MAGNETIC STRUCTURE OF SMALL MONOCRYSTALLINE PARTICLES OF MnBi *ALLOY*

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The magnetic structure of particles of manganese-bismuth alloy of various sizes (from 100 down to a few microns) has been studied by the powder-pattern method. It was observed that with decrease of particle size, the magnetic structure changed in a systematic manner. In particles of a few microns or less in size, single-domain magnetic structure was observed.

1. INTRODUCTION

LANDAU and Lifshitz[1] showed theoretically that in ferromagnetic crystals there should exist a multidomain magnetic structure, with the magnetization vectors in different domains oriented along axes of easy magnetization. Furthermore this deduction has been verified experimentally. From very general theoretical considerations it follows that in small monocrystalline ferromagnetic particles, a single-domain magnetic structure is to be expected.[2,3] This single-domainedness should set in when the dimensions of the ferromagnetic crystal are such that a breaking up into domains no longer produces a decrease of the energy of the crystal. In the study of ferromagnetic powders, trends have in fact been observed that could be explained only on the assumption that on passage to fine particles, a single-domain structure comes into existence.[4] However, the single-domain structure has not hitherto been observed by a visual method. The aim of the present work was the observation and study of single-domain magnetic structure by the powder-pattern method.

According to the theoretical estimates of Kittel[2] and Kondorskiĭ,[3] in the common ferromagnetics a single-domain structure should appear at particle dimensions of order 10^{-5} to 10^{-6} cm. In the study of magnetic structure by the powder-pattern method, however, it is desirable to make the observations on comparatively large particles. The critical particle size, below which single-domain structure occurs, depends on the values of the magnetic anisotropy constant and of the magnetic saturation. Specifically, this size increases with increase of the magnetic anisotropy constant, since the latter contributes to increase of the wall energy and consequently to increase of the difficulty of wall creation by breaking up the ferromagnetic into domains. Decrease of the critical size with increase of the value of the magnetic saturation comes about because of the increase of the magnitude of the magnetic charges, whose energy is decreased upon creation of a domain structure. On the basis of these relations, we chose for study the alloy MnBi. This alloy possesses, at room temperature, the largest value of the anisotropy energy among all known ferromagnetics and a comparatively small magnetic saturation; consequently, the single-domain structure in this alloy should occur at comparatively large particle sizes.

2. SPECIMENS STUDIED AND OBSERVATION METHOD

The specimens studied had a cylindrical shape and were obtained by sintering pressed powders of manganese and bismuth at temperatures from 280 to 360° C. At the time of sintering there were formed separate (and mostly monocrystalline) grains of MnBi alloy, isolated from one another by layers made up of bismuth and manganese that had not reacted. The size of these grains varies with the conditions of preparation (temperature and duration of sintering) from a few microns to hundreds of microns. The specimen surface to be studied was prepared by mechanical grinding and subsequent polishing with velvet. To obtain powder patterns, a magnetic suspension prepared by Elmore's[5] method was used. Observations of the powder patterns were made with a type MP-5 microscope. Magnetization of the specimen was accomplished with an electromagnet, at fields up to 24,000 oe. In the observation of the powder patterns, and especially when they were being photographed, it proved necessary that the microscope, specimen, and electromagnet form a single unit. Therefore the specimen was clamped between the poles of the electromagnet, and the microscope tube was attached to the core of the electromagnet by means of a horizontal movable platform. Since the observations were made in strong magnetic fields, all metal parts of the optical apparatus (microscope, opaque-illuminator, and condenser) were made of nonferromagnetic materials.

3. RESULTS OF THE OBSERVATIONS AND THEIR ANALYSIS

a) Multidomain magnetic structure. In observations of powder patterns on the surfaces of the majority of the crystals, with various crystallographic orientations of the surface, it was observed that in particles of size greater than 50 μ, as a rule, multidomain structure was present. The form of the powder patterns was related in a systematic way to the crystallographic orientation of the specimen surface. The alloy MnBi, as is known, has a hexagonal structure at room temperature; it is therefore a uniaxial ferromagnetic. Consequently, if the hexagonal axis (the axis of easy magnetization) of a crystal of MnBi alloy was parallel to the surface of the specimen or made a small angle with it, then walls were formed on the surface between domains with antiparallel orientations of the magnetization. A view of such a magnetic structure is shown in Fig. 1a. The orientation of the magnetization in the domains is shown by arrows. On application of a magnetic field parallel to the axis of easy magnetization and on increase of it, the process of wall displacement is observed; domains in which the magnetization vector is parallel to the direction of the field absorb domains with antiparallel orientation of the magnetization (Figs. 1b and 1c). In a sufficiently strong field the regions with antiparallel orientation of the magnetization disappear, and the whole crystallite is magnetized uniformly (Fig. 1d). On diminution of the magnetic field, there appear regions with magnetizations oriented antiparallel to the field, and their volume increases. When the external field is zero, the domain-structure picture shown in Fig. 1a is observed; that is, the particle is demagnetized (its remanent magnetization is very small). The further process of reverse magnetization proceeds by wall displacement; that is, by diminution of the volume of regions with unfavorably oriented magnetization.

