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Phase transformations in Mn–Al permanent magnet alloys

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Phase transformation studies have been made of the Mn–Al alloys with compositions near the equiatomic range with or without small amounts of carbon, copper and nickel, using differential thermal analysis, X-ray diffraction and optical and electron microscopy. The high temperature hexagonal ε phase obtained by quenching, transforms to the ferromagnetic τ phase between 500 and 550° C and on further heating transforms back to the hexagonal phase between 750 and 950° C. Also, on controlled cooling of the ε phase from about 900° C, the ferromagnetic τ phase is formed between 800 and 670° C. TEM studies have shown the presence of the B19 ordered phase, ferromagnetic τ phase and Mn_5Al_8 precipitates even in quenched alloys.

1. Introduction

There has been considerable interest during the last few years in the study of manganese–aluminium alloys mainly because of the fact that these alloys exhibit permanent magnet properties and unlike Alnicos, do not contain strategic materials such as nickel and cobalt.

Mn–Al alloys near the equiatomic range, form a metastable ferromagnetic τ phase (fct) [1]. This phase can be obtained from a high-temperature disordered hexagonal ε phase by controlled cooling or by quenching and annealing at temperature between 400 and 700° C. However, due to the brittleness and instability of the τ phase, permanent magnets could not be developed for quite some time. The addition of a small amount of carbon has been shown [2–4] to improve the stability of the τ phase and to reduce the brittleness of the alloy considerably.

The development of useful permanent magnets from a Mn–Al system requires a clear understanding of the phase changes that take place. Techniques such as X-ray diffraction, optical and electron microscopy and dilatometry have been employed for the study of phase transformations for some alloy compositions [5–8]. However, a simple technique such as differential thermal analysis (DTA) seems to have not been employed for the transformation studies. Alloys containing small amounts of carbon, nickel and copper, etc. have been found to have beneficial effects as regards workability of the alloys. Hence studies of their transformation behaviour are important for selection of proper temperatures for heat treatment prior to and during working. In the present work, phase transformation studies have been made on MnAl, Mn–Al–C, Mn–Al–C–Ni and Mn–Al–C–Cu alloys employing DTA and XRD techniques and also optical and electron microscopy. The results of these studies are presented in this paper.

2. Experimental procedure

Requisite amounts of electrolytic manganese and aluminium with or without small additions of carbon, copper, nickel were melted in a high frequency induction furnace and cast into cylindrical billets using cast iron–sand moulds. The ingots were homogenized at 1000° C for 2 to 3 h. The compositions of the alloys are shown in Table I. Small pieces cut out from the homogenized ingots were solution treated at 1000° C for 1 h and quenched in water. The quenched samples were used for DTA analyses. DTA/DDTA curves were obtained for all the samples with a Netzch thermal analyser using Al_2O_3 as the reference material. The heating and cooling rates were kept at $10° min^{-1}$. DTA plots were also obtained on a few samples maintaining a heating–cooling rate of $5° min^{-1}$.

X-ray diffraction patterns were taken on samples quenched from 1000° C, quenched and tempered at 550 to 600° C for 20 to 30 min and on samples heated to and also cooled from ~ 900° C to different temperatures (corresponding to peaks observed in the DTA curves) at the rate of $10° min^{-1}$ using a Siemens X-ray diffractometer (Model D-500) using chromium target and vanadium filter.

Microstructural studies of the heat-treated samples were made from (i) optical microscopy (using 10% H_2SO_4 as the etchant) and (ii) transmission electron microscopy (TEM). Thin foils for TEM were obtained by "electrolytic blanking" followed by electrolytic thinning and polishing with double-jet

TABLE I Composition of the alloys (in wt %)

Alloy	Mn	Al	C	Cu	Ni	Ti
1	70.6	29.4	–	–	–	–
2	69.8	29.5	0.7	–	–	–
3	69.1	29.3	0.5	–	–	0.2
4	70.2	27.4	0.6	0.9	–	0.8

