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(54) IMPROVEMENTS IN AND RELATING TO MAGNETIC MATERIALS

(71) We, MATSUSHITA ELECTRIC INDUSTRIAL CO. LTD., a Japanese Company, of 1006 Kadoma, Osaka 571, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to bulk Mn—Al—C alloys which are magnetically anisotropic, to a method of making such alloys, and to permanent magnets made from such alloys.

Mn—Al alloys consisting of 60 to 75% Mn (this percentage, and all percentages given hereinafter are by weight) the remainder being aluminium, in which the ferromagnetic metastable phase (face-centred tetragonal, lattice constant $a = 3.94\text{\AA}$, $c = 3.58\text{\AA}$, $c/a = 0.908$ and a Curie point of 350 to 400°C; hereinafter referred to as the τ phase) can be obtained by heat treatment, such as by controlled cooling or quench-tempering, are known. The ferromagnetic τ phase is the metastable phase which appears between the high temperature phase (close-packed hexagonal, lattice constant $a = 2.69\text{\AA}$, $c = 4.38\text{\AA}$; hereinafter referred to as the ϵ phase) and the room temperature phase (a phase in which the alloy is separated into the $\text{AlMn}(\gamma)$ phase and the β -Mn phase). This intermediate phase was discovered by Nagasaki, Kono, and Hirone in 1955. (*Digest of the Tenth Annual Conference of the Physical Society of Japan*, Vol. 3, 162, October, 1955). However, such Mn—Al alloys possess magnetic characteristics which are low, for example of the order of $(\text{BH})_{\text{max}} = 0.5 \times 10^6 \text{ G.Oe}$, $\text{Br} = 2200 \text{ G}$, and $\mu_{\text{Hc}} = 600 \text{ Oe}$.

Since then, a method has been proposed in which the powdered alloy in the τ phase is sintered, and then pulverised, increasing the coercive force; however, the magnetic characteristics of these alloys in isotropic form, at best, were low, being of the order of $(\text{BH})_{\text{max}} = 0.6 \times 10^6 \text{ G.Oe}$, $\text{Br} = 1700 \text{ G}$, and $\mu_{\text{Hc}} = 1250 \text{ Oe}$. Moreover, since the products were formed from powder, their mechanical strengths were low, making them unsuited for commercial use.

A method has been proposed for improving the magnetic characteristics of these Mn—Al alloy magnets by applying a high degree of cold-working on the alloy in the τ phase, the ferromagnetic phase, to render them anisotropic. In this method, rod shaped Mn—Al alloys in the τ phase are sealed in nonmagnetic

stainless steel pipes, and subjected to cold-working, such as swaging, to an extent of 85 to 95%. This method is capable of producing an alloy which is magnetically anisotropic and which has magnetic characteristics of the order of $B_r = 4280\text{G}$, $H_c = 2700\text{ Oe}$, and $(BH)_{\max} \div 3.5 \times 10^6\text{ G.Oe}$ in the direction of preferred magnetisation, that is, along the axis of the rod. However, Mn—Al alloys are very hard and brittle intermetallic compounds, so that cold-working of even less than 1% causes cracks or fractures in the alloys. Since the degree of anisotropy is dependent upon the extent of cold-working, it is necessary to cold-work the alloy to a high degree, normally more than 80%, to achieve satisfactory magnetic characteristics; for this reason the cold-working operation must be carried out while the alloy is sealed in a nonmagnetic stainless steel pipe. A disadvantage of this method is that the Mn—Al alloy in the pipe must be reduced to a fine powder; it is moreover, difficult to obtain rods of uniform cross-section. The method is therefore costly and of little practical value.

A method has also been proposed for obtaining Mn—Al alloys which are magnetically anisotropic in rod form by subjecting the τ phase of the Mn—Al alloy to hydrostatic extrusion at a temperature below 200°C , but the magnetic characteristics of such alloys is poor, being of the order of $(BH)_{\max} = 2.5$ to $3.6 \times 10^6\text{ G.Oe}$ in the direction of preferred magnetisation. This method also requires a very intricate hydrostatic extrusion technique and is also impractical.

Manganese-aluminium-carbon alloys which have good magnetically isotropic characteristics are described in U.S. 3 661 567.

However, the further improvement of their magnetic characteristics by either cold-working as described above, or by powder forming have been unsuccessful, the magnetic characteristics being barely improved, or degraded, and improvement in their performance by way of anisotropisation could not be expected.

We have now prepared bulk Mn—Al—C alloys which are magnetically anisotropic, and which have unexpected magnetic characteristics; in particular they have a $(BH)_{\max}$ exceeding $4.8 \times 10^6\text{ G.Oe}$ and being as high as $9.2 \times 10^6\text{ G.Oe}$.

According to one aspect of the present invention we provide a bulk alloy which consists, by weight, of from 68.0% to 73.0% of manganese, and from $(1/10[\text{Mn}] - 6.6)\%$ to $(1/3[\text{Mn}] - 22.2)\%$ of carbon, the remainder being aluminium together with unavoidable impurities, where $[\text{Mn}]$ is the percentage of manganese, and which is magnetically anisotropic.

In a preferred embodiment, the alloy contains the compound Mn_3AlC , as herein defined. Mn_3AlC is a compound having a perovskite type face-centred cubic crystal structure (lattice constant $a = 3.87\text{\AA}$), but because its Curie point is 15°C , and it is non-magnetic at room temperature, it does not contribute to the intensity of magnetisation of the alloy. The term "face-centred cubic phase similar to Mn_3AlC " is used herein to include perovskite-type carbides or compounds having the same chemical characteristics as the carbides, but which are not perfectly formed carbides.

The preparation of an alloy according to the invention has been made possible by the discovery that in Mn—Al—C alloys, which ordinarily exhibit no plasticity, there exists a special phase having significant and useful plasticity in a specific temperature range, when the alloy has a particular composition and the combined carbon in the alloy exists in a particular state.

According to another aspect of the present invention, we provide a method of making the alloy of the invention, which comprises subjecting an Mn—Al—C alloy of the composition specified above and which is free of a grainy Mn_3AlC phase (as herein defined) to plastic deformation at a temperature of from 530° to 830°C whereby the alloy is rendered magnetically anisotropic.

The term "a grainy Mn_3AlC phase" is used herein to mean a phase consisting of Mn_3AlC and/or a face-centred cubic phase similar to Mn_3AlC which is/are finely dispersed in grainy or reticular form with a tetragonal (magnetic) phase as its matrix. If the alloy has a grainy Mn_3AlC phase, an alloy which is magnetically isotropic is obtained on deformation. The formation of such alloys is described in our co-pending Application No. 45507/74 (Serial No. 1,473,373).

