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PHASE TRANSFORMATION STUDIES ON Mn–Al–C ALLOY, BY DSC AND ELECTRICAL RESISTIVITY MEASUREMENTS

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Abstract

Phase transformation studies carried out on Mn–Al–C permanent magnet alloy employing DSC and electrical resistivity measurements, are reported and discussed. The transformation of the hexagonal Mn–Al phase (disordered and non-magnetic) to the ferromagnetic fct phase proceeds via the formation, in at least two stages, of the ordered orthorhombic phase. The activation energy for the formation of the fct phase is ≈ 34.65 kcal/mol. Microstructural changes occurring at various stages of the transformation are also studied.

Keywords: Mn–Al–C alloy, permanent magnet, phase transformation

Introduction

Manganese–aluminium alloys near the equiatomic range are known to exhibit permanent characteristics [1–4]. The high temperature (>900°C) phase (ε-phase) is disordered and has a hexagonal structure and is non-magnetic. ε-phase, on tempering around 500–600°C or on controlled cooling from above 900°C, transforms to a ferromagnetic τ-phase having fct structure. This phase exhibits a high coercive force and a high remanence and therefore, this alloy is useful for permanent magnet applications. Mn–Al alloys are, however, very brittle and also the preparation of the metastable ferromagnetic phase is rather difficult. The addition of a small amount of carbon (below 1 wt%) to a Mn–Al alloy has been found not only to reduce the brittleness of the alloy but also to improve the stability of the ferromagnetic phase [5–7].

The development of high energy product permanent magnets requires a knowledge of the phase transformations occurring in this alloy system. Earlier studies [4, 7–12] on Mn–Al alloys with or without minor alloying elements, employing X-ray diffraction (XRD), dilatometry, optical and electron microscopy, have provided considerable insight into the phase transformations as well

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as the mechanism of the transformations. Phase transformation studies by differential scanning calorimetry (DSC) and electrical resistivity measurements, however, have not been reported so far. Moreover, microstructural changes taking place in this alloy system during the various stages of the transformation are very interesting and a clear picture of these microstructural changes is lacking.

The present work thus aimed at looking at the transformation behaviour of the alloy using simple techniques such as DSC and electrical resistivity and also their corresponding microstructures.

Experimental

An alloy with a nominal composition of Mn 72, Al 27 and C 1 (all in wt%), was made by melting electrolytic manganese, commercial grade aluminium and graphite in a high frequency induction furnace and casting in cast iron/graphite moulds. The cast alloy was homogenized at 1000°C for 3 h. Samples in the form of 3 mm diameter rods of ~50 mm length were solutioned at 1000°C for 1 h and then quenched in oil. The quenched alloy was used for DSC and electrical resistivity studies. DSC runs were made from room temperature to 710°C (with 10–15 mg of the sample) on a Perkin-Elmer DSC-instrument, at heating rates of 3, 5, 10, 20, 30 and 40 deg·min^{-1}. Electrical resistivity measurements were made using a TER-2000 instrument (of Sinko Riku, Japan) from room temperature to 1000°C at a heating rate of 5 deg·min^{-1}. Measurements were also made during the cooling cycle with a cooling rate of 5 deg·min^{-1}.

XRD studies of the quenched, quenched+tempered (600°C/20 min) alloys were carried out by a Siemens X-ray diffractometer (model D-500) with CrK_α radiation. Microstructural studies of the quenched, quenched+tempered and also control-cooled (from ~1000°C) alloys were made using optical microscopy.

Results

The DSC curves of the quenched alloy at different heating rates are shown in Fig. 1. At low heating rates (5 deg·min^{-1}), two exothermic humps around 280 and 380°C and a strong exothermic peak at about 565°C have been observed. At higher heating rates (10, 20 and 30 deg·min^{-1}), a single broad exothermic hump and a strong exothermic peak in the temperature range 120–425°C and 525–700°C, respectively, have been obtained. It may also be noticed that at higher heating rates (Fig. 1c and 1d), the major exothermic peak is preceded by a shoulder (step).