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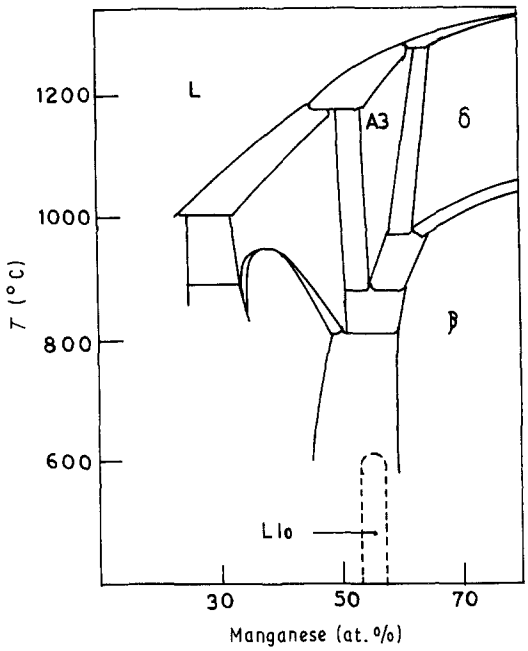

Figure 1 Phase diagram of Mn–Al alloy.

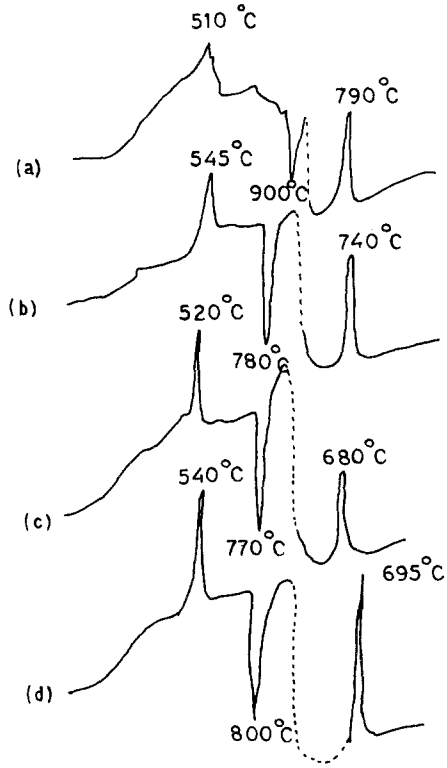

Figure 2 DTA curves of (a) Mn–Al, (b) Mn–Al–C, (c) Mn–Al–C–Ni and (d) Mn–Al–C–Cu alloys.