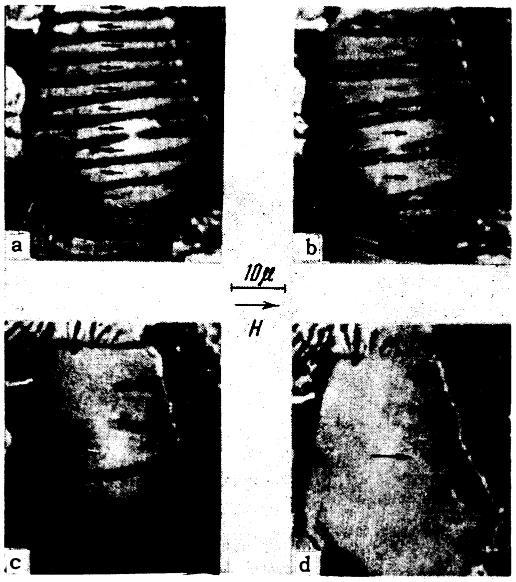

FIG. 1. Powder patterns on a particle with multidomain structure, in magnetic fields: a) H = 0; b) H = 1400; c) H = 3200; d) H = 7400 oe. The hexagonal axis makes a small angle with the observation plane.

If the specimen surface is close to the surface perpendicular to the hexagonal axis, then there appears a magnetic structure in the form of "stars" (Fig. 2). It may be assumed that the "stars" appear at points of termination of basic and closure domains on the crystal surface.

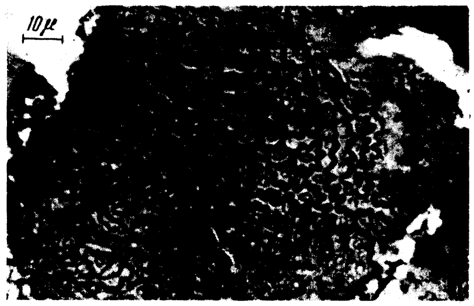

FIG. 2. Powder patterns on a particle with multidomain structure. The hexagonal axis makes an angle of nearly 90° with the observation plane.

The magnetic structures shown in Fig. 1a and in Fig. 2 have been observed in all uniaxial ferromagnetic crystals that have been studied (cobalt,[6] manganese antimony,[7] barium ferrite[8]). Thus in comparatively large crystals of MnBi alloy, there is observed a magnetic structure that is present in all magnetically uniaxial ferromagnetics.

b) Single-domain magnetic structure. In the investigation of the form of the powder patterns in finer monocrystalline particles of the MnBi alloy, it was established that in particles of size a few microns and below, the presence of a single-domain structure could sometimes be observed. The emergence of this structure could be shown by the peculiar form of the powder deposit and its behavior under the influence of a magnetic field. In such particles, for arbitrary changes of the magnetic field, it is impossible to observe a breaking up of the particle into separate domains. If the hexagonal axis of the crystal (the direction of easy magnetization) lies in or makes a small

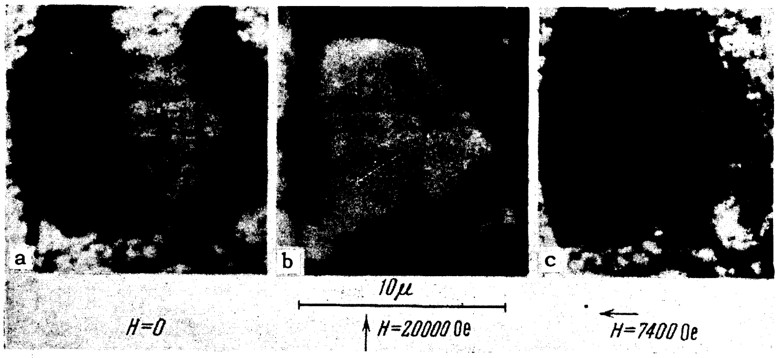

FIG. 3. Picture of the powder deposition on a particle with single-domain structure in a magnetic field. The hexagonal axis makes a small angle with the observation plane.

