

The effect of Ti or Zr additions on the microstructure and magnetic properties of MnAl-C alloys

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ABSTRACT

As-transformed and hot-deformed samples of MnAl-C alloys with Ti or Zr additions have been produced and characterized using magnetometry, X-ray diffraction, scanning electron microscopy and transmission electron microscopy. Both Ti and Zr additions in MnAl-C alloys form carbide primary phases, TiC and ZrC, which consume the carbon meant to be dissolved in the metastable τ -phase to stabilize it against decomposition. With these two additions, the Curie temperature of τ -phase increases while its stability against decomposition decreases. After hot deformation, the MnAl-C alloys with Ti or Zr additions have lower polarisation and remanence due to the reduced stability of the τ -phase. Adding extra carbon along with Ti to a MnAl-C alloy in order to compensate for the C lost on formation of TiC restored the original stability of the τ -phase. After hot-deformation, this alloy exhibited a lower polarisation and remanence owing to the unexpected formation of the γ_2 -phase.

Introduction

The intrinsic magnetic properties (anisotropy constant $K_1 > 1 \text{ MJm}^{-3}$ [1], saturation magnetization $\mu_0 M_s > 0.74 \text{ T}$ [2–4] and Curie temperature $T_c > 260 \text{ °C}$ [1,5,6]) of the τ -phase ($L1_0$, space group: $P4/mmm$) in Mn-Al system show its strong potential as a rare earth free permanent magnet [7–9]. This ferromagnetic τ -phase has a theoretical 110 kJm^{-3} maximum energy product ($(BH)_{\text{max}}$), which has the potential to plug the gap between hard ferrites and Nd-Fe-B [9]. Until now the best magnetic property was achieved through hot extrusion [6,10,11]. The ferromagnetic τ -phase with nearly equiatomic Mn-Al composition can be only obtained from the high temperature ϵ -phase ($A3$, space group: $P6_3/mmc$) by annealing the quenched high temperature ϵ -phase [12,13] or cooling at an intermediate rate from the ϵ -phase [5]. The metastable τ -phase decomposes into the disordered cubic β -Mn ($A13$, space group: $P4_132$) with excess of Mn and the ordered trigonal γ_2 -phase ($D8_10$, space group: $R3m$) with excess of Al after long-term annealing [5]. The existence of Mn_3AlC ($E2_1$, space group: $Pm\bar{3}m$) has been proved in the hot-deformed MnAl-C alloy [14].

The addition of carbon will enhance the stability of τ -phase against decomposition into the equilibrium phases [15–17]. One suggested mechanism to explain this effect is that the interstitial C atoms could inhibit the diffusion of Mn and Al atoms [16]. At the same time, the

addition of carbon also decreases the Curie temperature (T_c) [1]. Recent results have shown that Ni additions could further improve the stability of τ -MnAl-C [18]. The effect of Cu on the mechanical properties of bulk MnAl-C has been researched with the idea that reducing the stress necessary to deform the material may be one possibility to reduce the production costs [19,20]. Some experimental data suggest that adding Ti may increase the ductility of MnAl melt-spun ribbons [21]. Furthermore, the addition of Ti was also reported to improve the plasticity of the MnAl-C alloy with Cu addition, thus extending the lifetime of the extrusion die [19]. Zr addition has been reported to increase both saturation magnetization and coercivity of rapidly solidified MnAl-C alloys [22]. Although these reports show the potential benefit of Ti or Zr addition to MnAl/MnAl-C alloys, the microstructural mechanisms responsible for the effects are currently unclear.

The aim of the current work is therefore to confirm the influence of Ti and Zr additions to MnAl-C alloys by carrying out detailed characterisation of the microstructure and magnetic properties of materials in different states.

Experimental

The alloys with nominal compositions $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)_{100-x}\text{Ti}_x$ where $x = 0, 0.1, 0.5, 1$ and 2 , plus alloys with nominal compositions

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(Mn₅₃Al₄₅C₂)C_{0.26}Ti_{0.25} and (Mn₅₃Al₄₅C₂)Zr_{0.3} were produced by arc melting high purity elements (99.99% Mn and Al, 99.95% Ti, 99.9% C and Zr) under argon atmosphere. The as-cast material was encapsulated in a glass tube which was evacuated to 10⁻⁷ bar and backfilled with 0.2 bar Ar. The material was homogenized at 1100 °C for two days and afterwards quenched into water. The following annealing was done at 500 °C for 1 h, which will be referred to as “as-transformed”. To compare the stability, some of the samples were held at 700 °C for 7 days before being quenched into the water.

The alloys with nominal compositions Mn₅₃Al₄₅C₂, (Mn₅₃Al₄₅C₂)Ti_{0.25}, (Mn₅₃Al₄₅C₂)C_{0.26}Ti_{0.25} and (Mn₅₃Al₄₅C₂)Zr_{0.3} were prepared by induction melting industrial pure Mn and Al elements (99.8% Mn and 99% Al) and the high purity Ti, Zr and C as before under argon atmosphere and were then cast into a cylindrical Cu mould of 11 mm diameter. The as-cast materials were homogenized using the same conditions as above. The homogenized samples were sectioned to 7 mm height cylinders, which were deformed at 700 °C after 10 min holding at 0.001 s⁻¹ deformation rate to a nominal logarithmic degree of deformation of 1.386 (75% height reduction). These samples will be referred to as “hot-deformed”.