The activation energy (E_a) for the τ-phase formation has been determined by Kissinger's peak shift method (Fig. 2). An activation energy of 34.65 kcal/mol has been obtained.

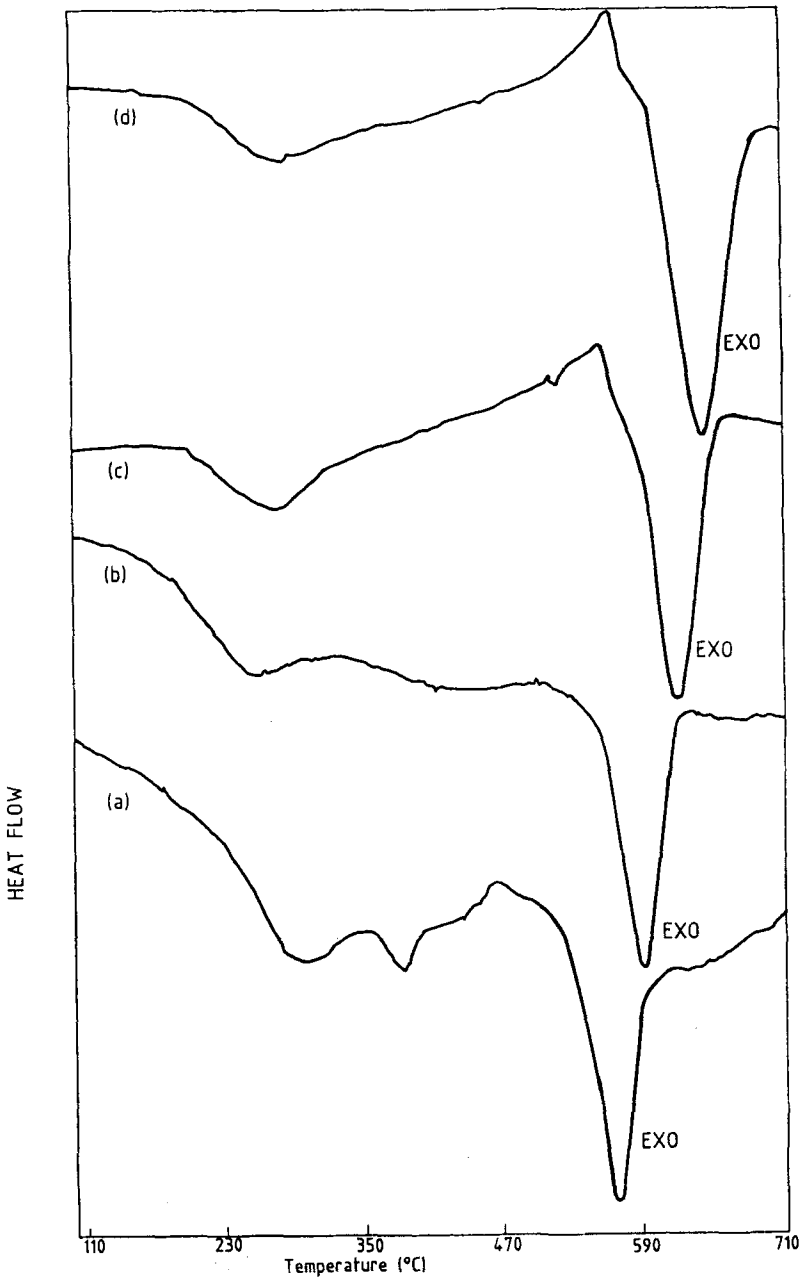

Fig. 1 DSC curves of Mn–Al–C alloy at different heating rates; a – 5 deg·min^{-1}; b – 10 deg·min^{-1}; c – 20 deg·min^{-1}; d – 30 deg·min^{-1}