angle with the specimen surface, then the magnetic powder collects at the edge of the particle where the poles are located. A view of such a magnetic structure is shown in Fig. 3a, where the powder collects at the left and right edges of the particle. If the particle under study is placed in a magnetic field oriented perpendicular to the direction of easy magnetization, then there is observed a displacement of the powder collected at the crystallite edges, in proportion to the strength of the field; this indicates a rotation of the magnetization vector under the influence of the magnetic field. In a strong field, as is clear from Fig. 3b, the powder collects at the upper and lower edges of the particle. This shows that the magnetization vector J_s in the particle is directed parallel to the external field. The property of single-domain structure is displayed also when the particle under study undergoes magnetization reversal in a direction parallel to the axis of easy magnetization (or its projection on the specimen surface). Thus on application of a field oriented antiparallel to the direction of the J_s of the particle, and on gradual increase of it, the powder, which in the initial state was at the edge of the particle, begins gradually to spread over the whole surface of the crystal. In Fig. 3c is shown a view of such a powder distribution in a demagnetizing field of 7400 oe. On further increase of the field, there occurs an instantaneous displacement of the powder to the edges of the crystal. The powder behavior described is caused by the fact that under the influence of the field, there occurs a rotation of the magnetization vector through 180°. In the course of this rotation there appears a vertical component of magnetization, which causes a spreading of the powder over the whole surface of the crystal. The field at which there occurs a displacement of the powder from the middle to the edges of the crystal corresponds to an irreversible rotation of the magnetization vector and is close to the coercive force of the particle. In the present case it amounts to thousands of oersteds. (In the case of the displacement process, the coercive force amounts to hundreds of oersteds.) Thus in MnBi alloy, in particles of the size of a few microns and below, there can occur a single-domain magnetic structure which is preserved in the process of magnetization reversal of the crystal.

c) Intermediate magnetic structure. Of considerable interest are particles of MnBi alloy whose size is a little larger than the critical size. In this case it is possible to produce either conditions under which the process of magnetization reversal of a particle will be accomplished by the usual method, i.e., by formation of nuclei of reversed magnetization and by wall displacement, or other conditions such that the process of magnetization reversal will occur by rotation of the vector magnetization (cf. Fig. 3). Thus, for example, in one of the crystals studied, by choice of the size of the magnetic field* used for initial magnetization of the particle, conditions were produced under which the process of magnetization reversal proceeds variously as follows:

1. The particle is magnetized in a field of 5000 oe. In this field the whole powder collects at the edges of the crystal, which indicates a uniform magnetization of the particle (particle magnetized to saturation). On diminution of the field, closure domains appear; they grow and are converted to domains with antiparallel orientation of the magnetization. In the state of remanent magnetization, the crystal is broken up into several regions with antiparallel orientations of the magnetization. On change of sign of the field, the process of magnetization reversal of this particle occurs by wall displacement, as in an ordinary ferromagnetic with multidomain structure.

2. The particle is magnetized in a field of 20,000 oe. In this case the single-domain magnetic structure is preserved both on diminution of the field and on change of its sign. In a field of 20,000 oe, the magnetic powder collects at the edges of the crystal. Decrease of the field causes a movement of the powder on to the whole surface of the crystal.

*A similar case was treated in detail in reference 9.

After change of the sign of the field and increase of it to 4000 oe, the whole surface is uniformly covered with powder. Upon a further small increase of the field, there occurs an instantaneous clearing of the particle surface, as the powder again collects near the particle edges. Such a movement of the powder is possible if the magnetization-reversal process under observation occurs by rotation of the magnetization vector.

Thus a strong magnetic field can in some cases completely eliminate the possibility of formation of nuclei of reversed magnetization in the process of change of magnetization around a hysteresis loop. Nuclei of reversed magnetization can be formed anew by certain treatments of the crystal, for example by commutation of a constant magnetic field of decreasing amplitude.

The intermediate magnetic structure under consideration is apparently not the only one possible. However, it may be assumed that in all intermediate magnetic structures, the conditions for formation and growth of nuclei of reversed magnetization play a large part.

d) Irreversible reorganization of the magnetic structure on change of temperature. On change of temperature there is to be expected a reorganization of the magnetic structure, and this may be in part irreversible. This irreversibility of the change of magnetic structure shows up especially graphically in crystals of MnBi alloy whose sizes are close to the critical. At room temperature such a crystal has a single-domain structure (Fig. 4a), which is shown by accumulation of the powder at the edges of the crystal in zero field. If the crystal is cooled to the temperature of liquid nitrogen (– 196° C) and then heated to room temperature, thereafter a multidomain structure is observed on its surface. In Fig. 4b can be seen the deposition of powder at the walls between domains and on the edges of the crystal.