According to a further aspect of the present invention, we provide a permanent magnet made by magnetising an alloy of the invention.

Such a permanent magnet may have a specific gravity as low as 5.1, and a magnetic energy per unit weight which is 2 to 3 times that of an anisotropic (Ba,Sr) ferrite magnet, 1.5 to 2 times that of an AlNiCo magnet, and comparable to the best permanent magnets known.

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Other features and advantages of the invention will appear from the following description of embodiments thereof, given by way of example, and the accompanying drawings, in which:—

5 Figure 1 is a graph showing the relationship between the particle diameter of the crystals and the carbon content in Mn—Al—C alloy castings consisting of 72.0% Mn and 0.1 to 2.5% C, the remainder being Al;

Figure 2 is a reproduction of a photograph of an optical microstructure of the $\epsilon_c(M)$ phase;

10 Figure 3 is a graph showing the relationship between the time and the degree of deformation in the direction of application pressure when a monocrystal in the $\epsilon_c(M)$ phase was subjected to plastic deformation;

Figures 4a, 4b and 4c are diagrams showing stages in the change of a crystal structure undergoing the transformation: $\epsilon_c \rightarrow \epsilon_c' \rightarrow \tau_c$;

15 Figure 5 is a reproduction of a photograph of an optical microstructure of the $\tau_c(M)$ phase;

Figure 6 is a graph showing the variation of saturation deformation with respect to the direction of applied pressure;

20 Figure 7 is a graph showing the relationship between the proportion of Mn and in an alloy and its degree of anisotropisation; and

Figure 8 is a composition diagram of a Mn—Al—C ternary system.

25 It has been established that in Mn—Al—C alloys, the solubility limit of carbon in the magnetic phase, as determined by the measurement of lattice constants by means of X-ray diffraction and by measurement of the Curie point using a magnetic balance, is 0.6% for a composition containing 72% Mn, 0.4% for 70% Mn and 0.2% for 68.0% Mn; in general the solubility limit of carbon within the composition range of 68.0 to 73.0% Mn is represented by the mathematical relationship: $(1/10[Mn] - 6.6)\%$.

30 The solubility limit of carbon in the high temperature phase is substantially the same as the solubility limit of carbon in the magnetic phase at a temperature of 830°C, but in the temperature range of from 900° to 1200°C, the solubility limit of carbon is greater than $(1/10[Mn] - 6.6)\%$ of carbon; however, by quenching from a temperature above 900°C, an ϵ phase can be obtained in which a quantity of carbon exceeding $(1/10[Mn] - 6.6)\%$ is forced to dissolve.

35 The high temperature phase at which carbon can be forced to dissolve in amounts exceeding the solubility limit in Mn—Al—C alloys, that is exceeding $(1/10[Mn] - 6.6)\%$, is designated the ϵ_c phase, to distinguish it from the ϵ phase of the high temperature phase containing carbon in amounts not exceeding the solubility limit. Also, the ferro-magnetic phase in which the force-dissolved carbon exceeds the solubility limit is designated the τ_c phase, to distinguish it from the τ phase of the magnetic phase containing carbon in amounts not exceeding the solubility limit. By subjecting the alloys to the ϵ_c phase to a tempering step, the phase structure in which the phase of Mn_3AlC and/or of a face-centred cubic phase similar to Mn_3AlC , is finely dispersed in grainy or reticular form in these alloys, with the τ_c phase forming the matrix. However, Mn_3AlC aligned in lamellae parallel to the special crystal plane of $\epsilon_c(0001)$ and at intervals of 1—10 μ is deposited in the ϵ_c phase if in the process of quenching, cooling is gradual. Precipitation of the lamellae is preferably effected either by cooling the alloy from a higher temperature to a temperature in the range of from 900°C to 830°C at a cooling rate of not more than 10°C/min. followed by quenching, or by holding the alloy in a temperature range of from 830° to 900°C for at least 7 minutes, preferably more than 10 minutes, followed by quenching. It has been established by optical microscopic observation and X-ray diffraction that this lamellar Mn_3AlC has a crystalline orientation relationship of

$$\epsilon_c(0001) \parallel Mn_3AlC(111)$$

55 Furthermore, it was confirmed by electron microscope examination, though not distinctively by optical microscope examination, that the ϵ_c phase was at intervals of 1 to 10 μ between the lamellae of Mn_3AlC , and that the phase of the Mn_3AlC and/or face-centred cubic phase similar to Mn_3AlC was deposited on the plane of $\epsilon_c(0001)$, separated from each other by a distance of 0.1 to 1 μ .

60 The heat treatment for causing the Mn_3AlC phase and/or the face-centred cubic phase similar to Mn_3AlC to be deposited in lamellae as described above, is designated the M treatment, and the ϵ_c phase containing the lamellar Mn_3AlC

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phase and/or a face-centred cubic phase similar to Mn_3AlC deposited by the M treatment is identified as the $\epsilon_c(M)$ phase.

By tempering the alloy of $\epsilon_c(M)$ phase, the matrix ϵ_c is transformed to the τ_c phase, but the lamellar Mn_3AlC phase and/or face-centred cubic phase similar to Mn_3AlC remains unchanged; the grainy Mn_3AlC phase is barely appreciable.

The τ_c phase containing the lamellar Mn_3AlC phase and/or face-centred cubic phase similar to Mn_3AlC is identified as the $\tau_c(M)$ phase. Isotropic Mn—Al—C alloys including the $\tau_c(M)$ phase as the isotropic matrix have a low level of magnetic characteristics, of the same order as the magnetic characteristics of isotropic Mn—Al alloys. The magnetic characteristics of Mn—Al—C alloys is however affected by the condition in which carbon is present, as mentioned above. Similarly, the magnetic characteristics and workability of anisotropic Mn—Al—C alloys rendered anisotropic by plastic deformation at an elevated temperature, are also dependent on the carbon conditions.

In a preferred embodiment of the method according to the invention, the deformed alloy is subjected to tempering at a temperature of from 480°C to 750°C.

In another preferred embodiment, an alloy which is magnetically anisotropic is made by subjecting a starting alloy which contains from 68.0% to 70.5% of manganese to quenching from a temperature of at least 900°C, and to plastic deformation at a temperature of from 600°C to 780°C. More preferably, the quenched alloy is subjected to tempering at a temperature of from 480°C to 750°C before deformation.

In order that the invention may be more fully understood, the following Examples are given by way of illustration only.

Example 1.

A monocrystal consisting of ϵ_c phase Mn—Al—C alloy having a composition consisting of Mn 72.28%, Al 26.64% and C 1.08%, as chemically analysed, was manufactured.