The chemical composition was analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). The nominal compositions with their corresponding actual compositions from the ICP results of alloys are shown in Table 1, indicating that the actual composition is very close (±0.9 at%) to the nominal one.

The microstructure was investigated using a Gemini Leo 1530 field emission gun scanning electron microscope (FEGSEM) equipped with backscattered electron (BSE) and secondary electron (SE) detectors. Standard metallographic grinding and polishing techniques were used to prepare the samples for FEGSEM investigations. X-ray diffraction (XRD) patterns were carried out on polished samples using a Bruker diffractometer with Co-K_α radiation ($\lambda(K_{\alpha 1}) = 1.78919 \text{ \AA}$; $\lambda(K_{\alpha 2}) = 1.79321 \text{ \AA}$). The refined lattice parameters and phase weight fractions were obtained using the Rietveld refinement method by analysing the 2 θ range of 20 – 120° in the software FullProf [23].

Lamellae for transmission electron microscopy (TEM) were fabricated using a dual beam SEM/focused-ion-beam (FIB) instrument (FEI Helios Nanolab 600). Regions of interest were covered by Pt deposition and lamellae were cut using 30 kV Ga ions, extracted and attached to TEM Mo-grids. Electron-transparent windows in the lamellae were thinned by 5 kV Ga ions. The lamellae were then investigated using a FEI Tecnai T20 G² instrument operated at 200 kV equipped with energy-dispersive X-ray spectroscopy (EDX) detector.

Magnetic hysteresis loops of the as-transformed alloys were obtained by using an in-house-built VSM at applied fields up to 5.6 T. The magnetic measurements of hot-deformed samples in radial direction were carried out using a Quantum Design PPMS device with a vibrating sample magnetometer (VSM) measuring head at applied fields up to 14 T. The hysteresis loop data were corrected by demagnetization factors according to the reference [24]. To determine the Curie temperature of the materials, thermomagnetic $M(T)$ curves were gathered up to 450 °C using the PPMS with the furnace option under an applied field of 0.1 T. Local minima in the first derivative of the $M(T)$ curves were taken as T_C .

Table 1
The nominal compositions and actual compositions of alloys.

Melting method	Nominal composition	Actual composition
Arc melting	Mn ₅₃ Al ₄₅ C ₂	Mn _{52.62} Al _{45.54} C _{1.84}
Arc melting	(Mn ₅₃ Al ₄₅ C ₂)Ti _{0.5}	(Mn _{52.68} Al _{45.66} C _{1.66})Ti _{0.49}
Arc melting	(Mn ₅₃ Al ₄₅ C ₂)Ti ₁	(Mn _{52.29} Al _{45.87} C _{1.84})Ti _{0.94}
Arc melting	(Mn ₅₃ Al ₄₅ C ₂)Ti ₂	(Mn _{52.48} Al _{45.72} C _{1.80})Ti _{1.96}
Arc melting	(Mn ₅₃ Al ₄₅ C ₂)Zr _{0.3}	(Mn _{53.06} Al _{45.44} C _{1.51})Zr _{0.28}
Induction melting	(Mn ₅₃ Al ₄₅ C ₂)Ti _{0.25}	(Mn _{52.53} Al _{45.65} C _{1.82})Ti _{0.23}
Induction melting	(Mn ₅₃ Al ₄₅ C ₂)Zr _{0.3}	(Mn _{53.18} Al _{44.86} C _{1.96})Zr _{0.32}

Results and discussion

Ti addition

As-transformed

Microstructures with primary phases. After annealing the homogenised (Mn₅₃Al₄₅C₂)_{100-x}Ti_x alloys at 500 °C for 1 h, the ternary alloy (x = 0) fully transformed to τ -phase (Fig. 1a). The alloys with x from 0.1 to 2 and (Mn₅₃Al₄₅C₂)C_{0.26}Ti_{0.25} additionally show grains of a primary phase. The small bright particles (in Fig. 1b-f) and large dark particles (Fig. 1d-f) both consist of the primary phase with the same crystal structure, which will be identified below. Both large and small primary phase particles protrude slightly from the surface of the sample, as can be seen from the pairs of SE and BSE images in supplemental Fig. S1. The apparently different BSE intensity of the small and large particles may be because the small particles became electrostatically charged by the incident electrons and therefore appear bright. The size of the primary phase particles varies with the Ti content of the alloy. With x = 0.1, the size of the particles ranges from 100 nm to 1 μ m. With x = 2, the upper limit of the size reaches to about 20 μ m (Fig. 1f). The γ_2 -phase appears in alloys with x = 0.5 to 2, and the size and the volume fraction of γ_2 -phase become larger with increasing Ti content (Fig. 1d-f). The increase of the γ_2 -phase fraction can be also noticed through the increase of the peak intensities in the XRD results (Fig. 2).