The result obtained can be understood if we take into account that the MnBi alloy at room temperature has a very large anisotropy constant, whose value decreases rapidly upon lowering of the temperature. The value of the saturation magnetization meanwhile changes very little. From this it follows (cf. Sec. 1) that on lowering of the temperature, there must be a decrease of the critical particle size at which the single-domain structure sets in. In consequence of this, the particle can become multidomain at a low temperature and can retain this structure on heating to room temperature. Irreversible reorganization of the domain structure on lowering of the temperature is also observed in crystals of MnBi alloy with multidomain and intermediate magnetic structures.

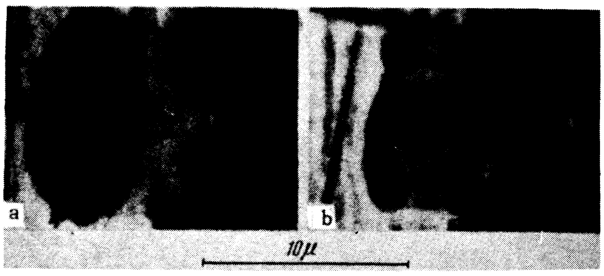

FIG. 4. Picture of the powder deposition on a particle: a) in the state of remanent magnetization; b) after a temperature cycle (+20, –196, +20 °C). The hexagonal axis makes a small angle with the observation plane.

4. CONCLUSION

Study of the magnetic structure of MnBi alloy has shown that crystals of size greater than 50 μ are multidomain. The process of magnetization reversal in them occurs in the same way as in all magnetically uniaxial ferromagnetics.[6-8] In particles of the same alloy of size 15 to 10 μ, it is possible in a number of cases to detect an intermediate magnetic structure. Magnetization reversal of such crystals, depending on the magnitude of the maximum magnetizing field, can occur either by wall motion or by irreversible rotation of the magnetization vector. In this case the single-domain structure, produced by a large field and retained on magnetization reversal, can be destroyed by commutation of a magnetic field of diminishing amplitude. In small particles of MnBi alloy (a few microns and below), a single-domain magnetic structure is observed. Such particles at room temperature do not break up into domains under any changes of the magnetic field. This single-domainedness can be destroyed by lowering the temperature, which causes a decrease of the critical size for the transition to single-domainedness at low temperatures. Thus the results presented in our work show that in monocrystalline particles of MnBi alloy, upon passage to small sizes, there occurs an essential change of form of their magnetic structure: instead of the multidomain structure, there appear an intermediate and a single-domain magnetic structure.

[1] L. D. Landau and E. M. Lifshitz, Physik. Z. Sowjetunion **8**, 153 (1935).

[2] C. Kittel, Phys. Rev. **70**, 965 (1946); Revs. Modern Phys. **21**, 541 (1949).

[3] E. I. Kondorskiĭ, Dokl. Akad. Nauk SSSR **70**, 215 (1950); **80**, 197 (1951); **82**, 365 (1952).

[4] E. V. Shtol'ts and Ya. S. Shur, Dokl. Akad.

Nauk SSSR **95**, 781 (1954); Ya. S. Shur, E. V. Shtol'ts, and G. S. Kandaurova, Izv. Akad. Nauk SSSR, Ser. Fiz. **21**, 1215 (1957), Columbia Tech. Transl. p. 1205; E. V. Shtol'ts, Ya. S. Shur, and G. S. Kandaurova, Физика металлов и металловедение (Physics of Metals and Metal Res.) **5**, 412 (1957).

[5]W. C. Elmore, Phys. Rev. **53**, 757 (1938).

[6]W. Andrä, Ann. Physik **15**, 135 (1954).

[7]R. Perthel and W. Andrä, Ann. Physik **19**, 265 (1957).

[8]Sixtus, Kronenberg, and Tenzer, J. Appl. Phys. **27**, 1051 (1956); C. Kooy, Philips Tech. Rev. **19**, 286 (1957-8).

[9]Ya. S. Shur, E. V. Shtol'ts, G. S. Kandaurova, and L. V. Bulatova, Физика металлов и металловедение (Physics of Metals and Metal Res.) **5**, 234 (1957).

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