were carried out to investigate the phase behaviour and stability. The furnace was heated to the needed temperature before the samples were inserted. To guarantee a fast cooling rate the quartz tubes were quenched into water.

The characterization of the crystal structure was done using the Rietveld refinement method on x-ray diffraction (XRD) patterns obtained with Co-K_α radiation ($\lambda(K_{\alpha1}) = 1.78919$ Å; $\lambda(K_{\alpha2}) = 1.79321$ Å; ratio 1:1) using a Bruker diffractometer. The refined lattice parameters were obtained by analysing the complete 2θ range of 20°–120°.

The microstructure and compositions of the materials were studied in a Zeiss LEO Gemini 1530 scanning electron microscope extended by a Bruker energy dispersive x-ray spectroscopy (EDX) system. The samples were prepared for microscopy using standard metallographic methods. The compositions of the samples were determined by averaging EDX spot measurements of at least 10 points per phase. The experimental inaccuracy together with the statistic of the multiple measurements results in a measured composition deviation of less than 1 atomic percent.

The magnetic measurements were carried out using a Quantum Design PPMS device with a VSM measuring head. Applied fields up to 14 T were used to saturate the samples. Thermomagnetic data were gathered using the same device with an applied field of 0.1 T. The samples used were non-textured and the according demagnetisation factors were taken into account to determine the internal magnetic field, H_{int}, for the magnetisation curves.

3. Results and discussion

Ternary Mn-Al-Ga alloys with compositions $Mn_{55}Al_{45-x}Ga_x$ where $0 \leq x \leq 45$ (at%) including binary end members, were produced. The binary Mn-Al alloy was homogenized at 1100 °C for 48 h and was cooled at an intermediate rate from this temperature ("controlled cooling") in order to induce the $\varepsilon \rightarrow \tau$ transformation, which resulted in a single, metastable $L1_0$ phase. In ternary alloys with $5 < x \leq 9$ at% Ga the same heat treatment procedure led to the formation of a mixture of $L1_0$ and γ_2 phases, as shown by the XRD in Fig. 1a) for $Mn_{55}Al_{38.57}Ga_{6.43}$ (see Supplemental Fig. S1 for all alloys). The regions of the $L1_0$ and γ_2 phases can be clearly identified from backscattered electron images of the microstructure (Fig. 2). The γ_2 phase shows a fine poly-twinned structure which is expected as this phase forms via a solid state phase transformation from γ in the binary Mn-Al system [10]. In samples of these alloys which were rapidly quenched from 1100 °C, XRD analysis showed a mixture of γ_2 and ε phases (see Fig. 1b). This is evidence that the ε phase was present at 1100 °C and reveals that the $L1_0$ phase in controlled cooled samples forms via the $\varepsilon \rightarrow \tau$ transformation, as in binary Mn-Al. This $L1_0$ phase is therefore metastable in nature. The regions of the $L1_0$ phase consist of fine grains, as can be seen in the darker regions in Fig. 2). EDX analysis showed that the $L1_0$ phase had a composition of $Mn_{54.9}Al_{39.0}Ga_{6.1}$, which was close to the nominal composition of the alloy, whereas the composition of the γ_2 phase was $Mn_{51.6}Al_{41.3}Ga_{7.0}$ *i.e.* less rich in Mn. The Al:Ga ratio of both phases is similar (*cf.* 6.4 for $L1_0$ and 5.9 for γ_2) (values for the other two phase containing alloys are shown in Supplemental Table S1).

3.1. Formation of two $L1_0$ phases

Post annealing the samples with $5 < x \leq 9$ at% Ga at 500 °C for 24 h resulted in the transformation of the γ_2 into a second $L1_0$ phase, as shown by the disappearance of the γ_2 peaks in the XRD data (e.g. for $Mn_{55}Al_{38.57}Ga_{6.43}$ in Fig. 1a) and by backscattered electron images (Fig. 2). The composition of the second $L1_0$ phase was confirmed by EDX to be the same as that of the γ_2 precursor phase ($Mn_{51.6}Al_{41.3}Al_{7.0}$). These are remarkable results as, in the binary Mn-Al system, γ_2 is a thermodynamically stable phase at the annealing temperature used here, 500 °C. It appears that the addition of a few at% Ga to MnAl is sufficient to change the phase equilibria so that γ_2 transforms into a thermodynamically stable $L1_0$ phase, which is not observed in the Mn-Al binary system. After the heat treatments described above, ternary Mn-Al-Ga alloys with $5 < x \leq 9$ at% Ga therefore consist of two different $L1_0$ phases with different chemical compositions, one of which is thermodynamically stable whereas the other is metastable. It should be noted that ternary alloys with <5 at% Ga were not produced in this work and therefore the amount of Ga necessary for production of the stable $L1_0$ phase could even be less than 5 at% Ga.

3.2. Magnetic properties and lattice parameters

The two $L1_0$ phases differ in their magnetic properties and lattice parameters. The Curie temperature is sensitive to the composition, resulting in $T_C = 298$ °C for $Mn_{55}Ga_{45}$ and $T_C = 340$ °C for $Mn_{55}Al_{45}$. In the controlled cooled state, the Curie temperature of the metastable $L1_0$ phase was $T_C = 356$ °C, which is higher than in binary Mn-Al. After the post-annealing, the M(T) data of the ternary alloy shows an additional step, resulting from two Curie temperatures; $T_{C1} = 283$ °C for the thermodynamically stable phase and $T_{C2} = 352$ °C for the metastable phase (Fig. 3a).

In the controlled cooled state, the alloy $Mn_{55}Al_{38.57}Ga_{6.43}$, consisted of metastable $L1_0$ and γ_2. The saturation magnetisation (M_s) of the alloy in this state is $\mu_0 M_s = 0.44$ T. This value is low because only a fraction of the volume was occupied by the $L1_0$ phase and the γ_2 phase does not contribute to the magnetic moment. In the post-annealed state, the entire volume of $Mn_{55}Al_{38.57}Ga_{6.43}$ consists of the two $L1_0$ phases. The M_s of the alloy in this state ($\mu_0 M_s = 0.825$ T) is much higher than in the controlled cooled state (Fig. 3b), which confirms that the thermodynamically stable $L1_0$ phase contributes significantly to the magnetisation. The M_s is also significantly higher than that of either of the binary end members ($\mu_0 M_s = 0.807$ T for $Mn_{55}Ga_{45}$ and $\mu_0 M_s = 0.741$ T for $Mn_{55}Al_{45}$). The reason for this is likely to be that the thermodynamically stable $L1_0$ phase has a higher moment due to its lower Mn content. That M_s increases with decreasing Mn content has been reported for both binary Mn-Ga and Mn-Al [3,4]. The reason for this is that as the Mn content approaches 50 at%, a smaller fraction of Mn atoms is located on the Al/Ga lattice site. These atoms couple antiferromagnetically with Mn atoms on Mn sites and therefore tend to reduce the overall magnetic moment [11,12]. Separating the M_s of the two $L1_0$ phases was not possible in this case because the volume fractions of the phases in the sample taken for magnetic