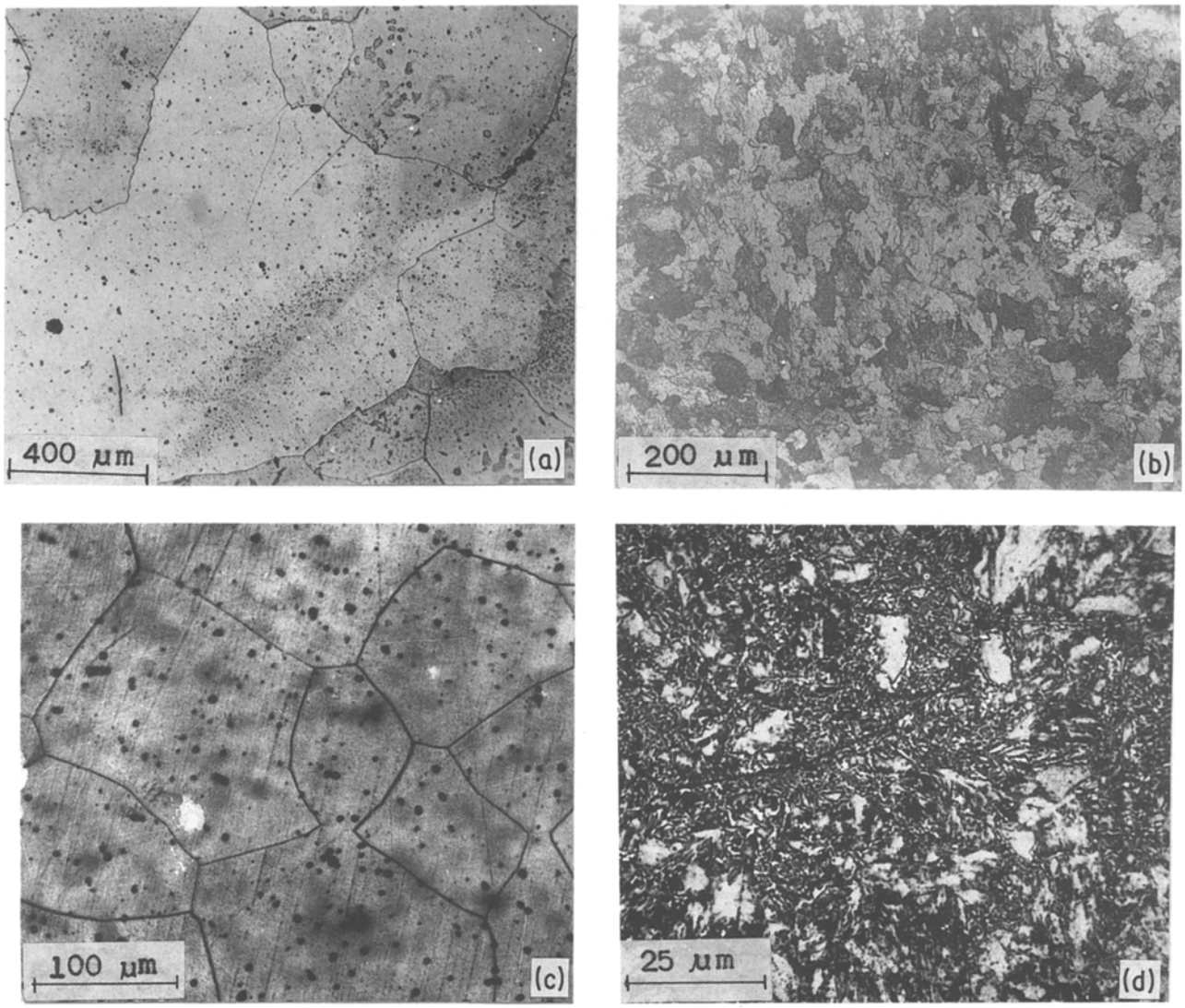

Figure 3 Microstructures of Mn–Al (a, b) and Mn–Al–C alloys (c, d). (a) Oil quenched from 1000° C , (b) oil quenched from 1000° C and tempered at 600° C for 30 min, (c) oil quenched from 1000° C, (d) oil quenched from 1000° C and tempered at 600° C for 20 min.

