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Some structural and magnetic properties of Fe–Al–C and Fe–Mn–Al–C alloys

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The remanence and coercivity of Fe–Al–C and Fe–Mn–Al–C alloys have been measured and studied as a function of ageing at 623 K. The resulting formation and growth of carbide precipitates of Fe_3AlC and Mn_3AlC in the same samples have been investigated by transmission and scanning electron micoscope techniques. The addition of Manganese to the Fe–Al–C alloy is shown to be severely deleterious to the magnetic properties of the resulting quaternary alloy; however, simultaneously, the electron diffraction and microscopic studies demonstrate that the structural order of the carbide precipitates is considerably improved. It is concluded that this observed decline in the magnetic properties of this alloy system is related to the formation of Mn_3AlC in preference to Fe_3AlC carbide precipitates.

1. Introduction

The permanent ferromagnetic alloy Fe–Al–C was first investigated by Snoek [1]. More detailed studies of the effects of compositional changes and heat treatments on the magnetic properties of this alloy were subsequently carried out at the Permanent Magnet Association, Sheffield [2] and by Mishima [3]. Recently, Briggs and Clegg [4] have reported further improvements in the magnetic properties of this alloy by evaluating the necessary preparational conditions to produce optimum values. Much of the interest in this alloy arises from its relatively low cost of production and its non-strategic constituents which make it an attractive proposition for applications in magnetic systems, particularly those in which long (> a few metres) bars are required.

Previous structural investigations of this material have been largely concerned with the highly tetragonal martensite that can be formed by various treatments of the alloy [5]. This usually requires quenching from temperatures in the region of 1473 to 90 K, the martensitic transformation temperature, M_s, occuring at approximately 190 K. The phase diagram of this system has been determined by Oshima and Wayman [5] who showed that it retained its antiferromagnetic austenitic structure at 1473 K but, due to its high carbon content, a carbide precipitate was formed during quenching by the process:

$$\text{austenite} \rightarrow \text{ferrite} + \text{carbide} \qquad (1)$$

The same effect was recently demonstrated to occur in thin film material by Parker *et al.* [6].

The incorporation of manganese in this alloy to form the quaternary Fe–Mn–Al–C has been investigated by Ham and Cairns [7] in an effort to produce an alternative to stainless steel. The structural properties of a similar alloy, differing only in that it contained an addition of a small quantity of nickel, was investigated in detail by James [8] who followed the ageing sequence involving the precipitation of the carbide $(FeMn)_3AlC$ from the solution treated structure. The latter worker further reported that the cubic lattice parameter of these carbide precipitates had a value which was intermediate between those of the isomorphous carbides Fe_3AlC and Mn_3AlC.

In the present work structural investigations of both Fe–Al–C and Fe–Mn–Al–C have been

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TABLE I

Treatment	Fe–Al–C		Fe–Mn–Al–C	
	B_r (T)	H_{cB} (A m^{-1})	B_r (T)	H_{cB} (A m^{-1})
Oil quenched	0.49	3.2×10^4	0.096	1.84×10^3
3 h aged at 623 K	0.80	1.36×10^4	0.124	1.2×10^3
120 h aged at 623 K	0.80	6.4×10^3	0.055	0.8×10^3

made using transmission and scanning electron microscope techniques in an attempt to relate the structural properties of these alloys to their observed contrasting magnetic behaviour.

2. Experimental details

The alloys used in this work were prepared in a vacuum induction furnace from constituents of 99.9% purity by casting in cylindrical shell moulds having a diameter of 1.25 cm and a length of 15 cm. One of the two alloys produced by this method was Fe–7.7% Al–1.77%C and the other differed mainly in that half of the iron atoms were replaced by manganese ones to yield the quaternary Fe–40% Mn–18% Al–1.77%C (where all percentages are by weight). The increased aluminium content in this alloy was necessary to produce bars of the desired length. All ingots were subsequently solution treated at 1473 K in an argon atmosphere prior to quenching in oil at 293 K. The bars of each alloy were aged at 623 K for periods of 3 and 120 h. For the investigation of their magnetic properties, samples were prepared by cutting cylinders of 5 cm length from the ingots. The end faces of these cylinders were mechanically ground in order to reduce the flux leakage during examination of their magnetic parameters. These measurements were carried out on a hysteresigraph following the specifications of BS 5884.