The various factors involved in obtaining the ϵ_c monocrystal of this Mn—Al—C alloy were studied and it became clear that the growth of the monocrystal is dependent on carbon content. It is a necessary condition for obtaining the ϵ_c monocrystal, in an alloy containing Mn 68.0 to 73.0%, that the amount of carbon must fall in the range of (1/10 Mn - 6.6)% to (1/3 Mn - 22.2)%, and that the process of heating to above 1,380°C, which is the melting temperature required to force the carbon to melt in its solid solution, should be carried out at least for one cycle. It was found, for example, that in the material in which the amount of carbon in solid solution was less than (1/10 Mn - 6.6)%, the growth of crystals in the alloy took place with difficulty; on the other hand, in Mn—Al—C alloys in which carbon, in an amount in excess of the solubility limit of (1/10 Mn - 6.6)% was forced to dissolve into the solid solution at a melting temperature of above 1,380°C, coarse grains of the crystal were apparent. In this way, the ϵ_c monocrystal can be obtained by cooling the molten alloy from one end thereof by the Bridgman method or by use of a chill mould.

As regards the growth of crystals from the ϵ_c phase, in the case of polycrystals formed in ordinary casting conditions, Figure 1 shows that in material containing carbon in amounts above the solubility limit, the increase of crystal grain size becomes marked, the crystal grain size increasing with the increasing proportion of force-dissolved carbon; but as the amount of carbon exceeds (1/3 Mn - 22.2)%, the excess carbon forms aluminium carbide Al_4C_3 , which is undesirable. For these reasons, the required amount of carbon to obtain ϵ_c monocrystals is limited to the range of (1/10 Mn - 6.6)% to (1/3 Mn - 22.2)%, as described above.

To force the carbon to go into solid solution, a temperature exceeding 1,380°C must be used. At melt temperatures below 1,380°C, it is not possible to force the carbon to dissolve into solid solution in amounts exceeding the solubility limit.

Accordingly, to obtain the ϵ_c monocrystals, the respective component elements were mixed and alloyed by heating them above 1,380°C, and then, monocrystallised. Further, a Mn—Al—C alloy in which carbon was preliminarily dissolved into solid solution at a temperature above 1,380°C, was remelted and monocrystallised. In this latter case, the heating temperature for ϵ_c monocrystallisation was not necessarily required to be above 1,380°C, and heating to a temperature above the melting point of 1,210°C to 1,250°C was sufficient.

The temperature control conditions for obtaining the ϵ_c monocrystal by cooling the molten Mn—Al—C alloy from one end were chosen as follows:

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The molten metal was solidified at a rate of 0.5 to 10 cm/hr, with a temperature gradient of 5 to 200°C/cm in the temperature range of 1,150°C to 1,250°C, or solidified from one end at a cooling rate of 10 to 100°C/hr in the same temperature range; the monocrystal was then cooled to 900°C, and thereafter quenched from a temperature of 900°C to a temperature below 500°C by cooling it over that temperature range at a cooling rate of 300° to 3,000°C/min. In this way there could be easily obtained an ϵ_c monocrystal in the shape of a cylinder of 35 mm external diameter.

From the ϵ_c monocrystal obtained in this way, there was cut a cubic test piece of 8 × 8 × 8 mm having surfaces of (0001), (1100) and (1120). This ϵ_c monocrystal was tempered at 600°C for 1 hour. The magnetic characteristics of the tempered test piece were measured; the material was found to be magnetically isotropic with magnetic characteristics as follows: $B_r = 2,750$ G, $H_c = 1,350$ Oe, and $(BH)_{max} = 1.1 \times 10^6$ G.Oe. These values are similar to those obtained with isotropic Mn—Al—C alloy magnets of the ordinary polycrystal type. By optical microscope observation of the structure of the test piece after tempering, a finely dispersed grainy or reticular deposition of the Mn_3AlC phase was observed, as in the structure of the ordinary isotropic magnet. From the result of the X-ray diffraction, however, it was confirmed that since the intensity of diffracted lines from the Mn_3AlC phase differed, depending on the diffracting surfaces of the test piece, there existed a small amount of the Mn_3AlC phase oriented in its relationship to the ϵ_c phase before being tempered as expressed by $\epsilon_c(0001) // Mn_3AlC(111)$.

Other test pieces, subjected to similar treatment as described, with other surfaces cut and with different tempering conditions, were found to be isotropic and no improvements in their magnetic characteristics were obtained by such treatment.

Example 2.

An ϵ_c monocrystal obtained as in Example 1, was subjected to the M treatment in which it was held at a temperature of 830°C for 20 minutes, and was then quenched from this temperature at a cooling rate of 300° to 3,000°C/min. The monocrystal thus obtained had a phase, identified as $\epsilon_c(M)$ monocrystal, in which the Mn_3AlC phase was orderly deposited in the shape of lamellae on the (0001) plane of the ϵ_c monocrystal, as described above. The orientation was found to be:

$$\epsilon_c(0001) // Mn_3AlC(111)$$

as described above, confirmed by X-ray diffraction, X-ray microanalysis, optical microscopy and chemical analysis.

Figure 2 is a reproduction of an optical photograph of the microstructure of magnification indicated in the Figure, and about 1,000 in the original, showing the deposit phase of the Mn_3AlC as lamellae in the matrix of ϵ_c .

After determining the crystal orientation, by reference to the lamellar structure and X-ray diffraction, a cubic test piece was cut from the $\epsilon_c(M)$ monocrystal obtained as described, the test piece being 8 × 8 × 8 mm and having surfaces of (0001), (1100) and (1120). The test piece was subjected to tempering at 570°C for 1 hour to obtain the $\tau_c(M)$ phase. By optical microscopic observation and X-ray diffraction it was ascertained that the ϵ_c phase of the matrix was transformed into the τ_c phase by this tempering step, but the lamellar structure was not destroyed.

The magnetic characteristics of the test piece of $\tau_c(M)$ phase were fully isotropic, and were: $B_r = 2,550$ G, $H_c = 800$ Oe, and $(BH)_{max} = 0.67 \times 10^6$ G.Oe. These values were lower than the magnetic characteristics of a normal isotropic Mn—Al—C alloy magnet of the polycrystalline type. Other test pieces were prepared with different face cuts and treated in different conditions, but were all found to be isotropic, with no improvement in magnetic characteristics.

Example 3.