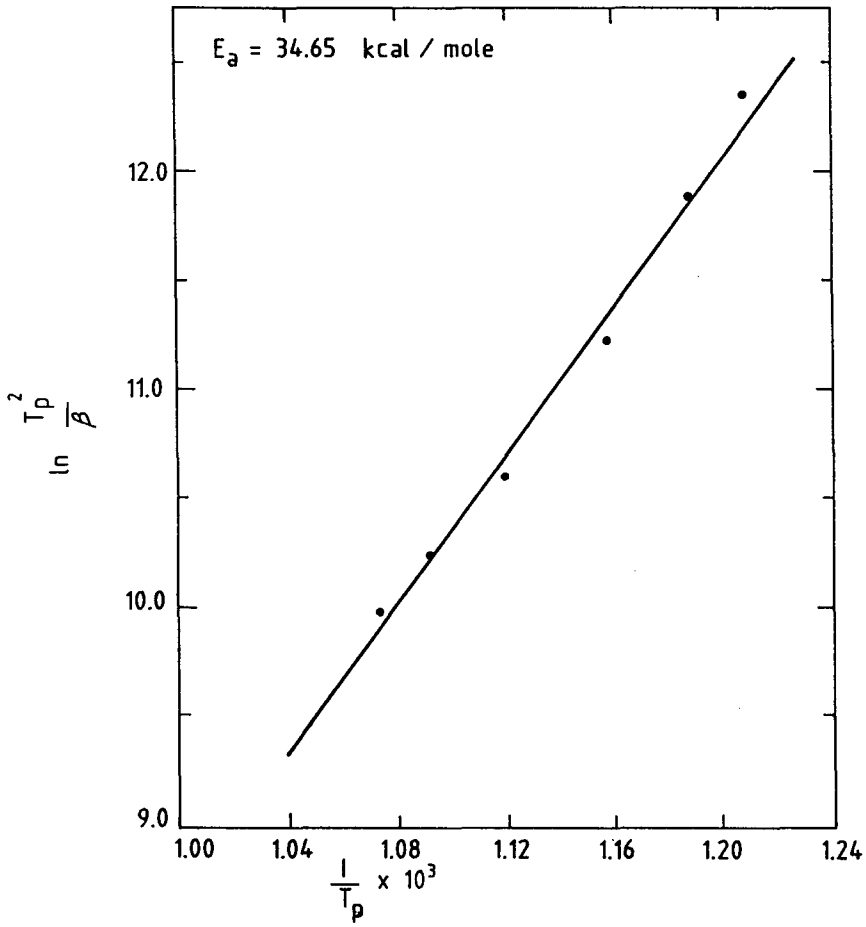

Fig. 2 Kissinger plot for the determination of activation energy (E_a) for τ-phase formation

The DSC curve of the quenched+tempered (at 600°C for 20 min) alloy is shown in Fig. 3. A small endothermic hump at about 307°C has been observed.

The variation of the electrical resistivity of the quenched alloy at a heating rate of 5 deg·min^{-1} is given in Fig. 4. During the heating cycle, a small change in the resistivity at about 215°C and sharp changes at 565 and 830°C, have been observed. On cooling from 1000°C at a rate of 5 deg·min^{-1}, electrical resistivity measurements have shown sharp changes at about 685 and 310°C.

The X-ray diffraction data as obtained from the diffractograms of the alloy a) oil quenched from 1000°C b) oil quenched+tempered at 600°C for 20 minutes and c) cooled from 1000 to 500°C at a rate of 4 deg·min^{-1} are given in Tables 1–3, and the corresponding microstructures are shown in Fig. 5. Whereas the quenched alloy shows large grains of the hcp phase (as identified by XRD),

