JOURNAL OF MATERIALS SCIENCE 19 (1983) 1261–1266

Magnetic domain structure of isotropic MnAlC permanent magnet alloys

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Observations of the magnetic domain structure were made on an isotropic MnAlC alloy (of the following composition: 73.0 wt % manganese, 26.4 wt % aluminium and 0.6 wt % carbon) homogenized at 1373 K for 1 h, quenched in water and tempered in the temperature range from 723 to 923 K. Observation of the magnetic domain structure was carried out by the Bitter powder pattern technique. It was found that the magnetic properties of the MnAlC alloy are closely related to the type of magnetic domain structure.

1. Introduction

The magnetic properties of the MnAlC alloy (69.5 to 73.0 wt % manganese, 26.4 to 29.5 wt % aluminium and 0.6 to 2.0 wt % carbon) are associated with the presence of the ferromagnetic phase τ which has an ordered superstructure of a tetragonal face-centered structure of the CuAu ($L1_0$) type [1–5]. That phase is formed during the heat treatment of a nonferromagnetic, high-temperature hexagonal phase ϵ [4, 6–8]. The process of formation of a metastable phase τ has been studied by X-ray structure analysis [4, 5] and neutronography [9] as well as by optical [4] and electron [10–15] microscopy. The present experimental data on the microstructure of the MnAlC alloy provide no comprehensive information concerning the mechanism of the phase formation during the various stages of the $\epsilon \rightarrow \tau$ transformation. The X-ray examinations show [5] that the crystals of the τ phase are not smaller than 5×10^{-7} to 10^{-6} m, and they have antiphase domains varying in thickness from 10^{-8} m at the initial stage of the tempering process to 10^{-7} m after 5 h tempering at 673 K. The study of thin foils of MnAl alloy in an electron transmission microscope by Jakubovics and co-workers [11, 15] has shown that narrow bands of the τ phase are separated by stacking faults having a slip vector $1/6\langle 1\,1\,2\rangle$ in the $\{1\,1\,1\}$ plane and have antiphase boundaries with the $1/2\langle 1\,0\,1\rangle$ slip vector. As a general rule it may be assumed that the τ phase has stacking faults, domain boundaries in ordered spaces. The occurrence of these defects was observed in the course of X-ray and neutronographic examinations [5, 9] and by electron microscopy [10–15].

So far in published works and patents on that subject two aspects of the problem have been examined: (1) the influence of chemical composition and of the final heat treatment on magnetic properties of the MnAlC alloy [6, 7, 16–18]; and (2) the mechanism of formation of the ferromagnetic τ phase in the alloy. Technological parameters of the entire production process, from melting to the final heat treatment, are usually defined by the metallographic structure of the finished product, i.e. grain size, structure homogeneity, diversification of crystallographic orientation of grains, the shape and the size of non-metallic inclusions, secondary phases, defects, etc. However all these factors affect the magnetic properties of the finished product only because of the presence of the domain structure in the alloy. The relation between the magnetic domain structure and metallurgical structure is much more easy to assess quantitatively than the realtion between the magnetic properties of a finished product and the processing conditions and metallurgical structure. Thus the present investigation should be focused on solving two essential problems, i.e. (1) what type of domain structure and what kind of behaviour in an external magnetic field would ensure optimum magnetic properties, and (2) how to induce that domain structure in the course of the MnAlC manufacturing process. The solution of these two basic problems should bring about a further improvement in the magnetic properties of that alloy.

So far, the changes occurring in the macroscopic domain structure during isothermal heat treatment have not been systematically studied [19, 20] and, despite the importance of the problem, only few papers have been published concerning electron microscope studies on the magnetic domain structure and magnetization processes in MnAlC thin films [12, 15]. The scarcity of information on the domain structure was the reason for studying the problem of domain structure during the various stages of heat treatment of the MnAlC magnet.