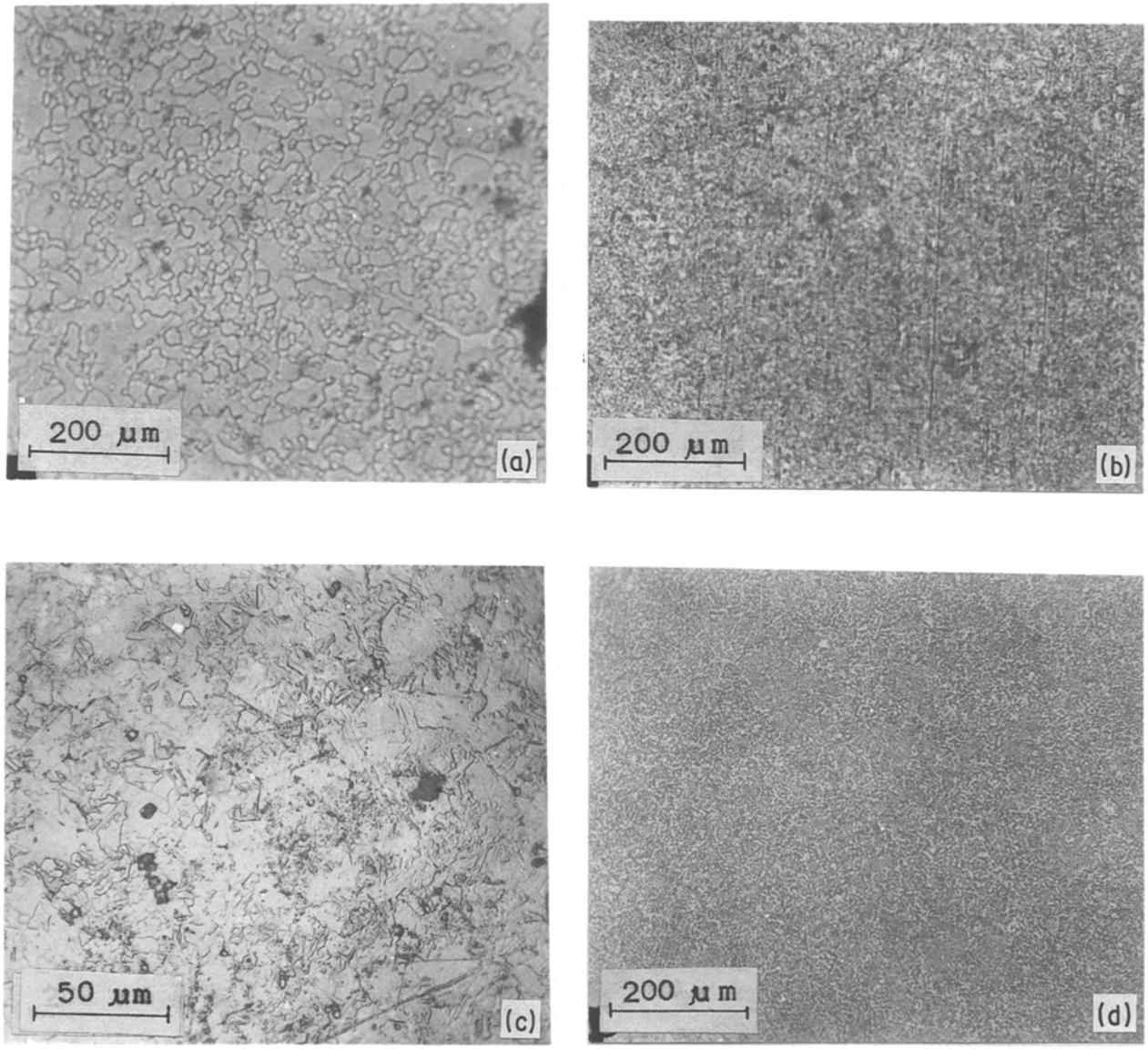

Figure 4 Microstructures of Mn–Al–C–Ni (a, b) and Mn–Al–C–Cu alloys (c, d). (a) Oil quenched from 1000° C, (b) oil quenched for 1000° C and tempered at 600° C for 20 min, (c) oil quenched from 1000° C, (d) oil quenched and tempered at 600° C for 20 min.

Struers Tenupol-2 using 10% perchloric acid in methanol as the electrolyte.

3. Results and discussions

3.1. Phase transformations during heating of the quenched alloys

The phase diagram for the binary Mn–Al system is shown in Fig. 1. It has been shown by optical microscopy and XRD that the Mn–Al alloys quenched from above 900° C contain single phase ε. On heating, the ε phase undergoes several phase transformations. The DTA curves of the various alloys (quenched) are shown in Figs 2a to d. The exothermic and endothermic peaks observed in the DTA curves have been analysed from XRD studies of samples similarly heated or cooled as in DTA. The first major exothermic peak observed in the temperature region 500 to 550° C has been found to be due to the transformation of the ε phase (h c p) to the ferromagnetic τ phase (fct). The endothermic peaks observed in the temperature range 750 to 900° C have been found, from XRD, to be due to the transformation of the τ phase back to the ε phase. The smaller humps observed in some of the alloys before the first major exothermic peak appeared to be attributable to ordering of the ε phase (A3-type) to the B19 type structure. The complete transformation of ε phase may be shown as [2, 7]

$$\underset{\text{A3}}{\varepsilon} \xrightarrow{\text{Ordering}} \underset{\text{B19}}{\varepsilon'} \xrightarrow[\text{Shear}]{\text{martensitic}} \tau \rightarrow \varepsilon$$

Heating

Two minor peaks (one exo- and one endo-) observed for the binary Mn–Al alloy between 700 to 850° C are probably due to the formation of MnAl(r) and β-Mn phases. A marked shift in the base line in DTA curve has been seen for all the alloys. This has been attributed to the large specific heat differences of the test and reference materials, since by taking tempered Mn–Al alloy as the reference material, there was hardly any shift in the base line.