For structural studies, discs of 0.5 cm thickness were cut from the ingots and were then mechanically polished with diamond paste down to a particle size of 0.25 μm. To remove the polishing damage and to reveal the carbide precipitates, the Fe–Al–C alloy was etched in a 5% nital solution for about 2 min, while, for the same purpose, the Fe–Mn–Al–C alloy was etched in Tucker's reagent for about 10 sec. In both cases, this etching not only revealed the grain structure of the material, but also preferentially dissolved the matrix thereby leaving the carbide preciptates standing in relief of the surface. This rendered these precipitates ideally suited to study by the reflection high energy electron diffraction (RHEED) technique in a JEM 120 transmission electron microscope operated at 100 kV. Additional structural information was obtained from the same samples using a Cambridge S600 scanning electron microscope. Finally, extraction replicas were obtained (for examination in the transmission electron micoscope) from the Fe–Al–C sample which gave rise to little evidence of micostructure in the RHEED or scanning electron micoscope studies, but which exhibited the best magnetic properties.

3. Results

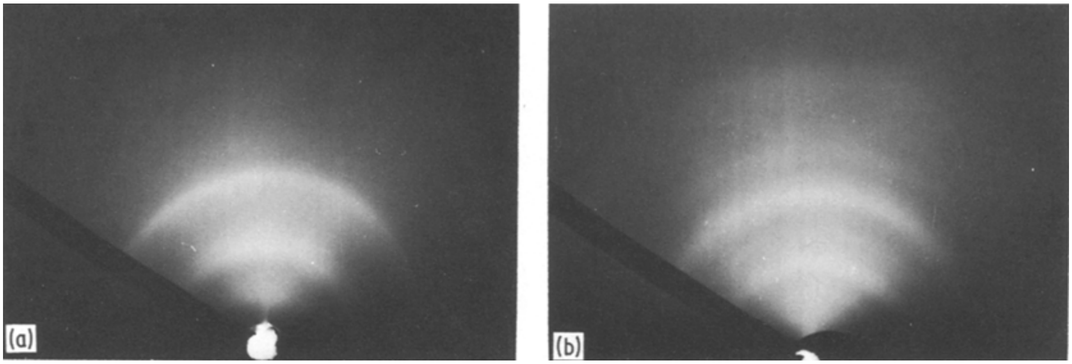
3.1. Magnetic properties

The measured values of the remenance (B_r) and coercivity (H_{cB}) of the ternary alloy Fe–Al–C are compared with those of the quarternary Fe–Mn–Al–C in Table I.

3.2. Structural properties

3.2.1. Fe–Al–C

The RHEED patterns obtained from etched surfaces of Fe–Al–C samples after oil quenching and after ageing at 623 K separately for 3 and 120 h are shown in Fig. 1a, b and c, respectively. The pattern corresponding to the oil quenched ingot (Fig. 1a) contains only two diffraction rings which are very diffuse and which arise from interplanar spacings of about 0.23 and 0.135 nm in a very disordered structure. These same two diffuse rings are also the main feature of the pattern obtained from the surface of the specimen which had been aged for a period of 3 h (see Fig. 1b). However, in this pattern there is some evidence of the formation of additional diffuse diffraction rings, these being associated with interplanar spacings of about 0.18 and 0.11 nm. A much more significant change in the diffraction pattern is produced when the ageing period is extended to 120 h. This is seen to produce a fine grain structure which is revealed by the sharp and continuous diffraction rings seen in Fig. 1c. The values of the interplanar spacings derived from this pattern are



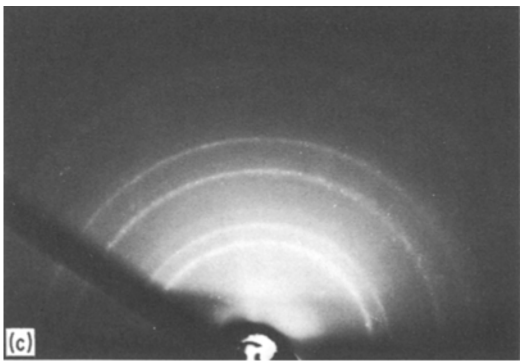


Figure 1 100 kV RHEED patterns from etched surface of Fe–Al–C alloy after (a) oil quenching, (b) ageing at 623 K for 3 h, (c) ageing at 623 K for 120 h.

given in Table II, in which they are compared with ASTM index data for Fe_3AlC.