Identification of TiC primary phases and lattice parameters of τ -phase. A TEM lamella which includes both nanometre-scale and micron-scale primary phases was cut from the (Mn₅₃Al₄₅C₂)Ti₂ alloy to analyse the primary phases. EDX spectra from the primary phases showed strong Ti peaks. As the quantification of C from EDX data is not reliable, C was excluded from quantitative analysis. The results showed that, of the elements quantified, the primary phases consist almost entirely of Ti (9 points show hundred percent of Ti and 3 points show average 1.10% Mn with the balance being Ti). The primary phases are therefore likely to be either a pure-Ti phase or a Ti-carbide. Confirmation was provided by selected area diffraction (SAD) patterns which were successfully indexed as the TiC phase ($B1$, space group: $Fm\bar{3}m$, prototype: NaCl, $a = 4.325 \text{ \AA}$ [25]) in the Fig. 3. Several primary phases with nanometre-scale or micron-scale and different incident angles have been tried and all results can be indexed as TiC phase. The melting point of TiC is 3160 °C and its enthalpy of formation ($\Delta H_f = -92.9 \pm 8.9 \text{ kJmol}^{-1}$ [26]) is strongly exothermic. During the solidification of the alloys, it is therefore likely that TiC will form first from the melt and will not be affected by the following heat treatments. For this reason, the TiC particles are referred to here as primary phases instead of precipitates.

For the alloys with x = 1 and 2, the XRD results show obvious γ_2 -phase peaks (Fig. 2). Minor peaks of TiC can be also seen in XRD results of these alloys. Phase weight fractions calculated by Fullprof are listed in the Table 2. With increasing Ti content, more TiC and γ_2 -phase are shown in the alloys, which are also noticed in the microstructural images (Fig. 1). The TiC and γ_2 -phase have not been noticed in the XRD results of the alloys with Ti ≤ 0.5 due to the resolution of the XRD. The γ_2 -phase is present in the alloy with x = 0.5 and in alloys with higher Ti concentrations. The Mn/Al ratios obtained from ICP are slightly lower for the alloys with x = 1 and 2 than the ratios of the alloys with x = 0 and 0.5. This may be caused by more Mn evaporation as a result of the higher energy required to melt alloys with higher Ti content. This lower Mn/Al ratio may be one reason for the existence of γ_2 -phase. The other possible reason is that, the formation of TiC did not consume all added Ti, and therefore more Ti was dissolved in MnAl-C, which may alter the phase equilibria.

The lattice parameters of the τ -phase are also shown in the Table 2. The a parameter increases with increasing Ti content, while c parameter decreases. The corresponding slight peak shift of τ -phase can be also

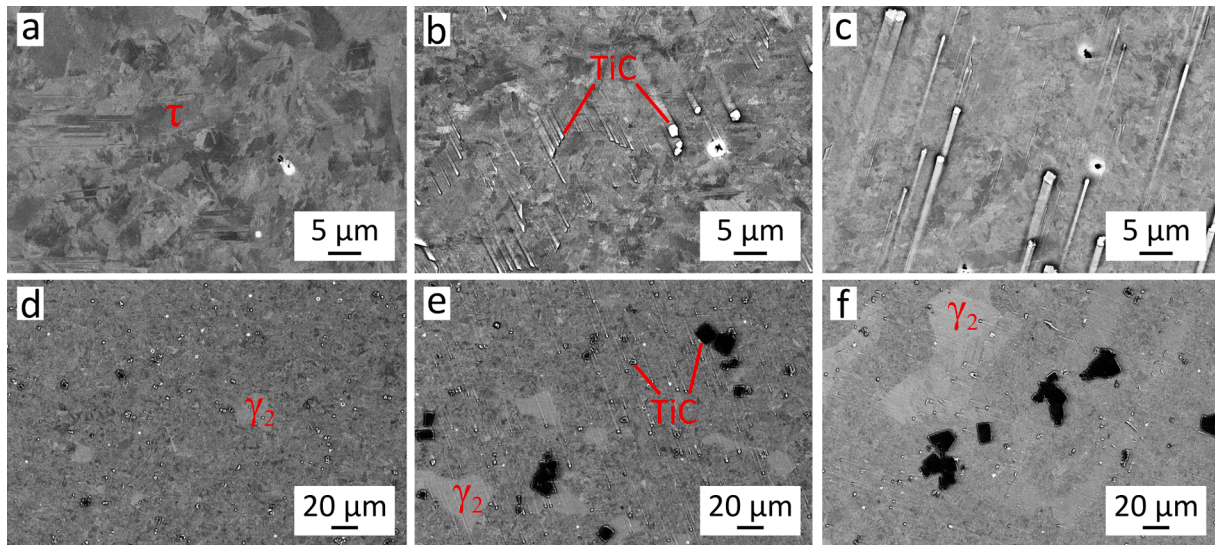


Fig. 1. Backscattered electron (BSE) images of $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)_{100-x}\text{Ti}_x$ where (a): $x = 0$, (b): 0.1, (d): 0.5, (e): 1, (f): 2 and (c): $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{C}_{0.26}\text{Ti}_{0.25}$ after annealing at 500 °C for 1 h. Small bright and big dark primary TiC phases, τ -phase and γ_2 -phase are marked.