3.2. Phase transformations during cooling

The ferromagnetic τ- phase in this system can also be obtained by cooling the alloy at a controlled rate ($\sim 10°\,\text{min}^{-1}$) from the high temperature single phase

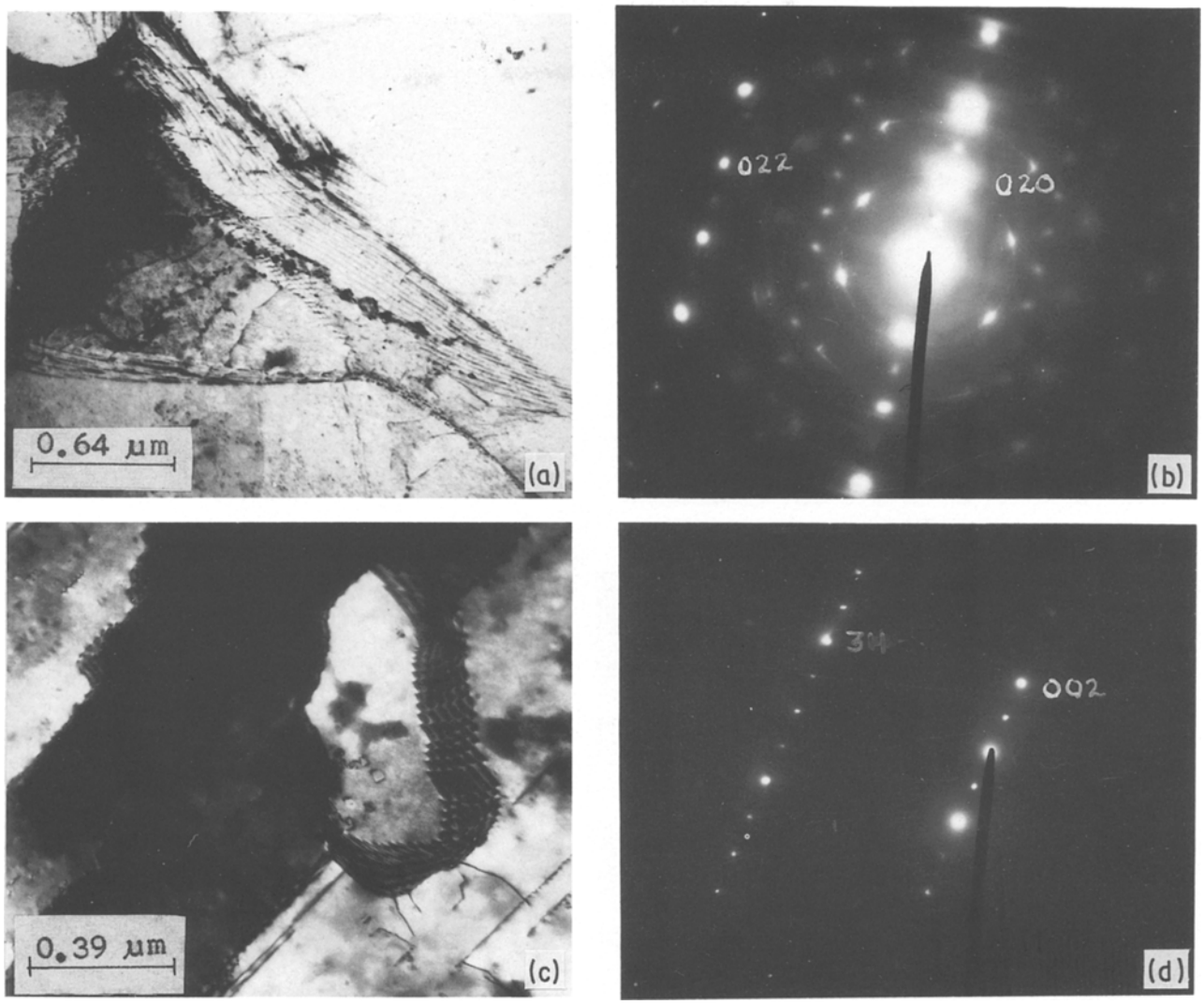

Figure 5 TEM micrographs and diffraction patterns of Mn–Al–C alloys. (a) Oil quenched from 1000° C, dislocation substructure of semicoherent boundary. Precipitate at boundary. (b) diffraction pattern from (a) superlattice reflections from three orientation variants. (c) oil quenched from 1000° C dislocation network at the semicoherent grain boundary. (d) diffraction pattern of ppt in (c) identified to be that of ε phase.

