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Structural, electronic and magnetic properties of the $Mn_{54-x}Al_{46}Ti_x$ (x = 2; 4) alloys

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ABSTRACT

The structural, electronic and magnetic behavior of the as-cast and annealed $Mn_{52}Al_{46}Ti_2$ and $Mn_{50}Al_{46}Ti_4$ alloys have been studied through electronic band structure calculations, X-ray diffraction and magnetic measurements in the temperature range 4–850 K and magnetic field up to 7 T. Band structure calculations show a preference for Ti atoms to occupy the Mn sites in the plane of Al atoms with their magnetic moments (−0.68 μ_B/Ti) coupled antiparallel relative to the Mn magnetic moments in the plane of Mn atoms (2.33 μ_B/Mn). The as-cast and annealed samples were phase mixtures with different values of the hard ferromagnetic τ phase content. Except the as-cast and annealed at 1050 °C $Mn_{52}Al_{46}Ti_2$ alloys, all the analyzed samples include, along with the τ and γ_2 phases, a soft κ phase (CsCl - structure type) with T_C around 530 K. The best magnetic characteristics were obtained for $Mn_{52}Al_{46}Ti_2$ alloy annealed at 470 °C for 6 h: M_S = 116 A m^2/Kg at 4 K and T_C = 668 K, in good agreement with the values reported in the literature for the τ phase of the MnAl system. The effects of the composition and of the preparation route on the electronic and magnetic properties are discussed in comparison with the properties of $Mn_{54}Al_{46}$ parent alloy.

1. Introduction

As potential free rare-earth permanent magnets, the nearly equiatomic Mn-Al alloys have been intensively investigated both experimentally and theoretically with the goal to improve their intrinsic magnetic properties [1–5]. Previous studies have shown that in the Mn-Al system a metastable phase (the tetragonal L10 phase or τ phase) with remarkable magnetic properties can be obtained, the most stable composition being $Mn_{54}Al_{46}$ [6–8]. The τ phase of Mn-Al is usually formed from the rapidly quenched metastable high temperature hexagonal ε parent phase [9–11] by annealing at temperatures around 500 °C [6,12,13]. In the equilibrium conditions, the metastable τ-phase decomposes into a phase mixture of the nonmagnetic stable γ_2 (Al_8Mn_5) and β-Mn-type phases [8]. It is worthwhile to note that pure τ phase of Mn-Al is difficult to obtain. Experimental data have shown that the τ phase is always accompanied by the γ_2 and β phases, their content depending on composition, preparation method and annealing temperature/time [12–15]. A high purity $Mn_{54}Al_{46}$ τ phase was recently obtained by arc-melting, melt-spinning and annealing [13]. The MnAl τ-phase exhibits appreciable intrinsic properties, such as a saturation magnetization ($\mu_0 M_s$) value of 0.75 T, an anisotropy constant (K_1) of 1.7 MJ/m^3, and a Curie temperature (T_c) of 650 K [16,17], with estimated maximum energy product at room temperature of 112 kJ/m^3 (14 MGOe) [4]. The $Mn_{54}Al_{46}$ alloy annealed at 450 °C for 60 min showed a saturation magnetization of 98.3 A m^2/Kg and Curie temperature of 661 K [12]. The highest reported experimental saturation magnetization of the $Mn_{54}Al_{46}$ alloy, 126 A m^2/Kg, was obtained for melt-spun samples annealed at 450 °C for 45 min [13]. A coercive field value of 0.36 T was reported for mechanically milled $Mn_{54}Al_{46}$ [18], while for crushed powder samples a coercive field of 0.5 T was obtained [13]. Electronic structure calculations performed on $Mn_{50}Al_{50}$ showed a Mn magnetic moment of 2.37 μ_B for the τ phase, resulting the theoretical value of 144 A m^2/Kg for the saturation magnetization [12].

The τ-phase stability enhancement was previously investigated by doping of the Mn-Al alloy with various elements (C, B, Ti, Fe, Ni, Cu, Zn, rare-earths) [5,7,11,19–29]. In $Mn_{50}Al_{46}Ni_4$ alloy was highlighted, along with the hard magnetic τ-phase, a soft magnetic κ-

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phase (CsCl-structure type) with a Mn magnetic moment close to that found in the τ-phase [28]. In the case of Ti doped Mn-Al, only two systems were studied, namely $Mn_{53.69}Al_{44.76}Ti_{1.55}$ and $Mn_{52.50}Al_{45.23}Ti_{1.68}Cu_{0.59}$ ribbons [24].

In the equiatomic τ-phase structure, the Mn and Al atoms are situated in alternating planes situated at $c/2$ distances [30]. The intralayer Mn-Mn exchange coupling is ferromagnetic [6,12]. However, the most stable composition for obtaining the Mn-Al τ-phase is Mn54Al46, which leads to the excess Mn atoms occupying the Al positions which are antiferromagnetically coupled to the Mn atoms situated in the other planes [30]. This causes an unwanted decrease of the magnetization per formula unit as only around 46% of the total atoms contribute to the magnetization [12,30]. This problem could be addressed by replacing the excess Mn atoms with elements having small magnetic moments, such as Ni or Ti, therefore reducing the weight of the antiferromagnetic Mn-Mn interaction to the total magnetic moment. Since the metallic radii of Al and Ti are close (1.432 Å for Al and 1.462 Å for Ti [31]), the Ti atoms could occupy both the Mn and Al sites in the τ phase lattice, and consequently the magnetic characteristics are expected to be modified in comparison with the parent Mn-Al binary alloy. The aim of this paper is to study the effect of Ti doping on the electronic, structural and magnetic properties of the bulk $Mn_{54}Al_{46}$ alloy.