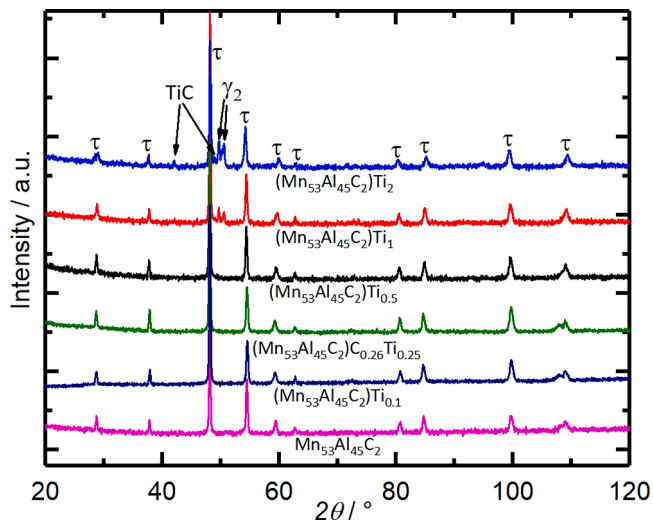


Fig. 2. XRD patterns of the as-transformed $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)_{100-x}\text{Ti}_x$ where $x = 0$, 0.1, 0.5, 1, 2 and $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{C}_{0.26}\text{Ti}_{0.25}$. The peaks of τ -phase, γ_2 and TiC are marked.

seen in the XRD results (Fig. 2). As the C concentration of the τ -phase decreases, the lattice parameter a becomes longer and c becomes shorter [10,27]. The formation of the TiC consumes the carbon which was meant to be dissolved in the τ -phase and therefore, as the Ti content in the alloy increases a larger fraction of TiC is formed and the C-content of the τ -phase decreases. The lattice parameter changes observed in the τ -phase are consistent with this reduced C-content.

It has been proved that the substitution of Ti for Mn in binary Mn-Al alloy induces the increase of a and decrease of c [28]. The fact that the $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Ti}_{0.1}$ shows the TiC phase (Fig. 1b) means that not all of the added Ti dissolves in the τ -phase, i.e., the Ti dissolved in the τ -phase is below 0.1 at.%. With higher Ti addition in the alloy, the amount of Ti dissolved inside the τ -phase may increase. In $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Ti}_2$ alloy, the content of Ti is higher than the content of C, and therefore an excess of Ti remains even if all the C forms TiC. EDX in the TEM shows 0.70 at.% Ti inside the τ -phase, and this number is higher than the amount of excess Ti (0.04 at.%), which also means the formation of TiC did not consume all C in this alloy. The Ti dissolved in τ -phase is a second contribution to

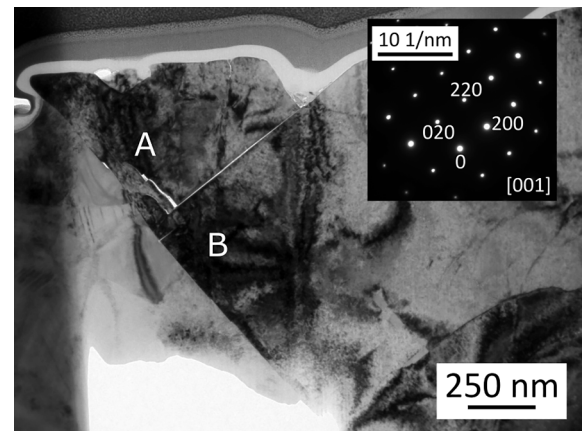


Fig. 3. Bright-field TEM image of the as-transformed $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Ti}_2$ alloy, the inset is the SAD pattern of both A and B positions marked in the TEM image, which can be indexed as TiC (zone axis [001]).

Table 2

The lattice parameters of the τ -phases and phase weight fractions (calculated using Fullprof) along with the Curie temperatures of $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)_{100-x}\text{Ti}_x$ where $x = 0$, 0.1, 0.5, 1, 2 and $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{C}_{0.26}\text{Ti}_{0.25}$.

Alloy	Crystal parameter of τ -phase (Å)		Phase weight fraction (%)			τ -phase T_C (°C)
	a (± 0.001)	c (± 0.001)	τ	γ_2	TiC	
$\text{Mn}_{53}\text{Al}_{45}\text{C}_2$	2.767	3.613	100.0			262
$(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Ti}_{0.1}$	2.764	3.616	100.0			264
$(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Ti}_{0.5}$	2.766	3.619	100.0			260
$(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{C}_{0.26}\text{Ti}_{0.25}$	2.771	3.607	100.0			278
$(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Ti}_1$	2.771	3.598	94.2	4.1	1.7	286
$(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Ti}_2$	2.779	3.576	72.0	23.9	4.1	336

the change of lattice parameters in alloys with higher Ti addition, especially for the $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Ti}_2$ alloy.

Magnetic properties. The hysteresis loops of the transformed alloys are shown in Fig. 4a. For the alloys with $x \leq 0.5$, the polarisation at an applied field of $\mu_0 H = 5.6$ T, $J_{5.6T}$, varies somewhat. With more Ti addition, because of the formation of γ_2 -phase, the fraction of the τ -phase become less and the $J_{5.6T}$ decreases rapidly.

The T_c of the ternary alloy produced here is 262 °C, and the T_c of the $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{C}_{0.26}\text{Ti}_{0.25}$ and $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Ti}_{0.1}$ are almost the same as this (Table 2 and Fig. 4b). For $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{C}_{0.26}\text{Ti}_{0.25}$, it is because more carbon was added to exclude the carbon-consuming effect of the formation of TiC. For $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Ti}_{0.1}$, the reason is that just a small amount of the supersaturated carbon was extracted to form TiC which did not affect the T_c too much. In contrast, with 0.5 at.% Ti, 1 at.% Ti and 2 at.% Ti, the T_c increases from 278 °C to 286 °C to 336 °C. With Ti addition, the amount of carbon dissolved in the τ -phase becomes less owing to the formation of TiC, thus leading to the increase in T_c [10].