(ε) region. The transformation sequence is given as [11]

$$\underset{(hcp)}{\varepsilon} \xrightarrow{\text{Shear}} \underset{(fcc)}{\text{Intermediate phase}} \xrightarrow{\text{Ordering}} \underset{(fct)}{\tau}$$

Cooling from 1000° C.

In the DTA curves, it can be seen that strong exothermic peaks appear in the temperature range 680 to 800° C. From XRD studies, these peaks have been found to be due to the transformation of the ε phase to the τ phase.

3.3. Phase analyses from XRD, optical and Electron microscopy

3.3.1. X-ray diffraction studies

The phase analyses of the samples after different heat treatments have been made from XRD. The alloys quenched (oil) from above 1000° C have a single phase, that of (MnAl, hexagonal). The quenched alloys after tempering at 500 to 700° C, have been found to have mostly the τ phase (fct). The alloys quenched from 1000° C to below 600° C and then tempered at 500 to 600° C for about 30 min have also shown lines corresponding mostly to that of the τ phase.

3.3.2. Optical microscopy

The microstructures of the binary Mn–Al and ternary Mn–Al–C alloys are given in Fig. 3. Mn–Al alloys oil quenched from 1000° C show large grains of the ε phase, whereas Mn–Al–C alloys show much smaller grains of ε phase on quenching, indicating that the carbon refines the grains. On tempering at 600° C, ε phase undergoes transformation to form fine precipitates of the ferromagnetic τ phase (Fig. 3d). The microstructures of Mn–Al–C alloys containing 1 to 2% Ni/Cu and a small amount of titanium as grain refiner, are given in Fig. 4. The alloys quenched from 1000° C have been found to have fine grained structure of the ε phase, which on tempering at 600° C have shown precipitation of very fine τ phase.

3.3.3. Transmission electron microscopy (TEM)

From X-ray analyses, the oil quenched specimens were found to be hexagonal A3 phase. The TEM studies show, however, regions of ordered B19 phase also. In the diffraction pattern, (Fig. 5b) the weaker spots correspond to the superlattice reflections from three orientation variants. The ring pattern is found to

