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Insights into formation and stability of τ-MnAlZ$_x$ (Z = C and B)

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ABSTRACT

The τ-phase MnAl alloys are promising candidate for rare earth free permanent magnets. In this study, In order to better understand the MnAl ε→τ phase transition mechanism in a continuous cooling process and metastable MnAl τ-phase high temperature stability, $Mn_{0.54}Al_{0.46}$, $Mn_{0.55}Al_{0.45}C_{0.02}$ and $Mn_{0.55}Al_{0.45}B_{0.02}$ alloys were systematically studied by *in situ* synchrotron X-ray powder diffraction (SR-XRD). The relationship between τ-phase formation tendency and different cooling rates of $Mn_{0.55}Al_{0.45}C_{0.02}$ was investigated. Besides, the high temperature stabilities of undoped τ-MnAl and carbon/boron doped τ-MnAl were studied. Differential thermal analysis (DTA) was also employed to study the phase transformation as well. The research results show that a high cooling rate of 600 °C/min leads to a 50/50 wt% mixture of ε- and τ-phase; almost pure τ-phase was obtained when cooled at a moderate cooling rate of 10 °C/min; while for a slow cooling rate of 2 °C/min, the τ-phase partially decomposed into β and γ_2 phases. No intermediate ε'-phase was observed during the ε→τ phase transition during the experiments. For the boron and carbon doped τ-MnAl, the 800 °C high temperature stability experiments reveal that C stabilizes the τ-MnAl while doped B destabilises the tetragonal structure and it decomposes into β- and γ_2-phases.

1. Introduction

Permanent magnets have been widely used in almost every aspect of the electrical engineering industry and our daily life, range from highly efficient electric power generators and motors to audio devices. Renewable energy technology like direct drive wind turbines and HEV/EV cars could possibly provide parts of the solution to the green economy growth [1]. Today the market leading magnets are NdDyFeB permanent magnets; however, the NdDyFeB magnets contain large amount of strategic heavy rare earth elements like Dy and Tb [2]. Given the current world consumption growth in NdDyFeB magnets, green energy critical important elements like Dy and Tb could be in severe shortage in the coming decades [3].

The ferromagnetic and metastable τ-phase MnAl, which crystallise in the AuCu-type structure ($L1_0$) [4], is considered a promising, relatively low density (5.1 g/cm^3) and low cost rare-earth free permanent magnetic material candidate [5,6]. The τ-phase MnAl has relatively high theoretical magnetic properties, with, saturation magnetization of 114 Am^2/kg, K_1 of 1.5 MJ/m^{3}and T_c of 650 K [7–9]. If the τ-phase MnAl was fully developed and could reach the theoretical value, it could partially substitute the costly NdDyFeB magnets. This would have a profound impact on low-cost green energy technologies.

There are mainly two proposed ε-τ phase transformation processes [10,11]. In practice, synthesis is either done by quenching and subsequent annealing (tempering) of a quenched ε-MnAl sample at 400–650 °C or by cooling from the melt at appropriate cooling rate (~10 °C/min) [12,13]. However, in the slow cooling process the ε-MnAl has to be cooled sufficiently fast to avoid decomposition into β and γ_2 which are the thermodynamically stable phases at low temperature (see Fig. 1) [14].

A small addition of carbon to the MnAl alloy has been proven to stabilize the τ-MnAl phase, thus preventing the τ-MnAl decomposition into unwanted β- and γ_2-phases [15,16]. Boron addition has been suggested to enhance the coercivity, H_c, by suppressing the MnAl grain growth, but B addition could also have a side effect of reducing the τ-MnAl stability, resulting in a material that is more

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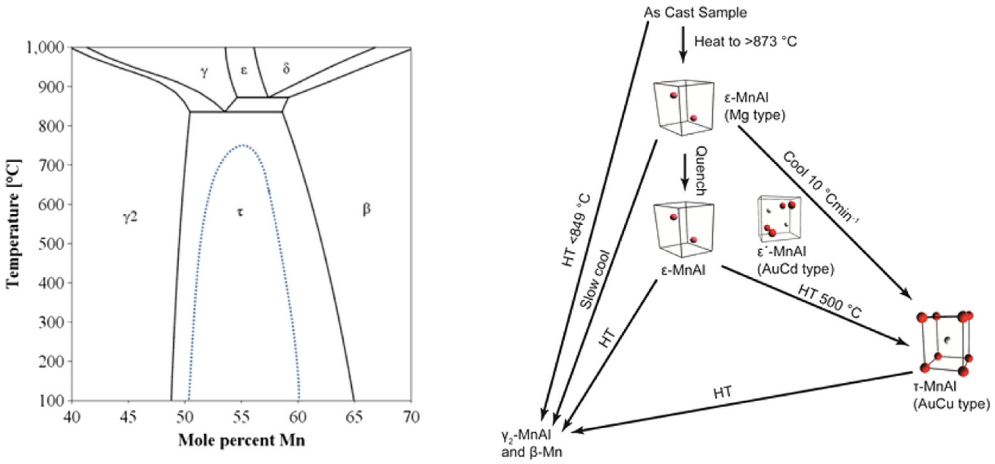

Fig. 1. a, Mn-Al phase diagram. b, Reaction scheme (white spheres Mn, red spheres Al pink spheres mixed sites).

easily decomposed into β- and γ_2-phases [17].