As the RHEED technique failed to provide any evidence for the presence of a phase or feature that might be responsible for the superior magnetic properties of the sample that had been aged for 3 h, an alternative investigation was undertaken in which extraction replicas were obtained from the etched surface of this particular sample. A transmission electron micrograph taken from such a replica is shown with its corresponding transmission electron diffraction pattern in Figs. 2a and b. The complete indexing of this pattern is also given in Table II.

A typical example of the topography of the etched surfaces of samples of this alloy is shown in Fig. 3, where this particular sample corresponds to that which was aged for 120 h. From this it can be seen that the grain structure is only made evident by the preferential etching at the grain boundaries.

3.2.2. Fe–Mn–Al–C

When an alloy was formed by replacing half of the atoms in the Fe–Al–C system by manganese, RHEED studies showed that even in the oil-quenched condition, the order of the precipitates in the quarternary alloy surpassed that of those in the ternary one after ageing for 120 h. This is demonstrated by the RHEED pattern shown in Fig. 4 in which the diffraction rings are seen to consist of discrete spots of widely differing intensity that suggests a preferred orientation

TABLE II Indexing of the electron diffraction patterns from Fe–Al–C

RHEED of 120 h aged sample (Fig. 1c)	Transmission pattern of 3 h aged sample (Fig. 2)	ASTM Index data for Fe_3AlC	
d-spacing (nm)	*d*-spacing (nm)	*d*-spacing (nm)	Intensity (%)
0.257	0.247	0.268	40
0.219	0.221	0.216	100
0.195	0.1905	0.189	80
0.155	0.171	0.168	40
–	0.150	0.153	20
0.131	0.135	0.133	80
0.125	0.126	0.125	40
	–	0.120	20
	0.115	0.114	80
	0.110	0.109	60
	0.106	0.104	40

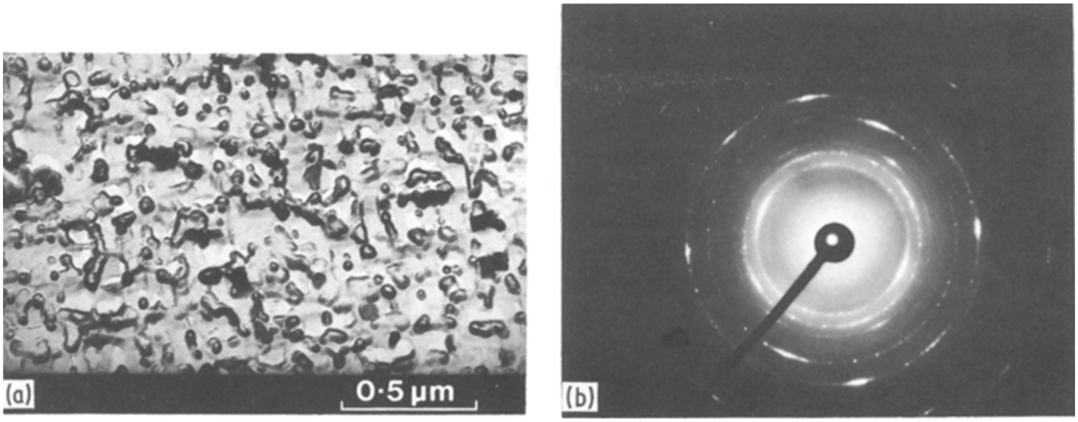


Figure 2 An extraction replica taken from a Fe–Al–C sample: (a) transmission electron micrograph, (b) transmission electron diffraction pattern.

effect rather than a larger grain size for this material. The complete indexing of this pattern is provided in Table III, where, in the absence of ASTM Index data for $(Fe, Mn)_3AlC$, the experimentally measured values are compared with the ASTM Index data for the separate carbides, Fe_3AlC and Mn_3AlC.

The improved crystalline quality of this alloy was demonstrated most convincingly when its etched surfaces were examined in the back-scattered electron emission mode of the scanning electron microscope. In particular, the grains of this structure exhibited strong crystallographic contrast which varied with the orientation of each grain with respect to the direction of the incident beam, as demonstrated by the two back-scattered electron images of the same area taken before and after a 20° tilt and shown in Fig. 5a and b, respectively.