A monocrystal of $\epsilon_c(M)$ phase Mn—Al—C alloy containing 72.10% Mn, 26.78% Al and 1.12% C, as chemically analysed, was manufactured as described in Example 2, and from this $\epsilon_c(M)$ phase monocrystal several cubic test pieces were cut, each of 10 × 10 × 10 mm, each having three surfaces respectively parallel to the three crystal planes (3304), (1120) and (3308). One of the test pieces was subjected to pressure, at a temperature of 550°C, of 30 kg/mm² in a direction

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perpendicular to the (3304) plane, using an oil hydraulic press. The test piece was deformed plastically to the $\tau_c(M)$ phase, with a rapid shrinkage in the direction of pressure which took place within several minutes after the pressure was applied; the deformation was rapid and marked. The effect is shown in Figure 3, where point A is the point of initial application of pressure, and point B is the onset point of deformation. The rapid reduction in dimension in the direction of pressure reached saturation at point C, at a value of 15% reduction, considered as the ratio of the length of the test piece before and after application of pressure. There was little further change, up to point D, even with pressure applied for an extended time. The magnetic characteristics of the test piece, after being subjected in this way to deformation at a raised temperature, were measured and found to be low, but by subjecting this test piece to tempering at a temperature of 570°C, an anisotropic magnet of excellent magnetic characteristics was obtained, the characteristics being oriented in one direction with the preferred direction of magnetisation at about right angles to the direction of pressure.

Detailed study was made of the phenomenon of rapid and marked plastic deformation of the $\epsilon_c(M)$ phase at raised temperature and of the phenomenon that, by tempering the test pieces after this deformation, anisotropic magnets oriented in one direction are obtained. Experiments similar to those described above were carried out, with different degrees of deformation, to examine the phase of the test piece in the course of the deformation process.

For convenience, a test piece deformed by pressure to point B, just before the rapid plastic deformation stage begins, will be designated S_1 ; a test piece deformed by pressure to a point E intermediate points B and C will be designated S_2 , a test piece deformed by pressure to just before point C, where the rapid plastic deformation ends, will be designated S_3 , and a test piece deformed by pressure to point D will be designated S_4 . The degrees of deformation in these test pieces were found to be: S_1 —1.9%, S_2 —7.3%, S_3 —14.6% and S_4 —15.0%. The degrees of elongation of the test pieces after being subjected to this deformation at raised temperature, were different in the different directions of measurement with each test piece; in particular, test pieces of S_3 and S_4 showed elongations in the direction corresponding to the direction perpendicular to (3308) before the pressure was substantial, but only small elongation was shown in the direction perpendicular to (1120) before pressure.

The phases of the four types of test piece were examined, after deformation, by X-ray diffraction; with test pieces S_1 , S_2 and S_3 , a quite new diffraction pattern was found and one which had not been previously observed from either the Mn—Al alloys or the Mn—Al—C alloys. This new diffraction pattern, on analysis, was found to be due to the existence of a new phase of orthorhombic structure having lattice constants of $a = 4.371\text{\AA}$, $b = 2.758\text{\AA}$ and $c = 4.528\text{\AA}$; such a crystal structure belongs to the B19 type (MgCd type) in the Struktur-Bericht type convention confirming the existence of a new phase differing from the usual phases ϵ , ϵ_a , τ , τ_a , or the phase of carbides such as Mn_3AlC . It was also established that this orthorhombic crystal phase was an order phase which made its appearance at the intermediary stage in the transformation $\epsilon_c \rightarrow \tau_c$ process, and the $\epsilon \rightarrow \epsilon'_c$ transformation is an order-disorder transformation, where ϵ'_c designates the order phase of the orthorhombic crystal.

In Table 1, the results of the X-ray diffraction of the ϵ'_c phase by the powder method are shown. With a test piece of S_1 material, only the diffracted lines from the new ϵ'_c phase were found, except for the diffracted lines due to the lamellar Mn_3AlC phase and, moreover, it was apparent that the ϵ'_c phase was a crystal oriented in one direction, and that between the ϵ_c phase of the matrix before the pressure and the ϵ'_c phase of the matrix after pressure, there exists crystal orientation relationships of

$\epsilon_c(0001) // \epsilon'_c(100), \epsilon_c[0001] // \epsilon'_c[100]$

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TABLE 1

Observed values		Miller indices	Calculated values	
Interfacial distance (A)	Relative intensity		Interfacial distance (A)	Relative intensity
4.587	5	001	4.582	7.4
3.162	8	101	3.163	17.3
2.764	3	010	2.758	7.0
2.363	14	011	2.363	24.9
2.292	16	022	2.291	12.4
2.186	44	200	2.186	41.0
2.077	100	111	2.079	100.0
2.033	38	102	2.029	49.9
		201	1.973	1.3
		012	1.762	0.8
1.712	3	210	1.713	11.4
		112	1.643	3.8
1.606	13	211	1.604	14.1
1.586	6	202	1.581	7.1
		003	1.527	1.0
		301	1.388	1.1
1.381	6	020	1.379	8.7
		212	1.372	0.7
1.338	11	013	1.336	17.3
		021	1.320	0.3
		121	1.264	1.6
		203	1.252	1.2
1.240	16	311	1.240	22.9
1.228	6	302	1.229	11.4
		022	1.181	3.7
1.167	16	220	1.166	15.1
		004	1.146	1.9
		122	1.141	23.2
1.1411	24	213	1.140	30.2

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With a test piece of S_2 material, the diffraction lines from the ϵ'_c phase and the diffraction lines from the τ_c phase were present and also the diffraction lines from the lamellar Mn_3AlC phase; the ϵ'_c phase and the τ_c phase were both oriented in one direction. With a test piece of S_3 , the diffraction lines were present from a small proportion of ϵ'_c phase and a large proportion of τ_c phase as well as the diffraction lines from the lamellar Mn_3AlC phase; the ϵ'_c phase and τ_c phase were both unidirectionally oriented as in the case of S_2 material. Between the unidirectionally oriented ϵ'_c phase and τ_c phase, there existed a specific crystal orientation relationship:

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$$\epsilon'_c(100) \parallel \tau_c(111).$$

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With a test piece of S_4 material, only the diffraction lines from the τ_c phase were found apart from the diffraction lines from the lamellar Mn_3AlC phase; the τ_c phase was found to be nearly unidirectionally oriented.

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The angle of the diffraction lines from the τ_c phase in the S_2 , S_3 and S_4 test pieces deviated somewhat from the angles of the diffraction lines from the ordinary τ_c phase in an isotropic Mn—Al—C alloy magnet, and some differences in lattice constants were observed.

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These test pieces after being deformed were subjected to tempering, at a temperature of 580°C , without pressure; the magnetic characteristics of the test pieces after tempering improved with the increasing tempering time; excellent anisotropic magnets with magnetic characteristics shown in Table 2 were obtained with tempering time of 18 hours with S_1 , 24 hours with S_2 , 30 hours with S_3 and 15 hours with S_4 .

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The right angle direction (1) referred to in Table 2 is a direction of measurement at right angles to the pressure direction and corresponding to the direction perpendicular to the (1120) plane before pressure, and right angle direction (2) is the direction of measurement at right angles to the pressure direction but corresponding to the direction perpendicular to the (3308) plane before the pressure.