2. Material and investigation procedure

The MnAlC alloy having a composition (wt%) 73.0 manganese, 26.4 aluminium and 0.6 carbon was induction melted in a Balzers furnace in an atmosphere of argon. Cast bars of the alloy were homogenized at a temperature of 1373 K for 0.5, 1.0 and 2.0 h and quenched in water. The specimens were then tempered at 723, 823 and 923 K for times ranging from 10 min to 20 h and cooled in air. The phase analysis of as-cast heat treated MnAlC alloy specimens was performed with an X-ray DRON-2 diffractometer. The magnetic properties during the various stages of heat treatment of the alloy (H_c, B_r, $(BH)_{max}$) were determined from the demagnetization curves by means of the Permagraph (Magnetik Elektro-Physik, Köln). An experimental confirmation of the domain structure in the alloy was obtained by the powder pattern technique, which revealed on the ferromagnetic τ phase surface the presence of local magnetic fields, generated by domain walls or by open domains, whose magnetization vector was nonparallel to the specimen surface.

3. Experimental results and discussion

The homogenizing conditions, defined in the course of initial trials and also based on the data in [6–8], i.e. homogenizing at 1373 K for 1 h and water quenching, enabled obtainment of a homogeneous ϵ phase. X-ray and microstructure examinations, as well as the fact that a magnetic colloidal suspension of fine Fe_3O_4 particles deposited on the specimens produced no powder patterns proved the nonferromagnetic character of the ϵ phase at room temperature. A subsequent heat treatment, i.e. tempering at 723 K proved ineffective, not even tempering at that temperature for 15 h produced a transformation of the paramagnetic ϵ phase into the ferromagnetic τ phase. The presence of the ϵ phase was confirmed by X-ray examination. Nor did the tempering at 823 K for 10 min lead to the transformation $\epsilon \rightarrow \tau$. The first peaks generated by the τ phase appear on the X-ray diffraction micrographs after 15 min of tempering at that temperature. This was also confirmed by the observation of the magnetic domain structure. A further prolongation of tempering time up to 30 min increased the degree of $\epsilon \rightarrow \tau$ transformation, but the pictures of domain structure still show the presence of the ϵ phase (bright spots not containing colloidal suspension, see Fig. 1a). The pictures of domain structure, as well as X-ray analysis, show the presence of two ϵ and τ phases. In specimens tempered at 823 K for 1 h the optimum magnetic properties were: $H_c = 86.9\,\mathrm{kA\,m^{-1}}$, $B_r = 270\,\mathrm{mT}$ and $(BH)_{max} = 99.4\,\mathrm{kJ\,m^{-3}}$. In that specimen the $\epsilon \rightarrow \tau$ transformation was completed, as is shown by X-ray analysis, observation of the microstructure and especially that of the magnetic domain structure (Fig. 1b). The powder pattern forms a network of small islets (we follow the terminology adopted in [19]) of a size of about 1.5×10^{-6} m. The observation also shows a coagulation of these islets which form short chaotically distributed chains. In that state the specimen is a single-phase material with a fine grained τ phase. The grain size grows with tempering time, and thus the specimens tempered for 1, 2 or 3 h have a similar phase composition and differ only by the size of grains. The specimens tempered for 2 and 3 h have large highly twinned grains. The increase in tempering time causes changes in domain structure too (Fig. 1c). There is a distinct increase in the size and the number of islets forming chains, and the islets which join each other inside the chains form continuous lines of powder suspension. As a result of the process a domain structure develops which is typical for uniaxial ferromagnetic materials, i.e. a labyrinth structure on planes perpendicular to the *c*-axis (Fig. 1d, spot A) and 180° walls on planes parallel to the magnetically easy direction (Fig. 1d, spot B).

In Fig. 2 the microstructure (Fig. 2a) is compared with the domain structure (Fig. 2b). The specimen was tempered for 30 min, and therefore,