In the current experimental results, just one Curie temperature was found in each corresponding alloy. This shows that the soft-magnetic κ -phase (B2, space group: $Pm\bar{3}m$) with T_c around 257 °C [28] was not present in the as-transformed alloys studied here.

Thermal stability. The addition of carbon will enhance the stability of τ -phase [15–17]. The metastable τ -phase in the binary Mn–Al alloys would fully decompose after 10 min at 700 °C, while with carbon (1.6 at. %) one third of the τ -phase will still remain after one week at 700 °C [17]. The same stability test was carried out on the ternary alloy produced here, with similar results (Fig. 5a). In addition to the remaining τ -phase in Fig. 5a, there are some aggregated areas of eutectoid structure β -Mn and γ_2 -phase. The formation of the TiC phase consumes the carbon which should be dissolved in the τ -phase and stabilize it and, as a result, the alloy with $x = 0.5$ at 700 °C after 7 days decomposes into β -Mn and γ_2 -phase entirely (Fig. 5b). As to the alloy $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{C}_{0.26}\text{Ti}_{0.25}$ (Fig. 5c) with more carbon which can be used to form TiC, the remaining τ -phase have the almost same fraction (about one third) compared to the ternary alloy. There are some aggregated areas of eutectoid structure β -Mn and γ_2 -phase plus some bright square TiC phases in Fig. 5c. The XRD results (supplemental Fig. S2) also show that the alloy with $x = 0.5$ fully decomposed into β -Mn and γ_2 -phase. Even for the $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Ti}_2$ alloy after 1 h at 500 °C, the β -Mn already forms along the grain boundaries of τ -phases and γ_2 -phases (supplemental Fig. S3). With Ti addition, the MnAl-C alloys will lose their original stability if additional C is not added to counteract the effect of forming TiC.

Hot-deformed

Microstructure and stability. Owing to the reduced stability of the τ -phase in the alloys with higher Ti addition, the decomposition of $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Ti}_{0.25}$ is more than both $\text{Mn}_{53}\text{Al}_{45}\text{C}_2$ and $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{C}_{0.26}\text{Ti}_{0.25}$ (Fig. 5d–f). In Fig. 5e and f, the small bright square particles are the primary TiC phases. One can also see the larger areas of other bright phases which are the β -Mn in Fig. 5d–f. In Fig. 5e the eutectoid structure of the β -Mn and γ_2 -phases is present. The grey areas are the recrystallized and non-recrystallized τ -phases. Some of the non-recrystallized τ -phases are marked with red “A” in Fig. 5d–f. Along the recrystallized τ -phase boundaries, the small precipitated β -Mn and Mn_3AlC are shown exemplarily for the hot-deformed ternary alloy in supplemental Fig. S4.

In the XRD results of the hot-deformed samples (supplemental Fig. S5), the hot-deformed $\text{Mn}_{53}\text{Al}_{45}\text{C}_2$ sample consists almost entirely of τ -phase plus a small fraction of β -Mn and Mn_3AlC . All three samples contain Mn_3AlC , and the $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{C}_{0.26}\text{Ti}_{0.25}$ contains the highest fraction as a result of the highest C addition. The $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Ti}_{0.25}$ shows the highest β -Mn content owing to the lowest stability of the τ -phase. The $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{C}_{0.26}\text{Ti}_{0.25}$ shows no obvious β -Mn peaks but the highest γ_2 -phase peaks, and the reason why this sample contains so much γ_2 -phase is not currently clear.

Magnetic properties. The Curie temperature results for all three hot-deformed samples (supplemental Fig. S6) still show one Curie temperature without any sign of the soft-magnetic κ phase. The measured temperature range here starts from the room temperature, which is higher than the Curie temperature (15 °C [29]) of Mn_3AlC . The similar Curie temperatures of the τ -phase in all three samples indicates that the remaining τ -phase contains approximately the same amount of dissolved C after deformation.

The hysteresis loops of three hot-deformed sample are shown in Fig. 6. The polarisation at 14 T, J_{14T} , of the hot-deformed $\text{Mn}_{53}\text{Al}_{45}\text{C}_2$ is higher than other alloys with Ti addition. This is because the decomposition of the τ -phases into β -Mn and γ_2 -phase in $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Ti}_{0.25}$ and the unexpected presence of the γ_2 -phase in $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{C}_{0.26}\text{Ti}_{0.25}$. The coercivity of the alloys with Ti addition are slightly higher than the ternary alloy, while the remanence is lower. In alloys with 0.25 at.% Ti content with or without extra carbon, the coercivity slightly increases while both polarisation and remanence decrease.