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TABLE 2

Test piece	Measuring direction	After deformation			After tempering		
		Br (G)	BHC (Oe)	BH _{max} (×10 ⁶ G.Oe)	Br (G)	BHC (Oe)	BH _{max} (×10 ⁶ G.Oe)
S ₁	Pressuring direction				1,100	450	0.3
	Right angle direction (1)				≈ 0	≈ 0	≈ 0
	Right angle direction (2)		Nonmagnetic		6,650	1,950	6.5
S ₂	Pressuring direction	≈ 0	≈ 0	≈ 0	750	300	0.1
	Right angle direction (1)	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0
	Right angle direction (2)	200	100	<0.1	6,850	2,150	7.2
S ₃	Pressuring direction	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0
	Right angle direction (1)	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0	≈ 0
	Right angle direction (2)	550	200	0.1	6,900	2,300	9.1
S ₄	Pressuring direction	950	500	0.2	1,400	600	0.3
	Right angle direction (1)	200	100	<0.1	500	200	<0.1
	Right angle direction (2)	4,300	1,650	1.3	6,700	2,250	6.8

Of these test pieces, the S₃ test piece after tempering was studied by X-ray diffraction, and found to be a τ_c(M) monocystal with its C axis, the easy axis of magnetisation of the τ_c phase of the matrix, oriented in a direction making an angle of about 82° to the pressure direction. The test piece was cut and its magnetic characteristics in the easy direction of magnetisation (C axis direction) were measured, they were found to be excellent as follows:—

$$Br = 7,000 \text{ G} \quad B_c H_c = 2,300 \text{ Oe} \quad BH_{\max} = 9.2 \times 10^6 \text{ G.Oe}$$

$$4\pi I_{10000} = 7,100 \text{ G} \quad I_c H_c = 2,350 \text{ Oe} \quad Br/4\pi I_{10000} = 0.98$$

(18)

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1,473,002

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- 5 A disc shaped test piece, containing the easy direction of magnetisation in a direction parallel to the major surface of the disc, was cut from this monocrystal test piece, and its magnetic torque was measured; the value of magnetic torque corresponding to an anisotropy constant, was found to be 1.07×10^7 dyne-cm/cm³. Similarly, the magnetic torque of the test pieces of S_1 , S_2 and S_4 after tempering were measured; the values obtained were 0.93×10^7 dyne-cm/cm³, 0.97×10^7 dyne-cm/cm³ and 0.95×10^7 dyne-cm/cm³ respectively. Since the degree of anisotropy is expressed by the ratio of the value of magnetic torque to that of the monocrystal, i.e., the value of 1.07×10^7 dyne-cm/cm³ above mentioned, all of these test pieces showed a very high degree of anisotropy, for example more than 0.9.
- 10 The crystal direction of the τ_c phase was substantially the same before and after tempering; the change in the crystal direction of the τ_c phase due to tempering was barely observable.
- 15 As a result of further detailed study of the phenomenon of rapid plastic deformation in the deformation of the $\epsilon_c(M)$ phase at elevated temperature, as described above and of the process of forming the unidirectionally oriented anisotropic material, it became evident that these phenomena are based on the $\epsilon_c \rightarrow \epsilon'_c \rightarrow \tau_c$ transformation occurring in specific crystal orientation relationships.
- 20 Thus, when a monocrystal in the $\epsilon_c(M)$ phase was subjected to pressure in the direction above mentioned, the matrix turns into a monocrystal of ϵ'_c having the crystal orientation relationships of

$$\epsilon_c(0001) // \epsilon'_c(100)$$

$$\epsilon_c[0001] // \epsilon'_c[100]$$

- 25 through an order-disorder transformation of $\epsilon_c \rightarrow \epsilon'_c$. This $\epsilon_c \rightarrow \epsilon'_c$ transformation corresponds to the process followed from point A to point B in Figure 3, and the dimensional reduction in the pressuring direction is not especially large.
- Furthermore, the ϵ'_c monocrystal is transformed to a τ_c monocrystal having the relationship of $\epsilon'_c(100) // \tau_c(111)$ through the $\epsilon'_c \rightarrow \tau_c$ martensitic transformation in which the specific (100) plane slides to the direction of [001] at a specific distance.
- 30 The sliding of the plane to the specific direction takes place rapidly in avalanche-like manner, and induces a rapid reduction in the direction of pressure, from point B to point C. Then, at the time when the sliding of the planes in the monocrystal is complete, that is to say, when all parts of ϵ'_c have been transformed into τ_c , as at point C, the reduction of dimension in the pressure direction ceases. After all the ϵ'_c has been transformed to τ_c , little further deformation occurs, even when pressure is continued.
- 35 Figures 4a, 4b and 4c are diagrams illustrating the change of crystal structure in the $\epsilon_c \rightarrow \epsilon'_c \rightarrow \tau_c$ transformation described above. Figure 4a represents the crystal structure of the phase of ϵ_c , Figure 4b the phase of ϵ'_c , and Figure 4c the phase of τ_c . The diagram of Figure 4a depicts a view of the ϵ_c phase observed from the directions perpendicular respectively to the (0001) and (1120) planes; Figure 4b depicts the phase of ϵ'_c observed perpendicular to its (100) and (010) planes and Figure 4c the τ_c phase perpendicular to its (111) and (110) planes. The solid lines designate respective crystal lattices; the dotted lines, the locational relationship of atoms; and the arrows, the direction of movement of the plane of the atoms. The double concentric circles indicate the positions of atoms of Mn or Al in the disorder structure; the single circles and the solid circles show the positions of atoms of Al and Mn respectively in the order structure. The positions of the carbon atoms in a state of solid solution are omitted.
- 40 The τ_c after deformation has poor magnetic characteristics, but becomes an anisotropic magnet with excellent magnetic characteristics after tempering.
- 45 It is apparent from the studies made that based on such a mechanism, the phenomenon of rapid plastic deformation takes place, and the unidirectionally oriented anisotropic magnet is formed. In accordance with this conclusion, the optical microstructure of the test piece after being subjected to deformation at elevated temperature was found to be quite uniform and smooth, although the existence of the lamellar Mn_3AlC phase was observed. Figure 5 is a reproduction of a photograph showing the structure. The magnification is apparent from the scale; in the original the magnification was 1,000. The fragmented or broken structure of the crystal due to slip lines or twin structure apparent in the structure of ordinary alloys after deformation was not present.
- 50 It became evident from the studies made that the rapid plastic deformation

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occurring in the deformation of the $\epsilon_c(M)$ phase is not a deformation due to slip or twin which is to be observed in normal plastic deforming of other metals or alloys, but a deformation based on the $\epsilon'_c \rightarrow \tau_c$ martensitic transformation. Accordingly, the limiting level of this deformation is based on a mechanism different from that occurring in the deformation due to the work hardening of metals or alloys. Furthermore, it was clear that the anisotropy of elongation of the test piece after being worked as described is due to the sliding of the specific plane to a specific direction of the $\epsilon'_c \rightarrow \tau_c$ transformation.