4. Discussion

It is clear from inspection of Table I that the addition of manganese to the Fe–Al–C system is severely deleterious to the magnetic properties of the quarternary alloy formed. In the as-quenched condition, the effect of the addition of manganese is observed to reduce the remanence by a factor of about 5 times and the coercivity by more than 15 times. Ageing for a period of 3 h produces an improvement in the remanence of both alloys. This may be explained by the ageing process providing sufficient energy for the process in Reaction 1 to proceed, thus promoting the growth of the ferrite phase which plays the more dominant role in the ferromagnetic behaviour. Simultaneously, the structrual order of the ferrite phase is expected to improve and this is likely to explain the observed decrease in coercivity. By extending the ageing period to 120 h, the transformation mechanism given by Reaction 1 is carried out to completion for both alloys. While the resulting reduction in the coercivity of each alloy is comparable, the remanence of the quaternary is observed to decrease considerably, as that

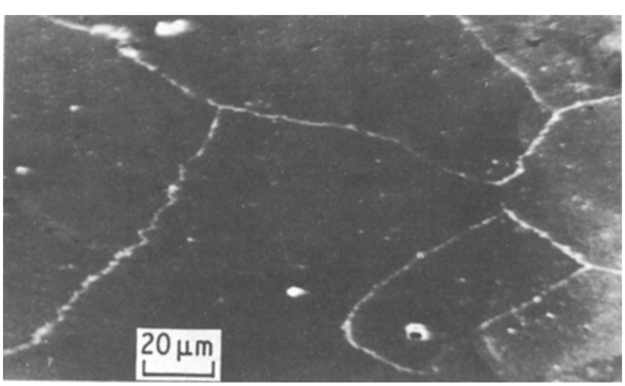


Figure 3 A scanning electron micrograph taken from an etched Fe–Al–C surface.

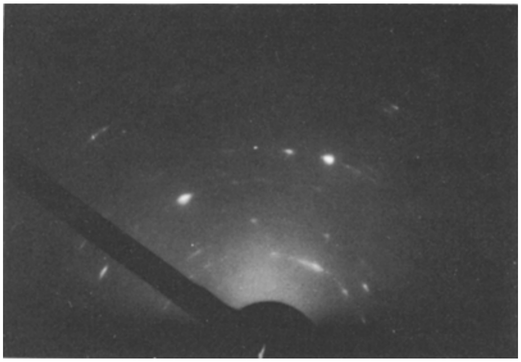


Figure 4 100 kV RHEED pattern from an etched surface of an Fe–Mn–Al–C alloy, as-quenched.

of the ternary remains unchanged. This can be explained by the fact that manganese has a greater affinity for carbon than does iron, with the result that prolonged ageing produces a greater proportion of isotropic Mn_3AlC which is known to have a lower Curie temperature and therefore a lower remanence.

Regarding the structural studies of the Fe–Al–C alloy, the RHEED examinations indicate that the crystalline order of the precipitates at the etched surfaces of the specimens in the as-quenched condition, and after ageing at 623 K for 3 h, was very poor. The RHEED pattern in Fig. 1c shows that by extending the ageing period to 120 h, the crystallinity of the structure at the etched surface of the sample is improved significantly, as is evidenced by the sharp, polycrystalline diffraction rings. These enabled the structure to be identified as that of Fe_3AlC as may be seen in Table II, in which the measured and ASTM Index data are compared. This observation suggests that the transformation process given by Reaction 1 has indeed proceeded to completion, with the carbide precipitates having reached their optimum size. It is to be noted that the diffuse rings seen in the RHEED patterns of Fig. 1a and b also gave rise to interplanar spacings which were consistent with this identification, though much less confidence can be placed on measurements taken from such diffuse patterns. In fact it was because of this last point that the extraction replicas were prepared from the sample which was aged for 3 h and which exhibited the optimum magnetic properties. The appearance of the extracted precipitates in orthogonal rows as seen in Fig. 2a is suggestive of spindal decomposition as is observed in the Alnico alloys [9]. The corresponding transmission electron diffraction patterns, seen in Fig 2b, consolidates the identification of the precipitated phase as Fe_3AlC, as is clear from Table II. The presence of arcs of intensity on specific parts of these diffraction rings may be taken as further evidence of the orientational relationship previously existing between the precipitates and the host grain of austenite. Finally, in discussing the structrual properties of this ternary alloy it was found that scanning electron micoscope studies could only reveal the presence of the grains of austenite by topographical contrast in the secondary emission mode at the preferentially etched grain boundaries (see Fig. 3).