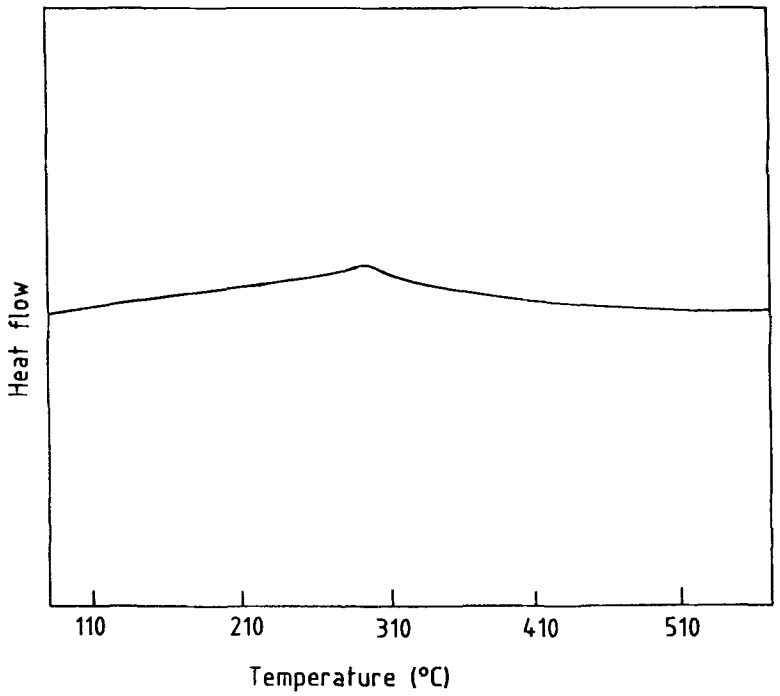

Fig. 3 DSC curve of quenched+tempered Mn–Al–C alloy; heating rate 20 deg·min^{-1}

the tempered alloy exhibits a martensitic structure (Fig. 5b) and this phase has been identified by XRD as the ferromagnetic fct phase. The control cooled alloy shows some peculiarities – a lamellar structure and a martensitic structure (Fig. 5c).

Discussion

The transformation of the high temperature ε-phase (hcp, disordered) to the ferromagnetic τ-phase (fct, ordered) has been reported to take place via the formation of an intermediate ordered phase (ε′) which is orthorhombic [4, 7, 11, 12]. The orientation relationships between the structures are [4, 7, 12]:

$$(0001)_\varepsilon \;||\; (100)_{\varepsilon'} \;||\; (111)_\tau$$

$$(\bar{1}100)_\varepsilon \;||\; (001)_{\varepsilon'} \;||\; (11\bar{2})_\tau$$

$$(11\bar{2}0)_\varepsilon \;||\; (010)_{\varepsilon'} \;||\; (\bar{1}10)_\tau$$

Table 1 XRD data of Mn–Al–C alloy, oil quenched from 1000°C

d / Å	I/I_1	Phase identified
2.34	20	ε (hcp)
2.19	30	ε (hcp)
2.07	100	ε (hcp)
1.60	9	ε (hcp)
1.35	7	ε (hcp)
1.24	65	ε (hcp)
1.14	40	ε (hcp)

Table 2 XRD data of Mn–Al–C alloy oil quenched from 1000°C and tempered at 600°C for 20 min

d / Å	I/I_1	Phase identified
3.59	10	τ (fct)
2.76	30	τ (fct)
2.19	100	τ (fct)
2.14	10	?
1.95	80	τ (fct)
1.80	30	τ (fct)
1.72	20	τ (fct)

Table 3 XRD data of Mn–Al–C alloy cooled from 1000 to 500°C at the rate of 4 deg·min^{-1}

d / Å	I/I_1	Phase identified
2.77	6	τ (fct)
2.20	100	τ (fct)
2.10	6	?
1.96	60	τ (fct)
1.81	3	τ (fct)
1.72	3	τ (fct)
1.33	11	τ (fct)
1.17	45	τ (fct)

Besides this, two other equivalent orthorhombic structures can be derived from a given hexagonal structure [12]:

$$(0\bar{1}10)_{\varepsilon} \;||\; (020)_{\varepsilon'} \text{ or } (\bar{1}10)_{\varepsilon'} \text{ or } (\bar{1}\bar{1}0)_{\varepsilon'}$$

$$(\bar{1}012)_{\varepsilon} \;||\; (112)_{\varepsilon'} \text{ or } (022)_{\varepsilon'} \text{ or } (\bar{1}12)_{\varepsilon'}$$