In the test pieces of S_1 and S_2 , dimensional reductions in the pressure direction were apparent after tempering, S_1 being found to have reduced by 5.5%, and S_2 by 6.0%, with respect to the dimension before tempering. A likely explanation of this phenomenon is that there is formed from ϵ'_c crystal, produced by transformation under pressure, directionally oriented τ_c crystal, produced by the $\epsilon'_c \rightarrow \tau_c$ transformation without pressure. To obtain unidirectionally oriented magnets having superior magnetic characteristics, however, it is necessary to proceed with deformation at elevated temperature up to a point just before reaching the saturation deformation, that is, just before point C in Figure 3.

Example 4.

A study was made of plastic deformation at elevated temperatures in a manner similar to Example 3, but with different directions of applied pressure, at different temperatures and with different pressures.

A hexagonal monocrystal of the $\epsilon'_c(M)$ phase of Mn—Al—C alloy having a composition of Mn 71.93%, Al 27.02% and C 1.05%, as chemically analysed, was manufactured as in Example 2, and from this $\epsilon_c(M)$ phase monocrystal, cubic or rectangular monocrystal test pieces were cut having sides of 5 to 12 mm. The test pieces were so cut out as to have three faces (a), (b) and (c) at right angles to each other, and in relation to the direction in which pressure was to be subsequently applied:

- face (a) perpendicular to the pressure direction,
- face (b) parallel to the crystal face containing the pressure direction and the $\epsilon_c[0001]$ direction, and
- face (c) at right angles to faces (a) and (b).

The cut test pieces were deformed by applying a pressure of 10 to 40 kg/mm², by means of a hydraulic press, at a temperature range of 500° to 850°C, and were then subjected to tempering in the temperature range from 550° to 650°C. The preferred direction of magnetisation of the test pieces after tempering was determined by X-ray diffraction, measurement of magnetic torque or measurement of the magnetisation curves in different directions, to determine the magnetic properties in the preferred direction of magnetisation.

Table 3 gives the conditions under which deformation was carried out including direction of pressure, temperature and degree of deformation in the pressure direction for each test piece, and the values of its magnetic characteristics in the preferred direction of magnetisation after tempering. The pressure direction was defined by angles θ_1 and θ_2 , where θ_1 is the angle between the pressure direction and the $\epsilon_c[0001]$ direction, and θ_2 is the angle between the projected pressure direction on the $\epsilon_c(0001)$ face and the $\epsilon_c[1\bar{1}00]$. For example, the pressure direction of $\theta_1 = 90^\circ$, $\theta_2 = 0^\circ$ is perpendicular to the $\epsilon_c(1\bar{1}00)$ plane and the pressure direction perpendicular to the $(3\bar{3}04)$ plane of Example 3 is expressed approximately by $\theta_1 = 55^\circ$, $\theta_2 = 0^\circ$.

TABLE 3

Test piece	Pressure direction		Temperature (°C)	Degree of deformation (%)	Br (G)	BH _c (Oe)	BH _{max} (×10 ⁶ G.Oe)
	θ ₁	θ ₂					
S ₅	0°	0°	600	- 0.8	3,300	1,400	1.8
S ₆	20°	0°	550	- 2.6	4,750	1,550	3.3
S ₇	35°	0°	550	-12.0	6,500	2,050	7.2
S ₈	55°	0°	500	- 0.2	2,900	1,500	1.6
S ₉	55°	0°	530	-14.8	6,900	2,250	9.0
S ₁₀	55°	0°	720	-14.5	6,800	2,200	8.1
S ₁₁	55°	0°	850	-14.0	2,600	1,600	1.4
S ₁₂	55°	0°	650	- 0.4	2,950	1,400	1.1
S ₁₃	55°	0°	600	-25.0	3,100	1,800	2.0
S ₁₄	70°	0°	580	-12.0	6,600	2,000	7.3
S ₁₅	90°	0°	530	- 2.0	6,250	2,300	7.6
S ₁₆	90°	0°	560	- 3.2	6,100	2,150	7.0
S ₁₇	35°	10°	830	-12.9	6,400	2,100	7.0
S ₁₈	35°	15°	550	-11.7	6,350	2,050	6.6
S ₁₉	70°	15°	600	-10.0	6,400	1,750	6.2
S ₂₀	55°	20°	650	- 6.2	4,150	1,500	2.3
S ₂₁	50°	30°	580	- 4.4	3,700	1,350	2.2
S ₂₂	90°	30°	560	- 0.5	3,300	1,300	1.7

Considering the symmetry of the hexagonal crystal, θ₁ and θ₂ were assumed to fall within the ranges of 0° ≤ θ₁ ≤ 90°, 0° ≤ θ₂ ≤ 30°. Pressure directions falling outside these angle ranges can be otherwise expressed as though they fell within these ranges, because of the symmetry of the hexagonal crystal.

Experiments carried out with different pressure directions showed that anisotropic magnets could be produced with most directions, but that large differences of magnetic characteristics were found, depending on the specific pressure direction employed, in particular, when the pressure direction was within the ranges of 35° ≤ θ₁ ≤ 90°, 0° ≤ θ₂ ≤ 15°, as defined above anisotropic magnets having excellent magnetic characteristics were obtained with (BH)_{max} in the preferred direction of magnetisation exceeding 6 × 10⁶ G.Oe. On the other hand, with the pressure directions θ₁ = 0, θ₂ = 0, and θ₁ = 90°, θ₂ = 30°, the magnets obtained were nearly isotropic, showing only a slight predominance in magnetic characteristics in the direction at right angles to the pressure direction. The preferred direction of magnetisation, where the maximum values of magnetic characteristics are obtained, varies, depending on the pressure direction used. For example, with θ₁ = 55° and θ₂ = 0°, test piece S₉ showed a preferred direction at an angle of about 82° to the pressure direction, and with θ₁ = 70°, and θ₂ = 0°, test piece S₁₄ showed a preferred direction at about 70° to the pressure direction. The samples were in the τ_c(M) phase, unidirectionally oriented, in which the τ_c[001]

axis was abounding in the preferred direction of magnetisation. In test piece S_{13} , with $\theta_1 = 90^\circ$, $\theta_2 = 0$, the preferred direction of magnetisation lay in the pressure direction, but not the $\tau_c[001]$ axis. However, the $\tau_c[001]$ axis was found in two directions making an angle of about 37° to the pressure direction, as the centre of symmetry.