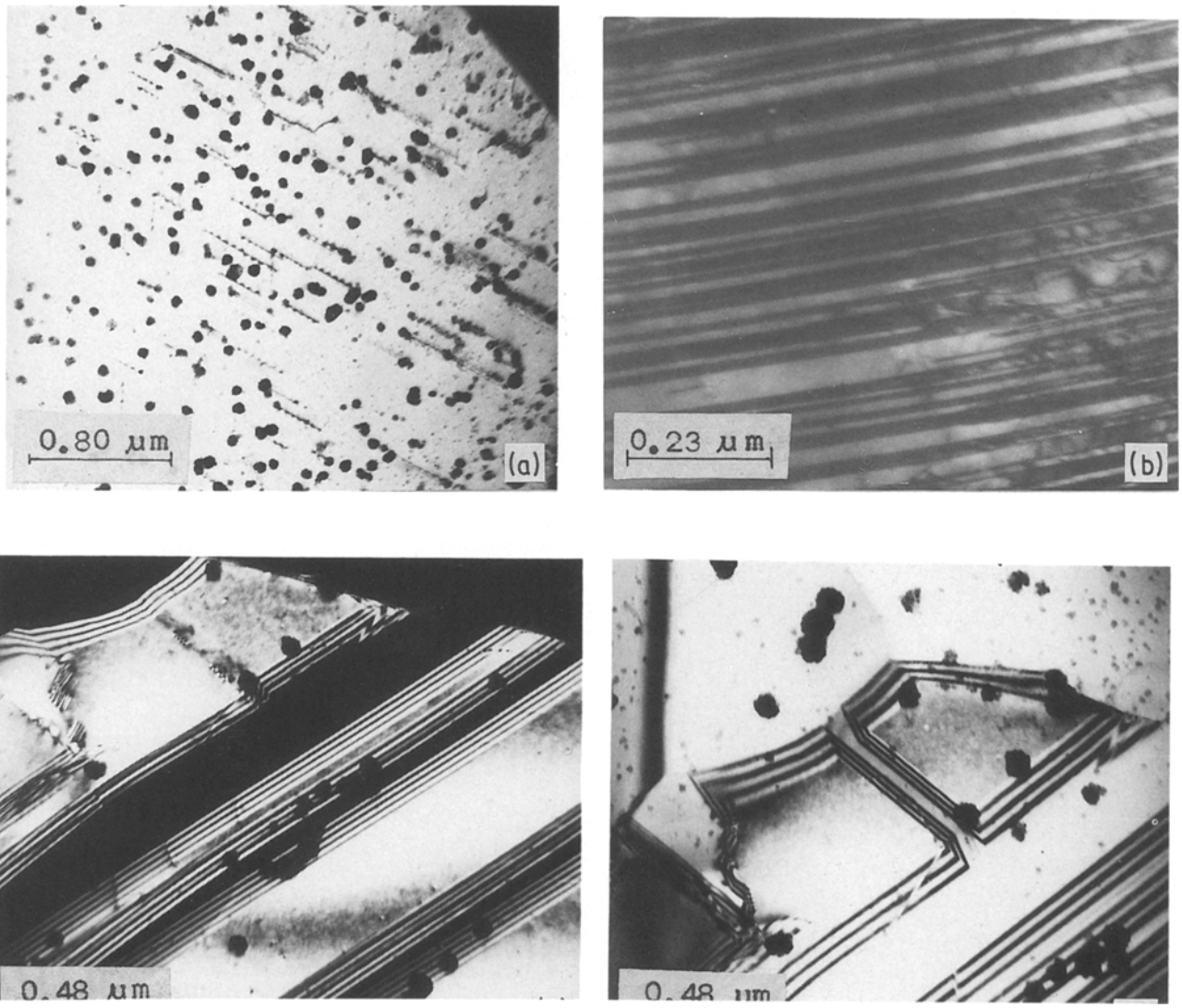

Figure 6 TEM micrographs of Mn–Al–C alloys. (a) Oil quenched and tempered at 600° C for 10 min. Dislocation and ppt in matrix, (b) oil quenched and tempered at 600° C for 10 min, showing twins, (c) dark field image of alloy OQ and tempered at 600° C for 10 min. Showing antiphase boundaries (APBS) and precipitates, (d) bright field image of alloy OQ and tempered at 600° C for 10 min APBs and precipitates.

be due to the Mn_5Al_8 precipitates. Dislocations and stacking faults were also observed in quenched alloys. The oil quenched alloys also contain the ferromagnetic τ phase, as found from the diffraction pattern (Fig. 5d).

The TEM micrographs of MnAlC alloys, quenched + tempered, are shown in Fig. 6. During the ordering and the Martensitic shear to form the ferromagnetic τ phase, from the ε phase twinning takes place in order to accommodate the localized stress arising from the shape and volume changes. In fact, in the case of tempered alloys, ordered twins have been observed (Fig. 6b). Both stacking faults and antiphase boundaries (conservative APBs) have been observed in the τ phase (Figs 6c and d). The APBs have a displacement vector $\boldsymbol{R} = \frac{1}{2}\alpha\,[0\,\bar{1}\,\bar{1}]$ or $\frac{1}{2}\,[101]$, $\bar{n}$ along [100].

4. Conclusions

The conclusions are as follows.

(i) Several phase transformations occur when quenched MnAl–C, Cu, Ni alloys are heated to or cooled from 900 to 1000° C. The ferromagnetic τ phase is formed between 400 and 550° C on heating (ε phase) and between 800 and 700° C during cooling.

(ii) The addition of small amounts of carbon, copper and nickel improves the stability of the τ phase and affects the phase transformation temperatures markedly.

(iii) Though X-ray diffraction studies could not reveal the ordering of the A3 → B19 phase, DTA has shown two minor peaks in two of the four alloys studied, indicating probably the ordering process.

(iv) TEM studies indicate dislocations and stacking faults in quenched alloys. Also found in quenched alloys are the B19 ordered phase, ferromagnetic τ phase and Mn_5Al_8 precipitates.

(v) Both stacking faults and antiphase boundaries have been observed in alloys tempered at 600° C.

(vi) DTA studies on the phase transformation are simple and ideally suited to establish the temperatures of heat treatment prior to and during hot extrusion of the alloys for developing anisotropic permanent magnets.

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