The applied pressure as a function of time during die-upsetting is shown for different alloys in Fig. S7. The peak of the curves represents the yield stress of the alloys and the data indicate that in $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Ti}_{0.5}$ and $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{C}_{0.26}\text{Ti}_{0.25}$ the flow stress is slightly lower than that of the ternary alloy. In the case of $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Ti}_{0.5}$ this may be

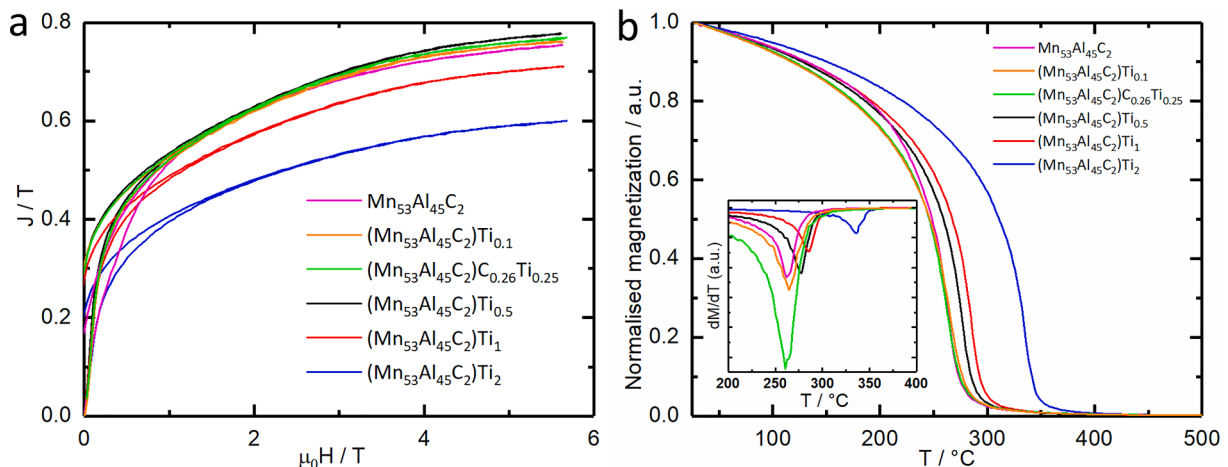


Fig. 4. The (a): hysteresis loops and (b): $M(T)$ curves of $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)_{100-x}\text{Ti}_x$ where $x = 0, 0.1, 0.5, 1, 2$ and $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{C}_{0.26}\text{Ti}_{0.25}$. The inset in (b) showing the first derivative of the $M(T)$ curves.

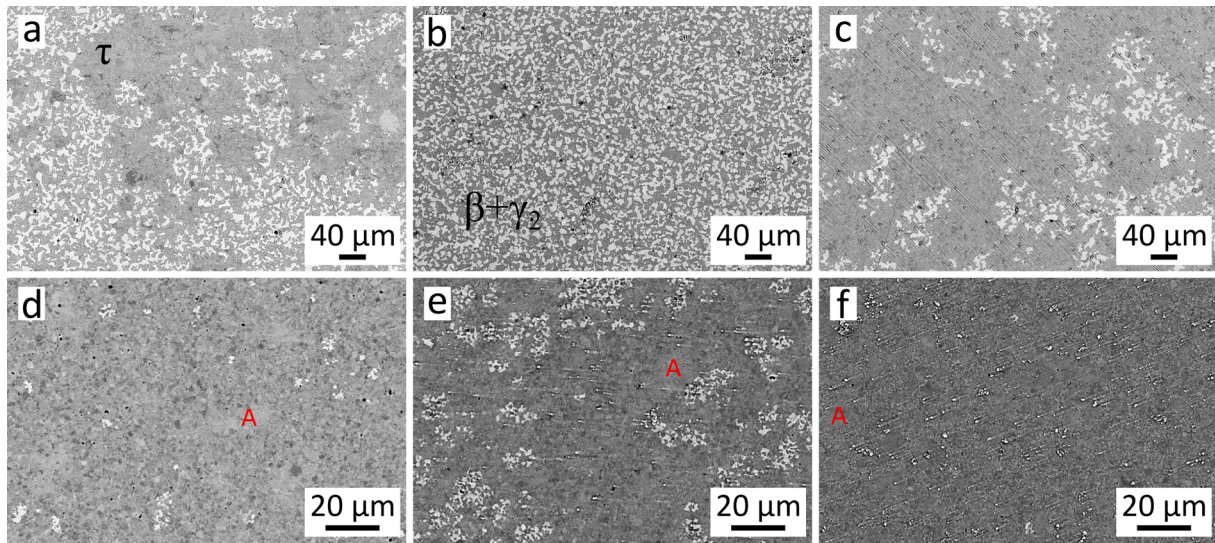


Fig. 5. The BSE images of (a): $\text{Mn}_{53}\text{Al}_{45}\text{C}_2$, (b): $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Ti}_{0.5}$, (c): $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{C}_{0.26}\text{Ti}_{0.25}$ after 7 days at 700 °C, and (d): $\text{Mn}_{53}\text{Al}_{45}\text{C}_2$, (e): $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Ti}_{0.25}$, (f): $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{C}_{0.26}\text{Ti}_{0.25}$ after hot deformation at 700 °C after 10 min holding by 75 % height reduction at 0.001 s^{-1} deformation rate. The τ -phase, β -Mn and γ_2 -phase are marked and some of the non-recrystallized τ -phases are marked with red “A”. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