The effect on the structure produced by incorporating manganese in the Fe–Al–C alloy is clearly demonstrated by the RHEED pattern shown in Fig. 4. This shows the improved

TABLE III Indexing of the RHEED pattern from Fe–Mn–Al–C

Measured d-spacing (nm)	ASTM Index Data					
	Fe_3AlC			Mn_3AlC		
	d-spacing (nm)	Intensity (%)	$(h\,k\,l)$	d-spacing (nm)	Intensity (%)	$(h\,k\,l)$
	–	–	–	0.3869	6	(1 0 0)
	0.268	40	(1 1 0)	0.2736	0.5	(1 1 0)
0.228	0.216	100	(1 1 1)	0.2234	44	(1 1 1)
0.193	0.189	80	(2 0 0)	0.1934	21	(2 0 0)
0.171	0.168	40	(2 1 0)	0.1730	2	(2 1 0)
	0.153	20	(2 1 1)	–	–	–
0.137	0.133	80	(2 2 0)	0.1368	27	(2 2 0)
0.128	0.125	40	(3 0 0)	–	–	–
	0.120	20	(3 1 0)	–	–	–
0.115	0.114	80	(3 1 1)	0.1166	100	(3 1 1)
0.110	0.109	60				
0.104	0.104	40				

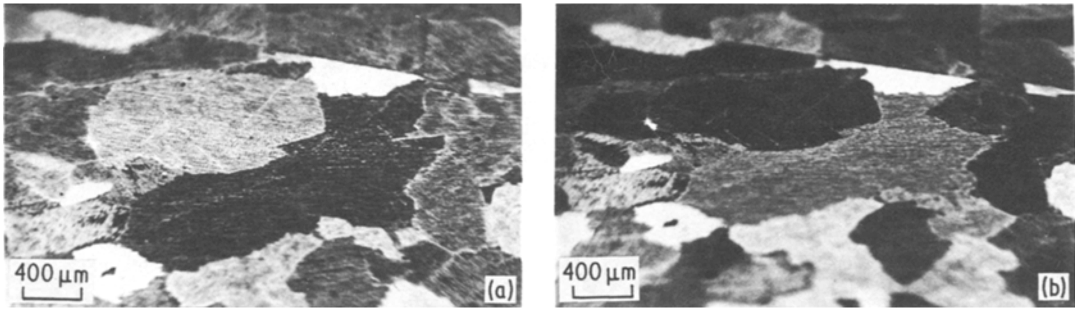


Figure 5 Back-scattered electron images of an etched surface of an Fe–Mn–Al–C alloy taken (a) before and, (b) after a 20° C tilt of the sample.

crystallinity of the carbide precipitates as is evidenced by the discrete spots now forming the diffraction rings. The wide variation in the intensities of different spots lying on these diffraction rings is attributed, not simply to an effect of grain size, but rather to the consequence of a large number of precipitates having the same orientation for a few specific directions of incidence of the electron beam in this alloy. Further, the grains of austenite were of much improved crystalline quality in this alloy, as was demonstrated by the fact that in this quaternary system, they were observed to exhibit strong crystallographic contrast when examined in the back-scattered electron image mode of the scanning electron microscope (see Fig. 5).

Inspection of Table III reveals that the measured interplanar spacings of the precipitated phase, in general, lie closer to those of Mn_3AlC than to those of Fe_3AlC, when comparing them with the ASTM Index data. This supports the earlier suggestion that manganese carbide is expected to be formed preferentially due to its greater affinity for carbon. Unfortunately, the inadequate accuracy of the RHEED technique [10] combined with the close proximity of the lattice parameters of the separate carbides [8], does not permit a definite estimate of the precise composition of these precipitates. However, in conclusion, this work demonstrates the strong structural dependence of the magnetic properties of these particular alloy systems.

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