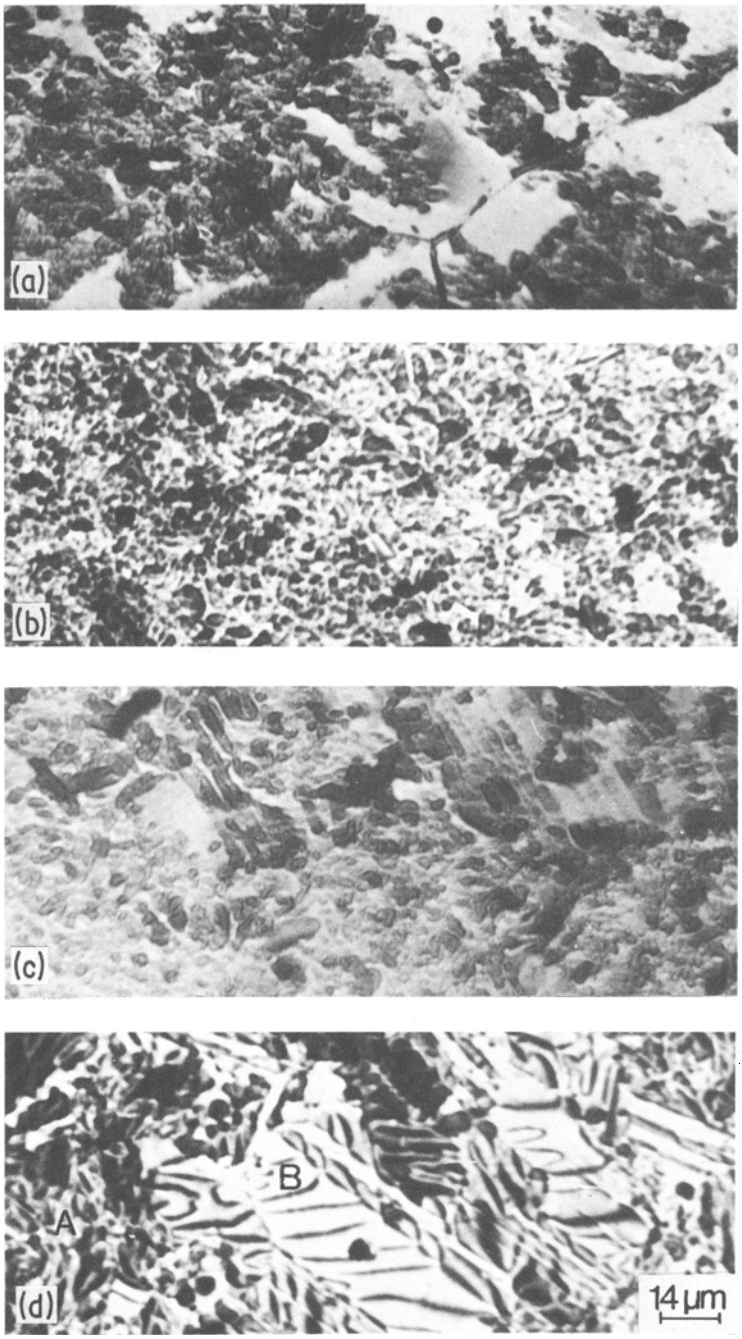

Figure 1 Changes in the domain structure of the MnAlC alloy (homogenized at 1373 K for 1 h and quenched in water) as a function of tempering time at 823 K: (a) 0.5, (b) 1, (c) 3, and (d) 15 h. A – a labyrinth structure, and B – 180° domain walls. The powder pattern method was used.

apart from the τ phase, clear and smooth spaces of the paramagnetic ϵ phase can be also distinguished (Fig. 2, spot C).

In order to reveal the growth of the ferromagnetic τ phase in regions covered by the paramagnetic phase ϵ of the MnAlC alloy, the powder pattern technique was also used (Fig. 3). The unetched but only mechanically polished surface of specimens was sprayed by colloidal suspension of fine Fe_3O_4 particles. As the photograph shows, the colloidal suspension accumulates only on the growing ferromagnetic τ phase (Fig. 3, spot E).