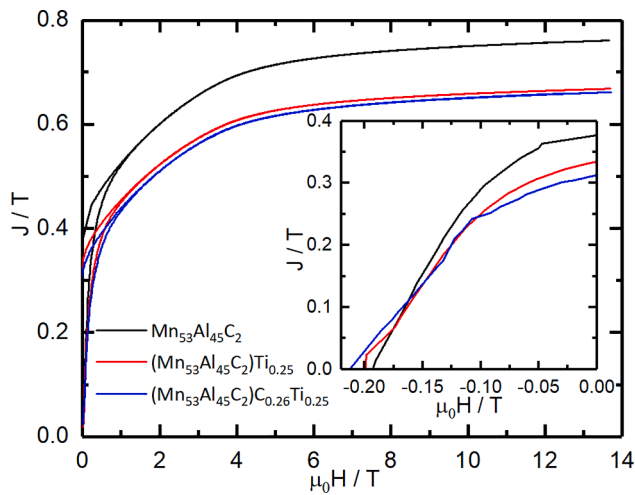


Fig. 6. Hysteresis loops of hot-deformed $\text{Mn}_{53}\text{Al}_{45}\text{C}_2$, $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Ti}_{0.25}$ and $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{C}_{0.26}\text{Ti}_{0.25}$ at 700 °C after 10 min holding by 75 % height reduction at 0.001 s^{-1} deformation rate and the inset showing the magnified image of the second quadrant.

because of the reduced fraction of interstitial C in the τ -phase, whereas for $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{C}_{0.26}\text{Ti}_{0.25}$, the formation of the γ_2 -phase may be responsible for the reduction of the deformation stress.

Zr addition

With Zr addition, the alloy also shows the primary phase particles (Fig. 7a) similarly to the case of Ti addition. The XRD result of the $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Zr}_{0.3}$ annealed at 500 °C for 1 h shows minor ZrC peaks (supplemental Fig. S8). The lattice parameters calculated from the XRD results by Fullprof show that after Zr addition, the a parameter of the τ -phase increases slightly from 2.767 ± 0.001 Å to 2.769 ± 0.001 Å, while the c parameter decreases from 3.613 ± 0.001 Å to 3.606 ± 0.001 Å, which shows the same trend with the Ti containing alloys because the formation of ZrC also consumes the carbon which was meant to be dissolved in the τ -phase. At the same time, the Curie temperature of the $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Zr}_{0.3}$ is 284 °C, which is higher than that of the ternary alloy, due to the extraction of C from the τ -phase [10].

A lamella was cut from the $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Zr}_{0.3}$ annealed at 500 °C for 1 h using the FIB. TEM was used to identify the primary phase. The EDX results show that the primary phases are 100% Zr ignoring the C content. The SAD patterns can be indexed as ZrC ($B1$, space group: $Fm\bar{3}m$, prototype: NaCl, $a = 4.691$ Å [25]). The inset of Fig. 8 is the diffraction pattern derived from the A part, whose zone axis is $[001]$. Hence, after Zr addition the alloys form ZrC primary phases. Geng *et al.* [22] have already noticed some extra peaks in the XRD results of $\text{Mn}_{53}\text{Al}_{45}\text{C}_2\text{Zr}_{0.1}$, which are the low-intensity peaks at $\approx 56^\circ$, 66° , and 82° 2θ (Rigaku Multiflex with Cu-K α radiation). These peaks are corresponding to the peaks of ZrC. The melting point of ZrC is 3532 °C and its enthalpy of formation ($\Delta H_f = -207.1 \pm 2.5$ kJmol $^{-1}$ [30]) is strongly exothermic. The ZrC also forms during solidification and will not change in the

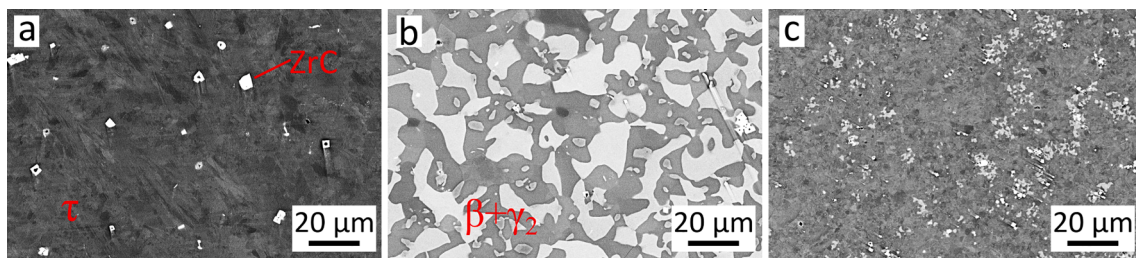


Fig. 7. BSE images of $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Zr}_{0.3}$, (a): annealed at 500 °C for 1 h, (b): annealed at 700 °C for 7 days and (c): hot-deformed at 700 °C after 10 min holding by 75 % height reduction at 0.001 s^{-1} deformation rate. The τ -phase, ZrC, β -Mn and γ_2 -phase are marked.