The magnetic characteristics of the $\tau_c(M)$ crystals, formed from the $\epsilon_c(M)$ monocrystals by deformation at raised temperature and tempering, depend on the degree of orientation of the $\tau_c(M)$ crystals, which in turn depends upon the direction of application of pressure. The orientation also depends on the orientation of the $\epsilon'_c(M)$ phase before being transformed: thus, when the pressure direction is within the range defined by $35^\circ \leq \theta_1 \leq 90^\circ$, $0^\circ \leq \theta_2 \leq 15^\circ$, the ϵ'_c phase of the matrix formed by the $\epsilon_c \rightarrow \epsilon'_c$ transformation is nearly unidirectionally oriented: the unidirectional or bidirectional τ_c phase was formed in the ensuing $\epsilon'_c \rightarrow \tau_c$ transformation. On the other hand, X-ray diffraction showed that with pressure directions $\theta_1 = 0^\circ$, $\theta_2 = 0^\circ$, and $\theta_1 = 90^\circ$, $\theta_2 = 30^\circ$ a multi-directional $\epsilon'_c(M)$ phase is formed, with resultant formation of the multi-directional $\tau_c(M)$ phase.

A substantially unidirectional $\epsilon'_c(M)$ phase is required to obtain anisotropic magnets having a $(BH)_{max}$ exceeding 6.0×10^6 G.Oe.

When different temperatures were used when applying pressure in directions falling within the ranges given of $35^\circ \leq \theta_1 \leq 90^\circ$, $0^\circ \leq \theta_2 \leq 15^\circ$, and within the temperature range of 530° to 830°C , anisotropic magnets having excellent magnetic characteristics with $(BH)_{max}$ exceeding 6×10^6 G.Oe were obtained; with temperatures below 500°C , anisotropisation did not occur, and there was almost negligible plasticity. Above a temperature of 850°C , the magnetic characteristics were nearly isotropic, with lessened plasticity. In addition the deformation velocity increased with rising temperature, up to 750°C .

The relationship between the degree of deformation and the magnetic characteristics was examined, and it was found that with test pieces subjected to pressure in directions falling within the range defined by $35^\circ \leq \theta_1 \leq 90^\circ$, $0^\circ \leq \theta_2 \leq 15^\circ$ the magnetic characteristics remained low when the test pieces were reduced beyond the degree of saturation deformation described in Example 3, or when the degree of deformation did not reach the value equivalent to one-tenth of this degree of saturation deformation.

The degree of saturation deformation is obtained by calculating, on the basis of the mechanism of transformation described in Example 3, the measured deformation in the pressure direction as saturation is approached, when the $\epsilon_c(M)$ monocrystal changes to the $\tau_c(M)$ monocrystal by the $\epsilon_c \rightarrow \epsilon'_c \rightarrow \tau_c$ transformation, brought about by slip of the plane of atoms as described in Example 3. Accordingly, the degree of saturation deformation differs, depending on the pressure direction. For example, changes of the degree of saturation deformation obtained with changes of θ_1 , keeping $\theta_2 = 0^\circ$, are shown in Figure 6. Test pieces deformed beyond the degrees of their saturation deformation showed isotropic elongation, did not have directionally oriented magnetic characteristics, and were all found by X-ray diffraction, to consist of a multi-directionally oriented $\tau_c(M)$ phase.

Example 5.

From the $\epsilon_c(M)$ monocrystal of Example 3, a test piece in the form of a cube $8 \times 8 \times 8$ mm was cut, having faces of (0001), (1100) and (1120). The test piece was held at a temperature of 500°C for 5 minutes. The phase structure of this test piece was examined by way of X-ray diffraction, which showed that the $\epsilon'_c(M)$ phase occupied a major part of the phase of the test piece. This test piece was placed under pressure and deformed at a temperature of 550°C , with a pressure of 35 kg/mm^2 in a direction perpendicular to (1100) plane. The magnetic characteristics of the treated test piece were measured. The magnetic characteristics in the pressure direction were:

$$Br = 5300 \text{ G}, \quad H_c = 2200 \text{ Oe}, \quad (BH)_{max} = 4.1 \times 10^6 \text{ G.Oe}$$

The same test piece was held at a temperature of 600°C for a further period of one hour, when an anisotropic magnet was obtained, having magnetic characteristics:—

$$Br = 5700 \text{ G}, \quad H_c = 2100 \text{ Oe}, \quad (BH)_{max} = 5.2 \times 10^6 \text{ G.Oe}$$

It was established that anisotropic Mn—Al—C alloy magnet can be obtained by deforming the $\epsilon'_c(M)$ phase material.

Example 6.

A Mn—Al—C alloy consisting of the unidirectional $\tau_c(M)$ phase and manufactured by the methods of Examples 3 and 4 was subjected to a plastic deformation at raised temperature with different directions of applied pressure.

Test piece S_3 of Example 4, consisting of the unidirectional $\tau_c(M)$ phase manufactured by plastic deformation at raised temperature and tempering, was again subjected to pressure, applying a pressure of 40 kg/mm² in the same direction as that of the initial application of pressure, at a temperature of 600°C. In this operation, hardly any deformation took place. Pressure application was continued, with the pressure further increased to 80 kg/mm², the test piece reduced by 8% in the direction of pressure, and isotropically elongated in the direction at right angles to the pressure direction. Measurement of the magnetic characteristics of the test piece after this pressure treatment showed that the unidirectional orientation of the $\tau_c(M)$ phase was effected, and the magnetic characteristic, in the preferred direction of magnetisation before applying pressure, gave a value of $(BH)_{\max}$ reduced to 3.8×10^6 G.Oe.

The test piece of S_3 of Example 3 consisting of the monocrystal in the $\tau_c(M)$ phase, after being tempered, was again subjected to pressure, applying a pressure of 40 kg/mm² in the direction parallel to the direction of easy magnetisation, which was nearly at right angles to the initial pressure direction, and at a temperature of 600°C. Rapid plastic deformation resulted, reaching a saturation similar to that of Figure 3. The degree of reduction in the pressure direction was -27%, while the elongation in the direction at right angles to the pressure direction was as much as 28% in the direction parallel to the initial direction pressure, but only about 1% elongation occurred in another direction at right angles, thus, a directional difference in elongation was evident. The magnetic characteristics of this test piece were measured and the preferred direction of magnetisation substantially shifted toward the direction in which the greater elongation took place, that is, the direction nearly parallel to the initial direction of pressure. The magnetic characteristics in the preferred direction of magnetisation observed before applying this pressure, that is, in the pressure direction, were appreciably reduced.