A similar comparison between the microstructure and the domain structure has been made for tempering temperatures of 923 K. In this case, after tempering for 10 min the coercivity of the

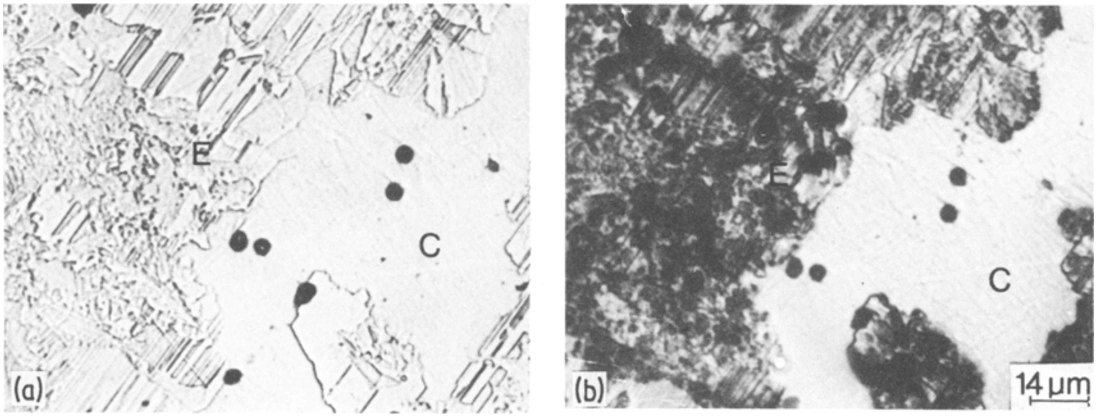

Figure 2 Comparison of microstructure (a) with magnetic domain structure (b) of the MnAlC alloy homogenized at 1373 K for 1 h, quenched in water, and tempered at 823 K for 30 min. E – uneven τ phase and the twins of τ phase, C -- phase ϵ. Composition of the etchant: 25 ml HCl, 8 ml HNO_3, 7.5 ml HF, 1 l H_2O. The domain structure was revealed by the powder pattern method.

specimens was 64.78 kA m^{-1}, while after tempering for the same length of time at 823 K the coercivity was zero. Optimum magnetic properties during the tempering process at 923 K, i.e. $H_c = 67.94\ \mathrm{kA\,m^{-1}}$, $B_r = 270\ \mathrm{mT}$, $(BH)_{max} = 9.93\ \mathrm{kJ\,m^{-3}}$ have been obtained after 15 min. Similarly, as in the case of optimum magnetic properties after tempering at 823 K, at 923 K the powder pattern shows a network of small islets of about 10^{-6} m in diameter. Longer tempering markedly worsens the magnetic properties. A shorter tempering time, which is needed in order to obtain the optimum magnetic properties at 923 K, in comparison with that of 823 K, is caused by a more rapid $\epsilon \rightarrow \tau$ transformation process. The observation of the microstructure and X-ray analysis have shown that the worsening of magnetic properties after longer tempering times at 823 and 923 K (5 and 9 h respectively) is connected with the phase transformation of the ferromagnetic τ phase into the nonmagnetic β phase. The amount of phase increases with the tempering time of the alloy at a given temperature (Fig. 4).

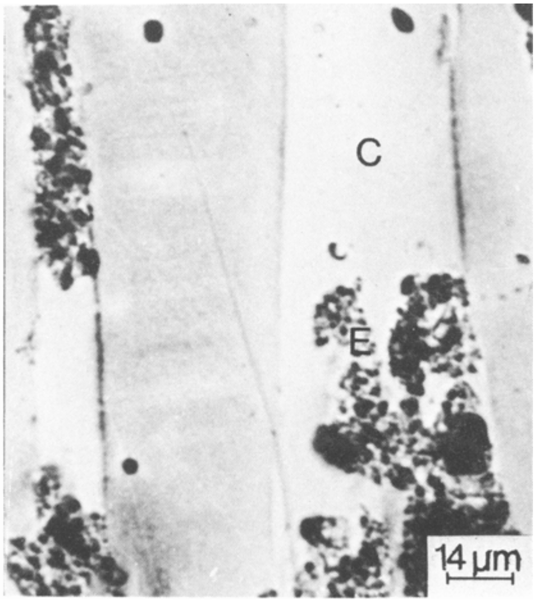

Figure 3 The growth of the ferromagnetic phase τ into the regions occupied by the ϵ phase of the MnAlC alloy (homogenized at 1373 K for 1 h and quenched in water). The surface of specimens was unetched. Observe the ϵ(C) phase and the uneven τ phase and the twins of τ phase (E). The τ phase revealed by the powder pattern method.