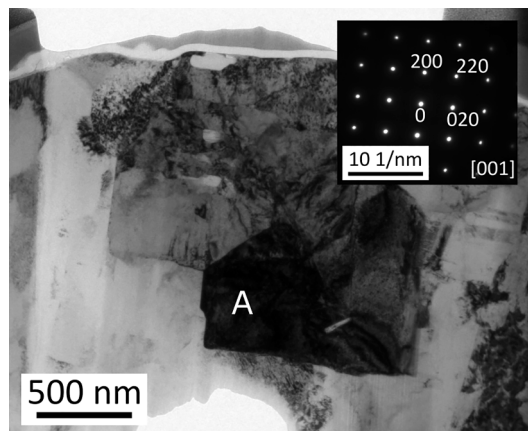


Fig. 8. The TEM image of the as-transformed $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Zr}_{0.3}$ alloy, the inset is the SAD pattern of A position marked in the TEM image, which can be indexed as ZrC (zone axis [001]).

following heat treatments.

The long-term annealing at higher temperature (700 °C for 7 days) was also conducted for investigating the stability of the τ -phase with Zr addition. The result shows that the τ -phase fully decomposed into the eutectoid structure of β -Mn and γ_2 -phase (Fig. 7b). In the microstructural image of hot-deformed $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Zr}_{0.3}$ (Fig. 7c), the grey areas are the combination of recrystallized and non-recrystallized τ -phases, and the coarse regions contain the eutectoid structure of the β -Mn and γ_2 -phase (see XRD results in Fig. S9). There are also some bright square ZrC particles appearing. Further decomposition occurred after hot deformation as a result of the lower stability of τ -phase due to its reduced carbon content. After hot deformation, the coercivity is almost the same for both alloys, however, the polarisation and remanence of $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Zr}_{0.3}$ alloy are less than those of $\text{Mn}_{53}\text{Al}_{45}\text{C}_2$ alloy owing to the decomposition (Fig. 9). The flow stress of the alloy $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Zr}_{0.3}$ is slightly lower than that of the ternary alloy (Fig. S7).

Conclusions

In MnAl-C alloys with Ti additions, TiC forms in the melt and consumes the carbon that is meant to be dissolved in the metastable τ -phase in order to stabilize it against decomposition into the equilibrium phases. The loss of the carbon dissolved in the τ -phase can be shown by the increase in Curie temperature. In addition, the resistance of the τ -phase against decomposition is decreased. After adding proportionately more carbon to balance the Ti addition, the stability of the τ -phase is restored. After hot deformation, the alloy with 0.25 at.% Ti addition and the alloy with 0.26 at.% C + 0.25 at.% Ti both have lower polarisation owing to the decomposition of the τ -phase and to the formation of γ_2 -phase, respectively. The Zr addition leads to the formation of ZrC. This also leads to higher Curie temperature and lower stability of the τ -phase due to the loss of dissolved C in the τ -phase.

The data indicated that the force necessary to die-upset the sample was slightly reduced for the alloys with Ti or Zr addition compared to the ternary alloy. This effect is likely to be due to the lower fraction of interstitial C dissolved in the τ -phase or to the presence of the equilibrium phases, β -Mn or γ_2 -phase. The small reduction in deformation force comes at the severe cost of reducing the magnetic properties due to the increased decomposition of the τ -phase or the formation of other non-ferromagnetic phases. Finally, it is not clear how the friction between the small, mechanically hard TiC/ZrC particles and the extrusion die would affect the lifetime of the die. In summary, the results here do not show a clear benefit of adding either Ti or Zr to MnAl-C alloys to either the magnetic or mechanical properties.

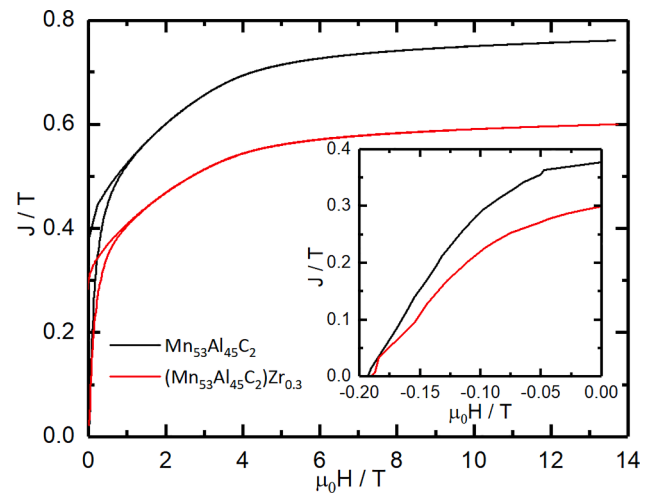


Fig. 9. Hysteresis loops of hot-deformed $\text{Mn}_{53}\text{Al}_{45}\text{C}_2$ and $(\text{Mn}_{53}\text{Al}_{45}\text{C}_2)\text{Zr}_{0.3}$ at 700 °C after 10 min holding by 75 % height reduction at 0.001 s⁻¹ deformation rate and the inset showing the magnified image of the second quadrant.

CRediT authorship contribution statement

Le Feng: Methodology, Investigation, Formal analysis, Writing – original draft, Writing - review & editing. **Kornelius Nielsch:** Writing - review & editing, Supervision. **Thomas George Woodcock:** Conceptualization, Investigation, Formal analysis, Visualization, Writing – original draft, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability.

All data needed to evaluate the conclusions in the paper are present in the paper and/or the [Supplementary Materials](#). Additional data related to this paper may be requested from the authors.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.rinp.2021.104756>.

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