2. Experimental and computational details

The $Mn_{52}Al_{46}Ti_2$ and $Mn_{50}Al_{46}Ti_4$ ingots were prepared by induction melting of the starting components under a purified Ar atmosphere. High purity Mn (99.95 wt%), Al (99.999 wt%) and Ti (99.99 wt%) were used as starting materials. The samples were turned and remelted repeatedly in order to ensure homogeneity. The water-cooled copper crucible provides a rapid cooling of the alloys after melting. The weight loss of the final materials was less than 1%. After melting, the samples were wrapped in tantalum foil, sealed in quartz tubes and annealed (TT) in an inert Ar atmosphere at 470 and 1050 °C for different times followed by quenching in water. The crystal structure of the alloys was investigated at room temperature by using a Bruker D8 Advance diffractometer with Cu K_α radiation. The phase percentages were determined using the FullProf software. Magnetization measurements were performed using an extraction magnetometer in the temperature range 4–800 K in applied external fields up to ±7 T. Electronic structure calculations were performed in the framework of the Local Density Approximation (LDA) of the Density Functional Theory [32] using the SPRKKR method. The calculation method is based on the KKR-Green's function formalism that makes use of multiple scattering theories. The details of the calculation method have been described in detail elsewhere [33]. The calculations have been done in the relativistic mode, i.e. all relativistic effects have been taken into account, including the spin-orbit coupling, in both ferromagnetic (FM) and antiferromagnetic (AFM) spin configurations. Exchange and correlation effects have been treated within the framework of the local spin density approximation (LSDA) using the parameterization of Vosko et al. [34]. The *k*-space integration was performed using the special points method [35]. The substitutional disorder in the system has been accounted for by means of the Coherent Potential Approximation (CPA) [36,37].

3. Results and discussions

3.1. XRD investigations

Because the highest τ phase content was obtained for the parent $Mn_{54}Al_{46}$ alloy annealed at 470 °C for 6 h [28], the $Mn_{52}Al_{46}Ti_2$ and $Mn_{50}Al_{46}Ti_4$ alloys were annealed under the same conditions. In order to see the influence of the annealing temperature on the structure and the magnetic properties, the two alloys were annealed also at a much higher temperature, namely 1050 °C for 1 h. The XRD patterns of the as-cast and annealed $Mn_{52}Al_{46}Ti_2$ and $Mn_{50}Al_{46}Ti_4$ alloys are shown in Fig. 1a and b), respectively. It can be seen that both as-cast and annealed alloys are phase mixtures. All the analyzed samples.

contain τ and γ_2 phases, while the $Mn_{50}Al_{46}Ti_4$ alloys contain an additional κ phase (CsCl–structure type). Results for the Rietveld refinement are given in Table 1. It is to note that the β-phase is not present in any of the investigated samples. The metallic radius of Mn, Al and Ti are 1.307, 1.432 and 1.462 Å respectively. Consequently, the substitution of Ti for Mn is expected to induce change of the lattice. Comparing the lattice parameters for the τ phase in the investigated alloys with those of the parent $Mn_{54}Al_{46}$ alloy ($a = 3.93$ Å and $c = 3.57$ Å [28]) one can see that the parameters a increases and c decreases as the Ti content increases. These results suggest that the Ti atoms are present in the lattice of the τ phases in all studied alloys. This aspect is well shown in Fig. 2, where the peaks corresponding to the τ phase are shifted to the left by increasing the doping content which indicates a change of the lattice parameters (see Table 1.).

The changes in the lattice parameters are expected to influence

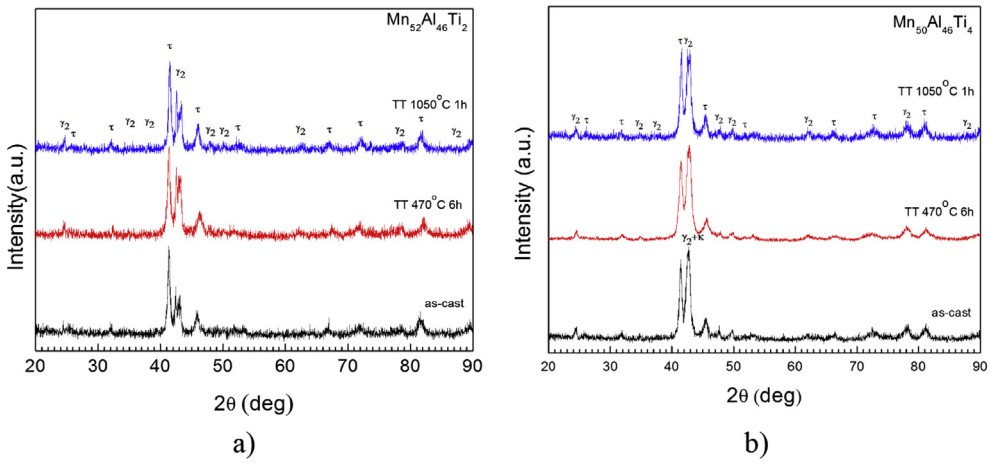

Fig. 1. XRD patterns of the as-cast and annealed $Mn_{52}Al_{46}Ti_2$ and $Mn_{50}Al_{46}Ti_4$ samples. The peaks corresponding to the τ and γ2 phases are indicated. For clarity the diffraction patterns have been shifted vertically.