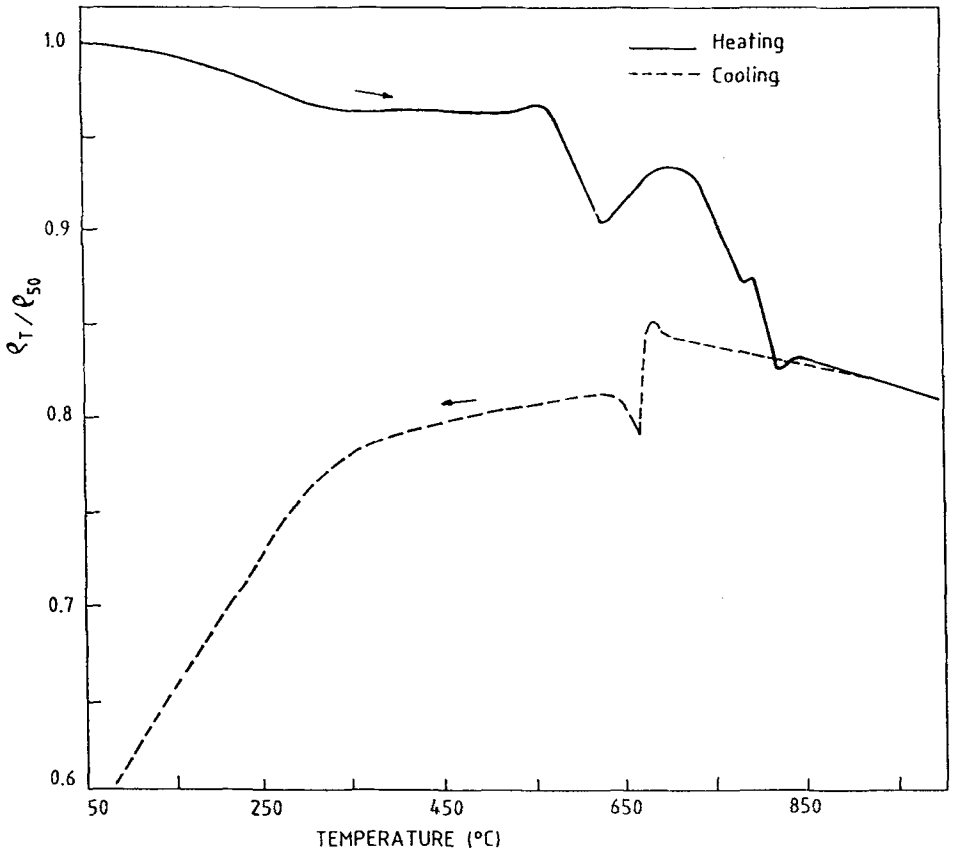

Fig. 4 Electrical resistivity of Mn–Al–C alloy

The exothermic humps observed below 450°C are attributed to the ordering process from the A3 (hcp) to the B19 (orthorhombic) phase. At low heating rates, particularly at 5 deg·min^{-1} or below, the two exothermic humps observed indicate the ordering process to take place at least in two stages, corresponding probably to the two different orthorhombic structures. It is, however, difficult to say whether or not during the ordering process, the third possible orientation results. From the XRD and microstructural studies, the strong exothermic peak observed in the temperature range 500–700°C, has been attributed to the formation of the ferromagnetic τ-phase (L1o). The shoulder (step) observed on the exothermic peak at heating rates of 20 deg·min^{-1} or more, appears to be due to the onset of the τ-phase formation before the completion of the ordering process.

When a DSC run is made on quenched+tempered Mn–Al–C alloy (ferromagnetic τ-phase), no phase transformation is expected up to at least 700°C.