To obtain the τ-phase from the ε-phase, the right synthesis conditions must be fulfilled, as discussed above. The transition itself is suggested to occur in two steps [16]. The first step is a reordering of all atoms from the hcp random arrangement (ε-phase) to an orthorhombic structure, known as ε′, via diffusion. The ε'-phase, Fig. 1a, is a layered structure isostructural with AuCd (B19-structure) [4,17]. The transition from ε′ to τ is a martensitic, diffusionless process and can therefore be very fast, and is hard to observe [16]. Fig. 2 shows the similarities between the ε′ and the τ-phase.

The τ-MnAl phase crystallizes in an ordered body-centred tetragonal structure, space group *P4/mmm*, the Mn atoms occupy the 1 *a* positions (0,0,0) and the Al occupy the 1 *d* positions (1/2,1/2,1/2) [18]. The Mn atoms at the 1 *a* position interact ferromagnetically with each other but there are always some additional Mn atoms at the 1*d* position that interact antiferromagnetically with the 1 *a* Mn atom. This stabilises the overall magnetic structure but leads to a decreased saturation magnetization. In the traditional three stage transformation process (ε→ε'→τ), the high temperature (hexagonal-close-packed, A3) ε-phase MnAl is typically obtained via quenching from 850 °C (e.g. melt-spinning). This is followed by annealing at moderate temperatures (400–700 °C). During the annealing process, ε-MnAl transforms into the intermediate ε′ through a diffusion process followed by the ε'→τ martensitic transformation [11]. In the quenching-annealing process, the ordering between Mn and Al atoms on the 1 and 1 *d* sites respectively, might be hindered, as a result, increase the antiferromagnetic interactions. This hindering of the Mn-Al ordering could be reduced in the "slow cooling process" which might explain why the directly obtained τ-MnAl phase has a higher saturation magnetization in comparison with other synthesis methods [19].

In our previous study, we found that the τ-phase MnAl could be directly formed during a natural cooling after drop synthesis process [19], however this τ-phase formation mechanism is not fully understood. In order to better understand the τ-MnAl formation conditions and high temperature stability, we performed high temperature *in situ* synchrotron X-ray powder diffraction. The relationship between τ-MnAl formation and different cooling rates was investigated. Furthermore, the influence of different doping elements (B and C) on the τ-MnAl temperature stability was systematically studied.

2. Experimental

2.1. Synthesis

Bulk $Mn_{0.54}Al_{0.46}$, $Mn_{0.55}Al_{0.45}C_{0.02}$ and $Mn_{0.55}Al_{0.45}B_{0.02}$ samples (~10 g each) were synthesized through the drop synthesis method [20]. The ingots were induction melted in a high purity argon atmosphere (400 mbar) from high purity raw materials, Mn (Institute of Physics, Polish Academy of Sciences, purity 99.999%), Al (Gränges SM, purity 99.999%), C (Highways international, purity 99.999%) and B (Wacher Chemie, purity 99.995%). Al was first melted with C or B respectively at 1000 °C, and Mn was dropped

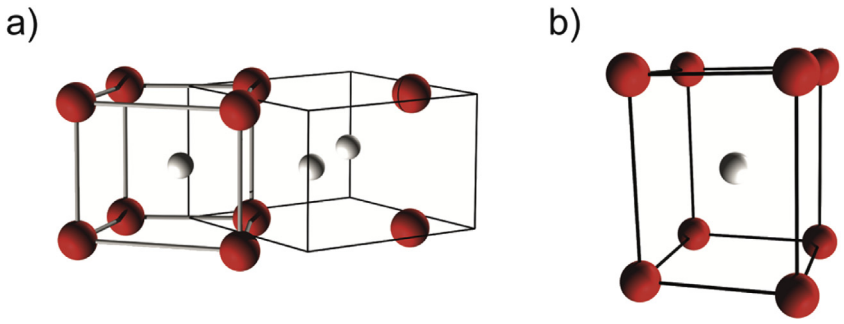

Fig. 2. The intermediate ε'-phase (a) and the τ-phase (b). The ε′-phase is has extra atoms added and connected to show the similarity to the τ-phase.