It should be emphasized that the magnetic properties of the MnAlC alloy, as of any other ferromagnetic material, are closely related to its magnetic domain structure. As the experimental results show, optimum magnetic properties in the MnAlC alloy are obtained when the domain structure is in the form of islets (Fig. 1b). The prolongation of isothermal tempering time leads, in the first stage, to the formation of chains of connected islets (Fig. 1c), and then to the development of a 180° Bloch wall structure or a labyrinth structure (Fig. 1d), and in consequence to a deterioration of the magnetic properties of the alloy. Similar results have been obtained in [19] for the carbonless MnAl binary alloy. The worsening of magnetic properties with simultaneous grain growth of the ferromagnetic τ phase should be

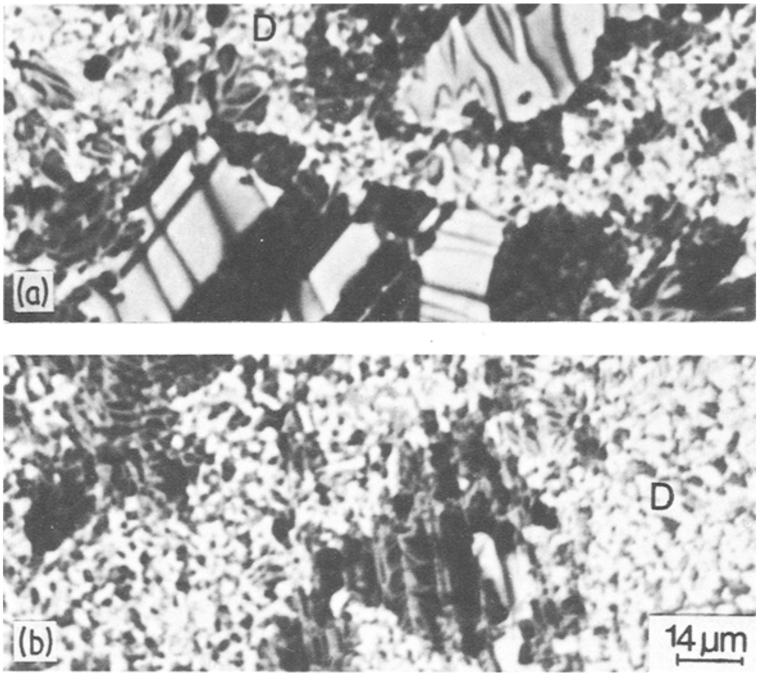

Figure 4 The growth of the β phase (D – bright spots) of the MnAlC alloy homogenized at 1373 K for 1 h and quenched in water as a function of tempering time at temperatures of 923 K: (a) 5, and (b) 9 h. Etched with the etchant given in Fig. 2.

attributed to the preponderance of domain wall shifting processes over the magnetization rotation vector.

The changes of domain structure on the surface of an isotropic MnAlC alloy observed in that work coincide with the data carried out by means of electron microscopy [12–15]. According to those observations the τ phase consists of finely dispersed areas orientated equally to each other. With the increase of tempering time the favourable increase of areas of equal orientation of crystallographic c-axis occurs. In the domain structure observed on the surface of MnAlC alloy it appears as a generation of islets, linkage of islets in chains, and then (at large grains of τ phase) generation of a multi-domain magnetic structure that is typical for uniaxial ferromagnetics

4. Conclusions

The powder pattern technique makes it possible to reveal the domain structure in the MnAlC alloy during various stages of the tempering process. Moreover, it was found that the relation between the magnetic properties of the MnAlC alloy and the type of domain structure observed on the surface of the specimen is not too small to be resolved by the Bitter pattern technique. The magnetic properties of the MnAlC alloy are closely related to the type of domain structure. The alloy has optimum magnetic properties when the type of domain structure occurs in the form of islets of about 1.5×10^{-6} m in diameter. The chain structure, and in particular the 180° wall structure, brings about a considerable worsening of magnetic properties.

Acknowledgements

This work has been supported by the Institute of Materials Science and Engineering, Warsaw Technical Unversity.

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Received 27 June
and accepted 26 July 1983