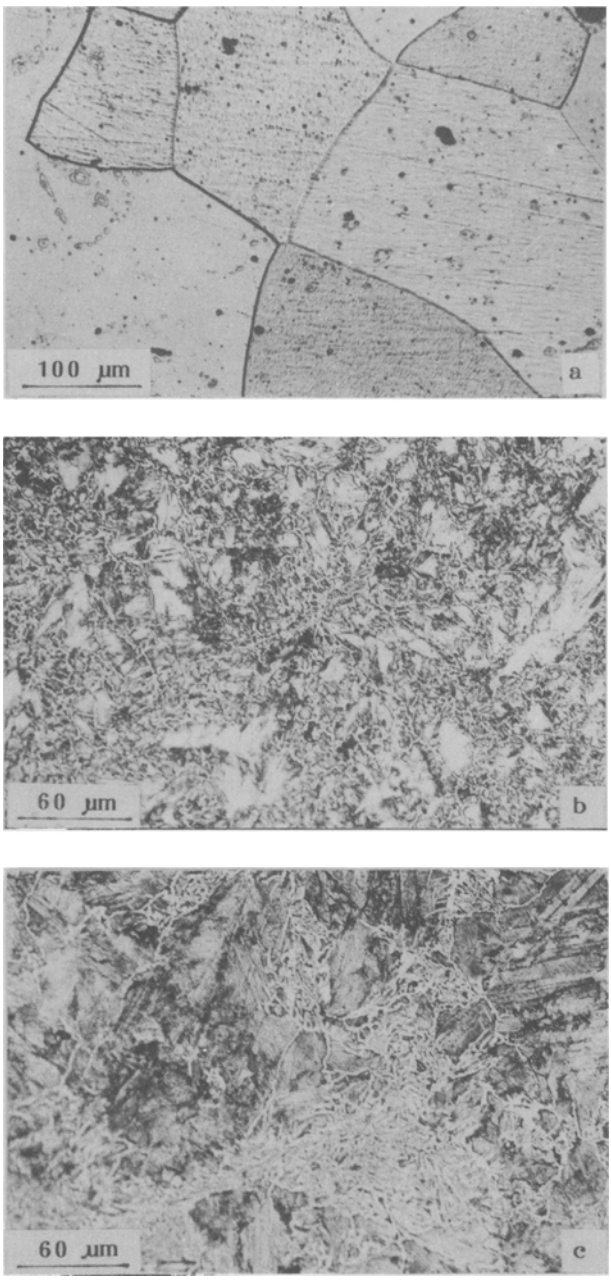

Fig. 5 Microstructures of Mn–Al–C alloy. a) oil quenched from 1000°C; b) oil quenched + tempered at 600°C for 20 min; c) cooled from 1000 to 600°C at the rate of 4 deg·min^{-1}

However, a small endothermic hump has been observed at ~307°C. This is indicative of the ferromagnetic to paramagnetic transition (Curie temperature) of the τ-phase, since it is known that a λ-type anomaly exists near the Curie temperature in the specific heat *vs.* temperature curves.

Electrical resistivity (ρ) measurements have shown a similar transformation behaviour as observed in DSC. Sharp changes in ρ at ~685 and 310°C are attributable to the τ-phase formation and the magnetic disorder-order (para- to ferro-) transformation, respectively.

Conclusions

* The formation of the ferromagnetic τ-phase (L1o) from the disordered hexagonal (A3) phase takes place via an intermediate ordered phase (B19).

* The B19 ordering of the A3 (disordered hcp) phase during tempering, takes place at least in two stages corresponding to different orthorhombic orientations.

* The activation energy for the formation of the ferromagnetic τ-phase is ~34.65 kcal/mol.

* The ferromagnetic τ-phase (L1o) is also obtained during controlled cooling of the hcp phase, from about 1000°C.

* The mechanism of the formation of the L1o phase during controlled cooling appears to be different from that during tempering (annealing) of the hcp phase at 500–650°C.

* The microstructures of the alloy control cooled from 1000°C exhibits a lamellar structure prior to the formation of the ferromagnetic phase (martensitic structure).

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Zusammenfassung — Beschrieben und diskutiert werden vorliegend die Phasenumwandlungsuntersuchungen an der permanentmagnetischen Legierung Mn–Al–C unter Anwendung von DSC- und elektrischen Widerstandsmessungen. Die Umwandlung der hexagonalen Mn–Al–Phase (ungeordnet und nicht magnetisch) in die ferromagnetische fct-Phase erfolgt – in mindestens zwei Schritten – über die Bildung einer geordneten orthorhombischen Phase. Die Aktivierungsenergie der fct-Phase beträgt ca 34.65 kcal/mol. Veränderungen der Mikrostruktur, die in verschiedenen Schritten der Umwandlung erfolgen, wurden ebenfalls untersucht.