By X-ray diffraction and electron-microscope observation, it was made clear that the phenomena of marked plastic deformation taking place as the monocrystalline test piece in the $\tau_c(M)$ phase is subjected to pressure in the preferred direction of magnetisation, and of the preferred direction of magnetisation shifting, were due to the reversibility of the $\epsilon'_c \rightarrow \tau_c$ transformation, involving the slip of the atomic plane in the direction opposite to that in which the slip of the atomic plane occurs in the transformation $\epsilon'_c \rightarrow \tau_c$ previously described.

As the monocrystal in the $\tau_c(M)$ phase formed by the $\epsilon'_c \rightarrow \tau_c$ transformation of Example 3 is put under pressure in the preferred direction of magnetisation, that is, in the direction of $\tau_c[001]$, the atomic plane parallel to the $\tau_c(111)$ plane defined by $\epsilon'_c(100) \parallel \tau_c(111)$, slips a specific distance, with stress in the direction of $\tau_c[112]$. This transfer is a slip in the direction opposite that of the transfer in the $\epsilon'_c[001]$ direction in the atomic plane parallel to the $\epsilon'_c(100)$ plane in the $\epsilon'_c \rightarrow \tau_c$ transformation, which corresponds to the $\tau_c \rightarrow \epsilon'_c$ transformation. Furthermore, a new unidirectional τ_c phase, different in crystalline azimuth from the τ_c phase before application of pressure, is formed by the ϵ'_c phase, formed by the $\tau_c \rightarrow \epsilon'_c$ transformation, slipping a specific distance, in the direction of the $\epsilon'_c[001]$, in the atomic plane parallel to the $\epsilon'_c(100)$ plane. This slip of the plane parallel to the $\tau_c(111)$ plane was apparent only on the atomic plane parallel to the $\tau_c(111)$ plane defined by the relationship of $\epsilon'_c(100) \parallel \tau_c(111)$, but the plane parallel to a group of $\tau_c(111)$ planes but of different surface direction showed no slip. The structure after being subjected to pressure, was examined by an optical microscope, and found to be a uniform smooth structure except for the lamellar Mn_3AlC phase, as described in Example 3, and there was no apparent structure having slip lines. The magnetic characteristics of the newly formed $\tau_c(M)$ phase in the preferred direction of magnetisation were measured and found to be:

$$Br = 6,850 \text{ G}, \quad H_c = 1,900 \text{ Oe}, \quad (BH)_{\max} = 7.0 \times 10^6 \text{ G.Oe}$$

The test piece of S_{11} of Example 4 and having two different $\tau_c[001]$ axes, was subjected to pressure, applying a pressure of 35 kg/mm² in the direction parallel to



one $\tau_e[001]$ axis, at a temperature of 600°C. Rapid plastic deformation was produced reaching saturation as in Figure 3, and a directional difference in elongation was observed. The test piece, after application of pressure, was examined by X-ray diffraction, which confirmed that the test piece was in a unidirectional $\tau_e(M)$ phase, that the direction of its $\tau_e[001]$ axis was parallel to the direction of one $\tau_e[001]$ axis observed before the pressure and which differed from the direction of pressure and that one $\tau_e[001]$ axis was moved to the other $\tau_e[001]$ axis by the pressure step. This change of $\tau_e[001]$ axis was found to be based on the reversibility of the $\epsilon'_e \leftrightarrow \tau_e$ transformation above described. The preferred direction of magnetisation of the test piece which had been deformed was found identical to the direction of the $\tau_e[001]$ axis, and its magnetic characteristics were found to be:

$$Br = 6,800 \text{ G}, \quad H_c = 1,850 \text{ Oe}, \quad (BH)_{\max} = 6.9 \times 10^6 \text{ G.Oe}$$

thus showing an improved Br, as compared with the magnetic characteristic in the preferred direction of magnetisation observed before deformation. It was found that it was difficult to bring about the $\tau_e \rightarrow \epsilon'_e$ transformation at a temperature other than 50°C above that which causes $\epsilon'_e \rightarrow \tau_e$ transformation, and that the deformation velocity of a test piece in the $\epsilon'_e = \tau_e$ transformation increases with increased temperature up to 750°C.

Example 7.

From a monocrystal in the ϵ_e phase having a composition of Mn 71.95%, Al 26.95% and C 1.10%, as chemically analysed, manufactured by a method similar to that of Example 1, cubic or rectangular test pieces were cut. These test pieces had different crystalline surfaces with sides of 5 to 12 mm. Each test piece was subjected to tests as in Examples 3 and 4. X-ray diffraction examination showed qualitatively tendencies similar to those observed in Examples 3 and 4, as regards the relationship between the pressure direction and the degree of deformation, the relationship between the pressure direction and the degree of anisotropisation, and the existence of the ϵ'_e phase.

Experimental results obtained with a test piece in the ϵ_e phase having no lamellar Mn_3AlC phase, as compared with the test results with the test pieces of Examples 3 and 4 in which Mn_3AlC was in lamellae, showed that its deformability was low: while in Examples 3 and 4, pressures of only 15 to 40 kg/mm² were required for deformation, in this case, pressures of 35 to 60 kg/mm², appreciably larger, were required, and the anisotropic material, because of the low orientation in its τ_e phase, was found to have magnetic characteristics inferior to those of Examples 3 and 4.

As an example, pressure was applied to a monocrystalline ϵ_e test piece of composition as mentioned above in the pressure direction corresponding to $\theta_1 = 90^\circ$, $\theta_2 = 0^\circ$ with a pressure of 50 kg/mm², at a temperature of 560°C. The degree of deformation in the pressure direction was found to be -1.9%, and measurement showed it to be nonmagnetic. The test piece, after pressure treatment, was examined by X-ray diffraction in various directions; only the diffraction pattern from the ϵ'_e phase was observed, and it was found to have its $\epsilon'_e[001]$ axis mainly in the pressure direction, but was not identified as a monocrystal. The phase was observed under an optical microscope, and a criss-crossing structure was observed on the surface of the test piece, and a crystal in the ϵ'_e phase differing in crystalline azimuth was also observed. The test piece which had been subjected to pressure was tempered at 570°C for 4 hours and as a result there was obtained an anisotropic magnet with its preferred direction of magnetisation in the pressure direction; its magnetic characteristics in the pressure direction were:

$$Br = 5,450 \text{ G}, \quad H_c = 2,200 \text{ Oe}, \quad (BH)_{\max} = 3.3 \times 10^6 \text{ G.Oe}$$

In the direction at right angles to the pressure direction, and corresponding to the $[11\bar{2}0]$ direction before application of pressure the magnetic characteristics were:

$$Br = 1,000 \text{ G}, \quad H_c = 600 \text{ Oe}, \quad (BH)_{\max} = 0.2 \times 10^6 \text{ G.Oe}$$

In another direction at right angles to the pressure direction the magnetic characteristics were:

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$B_r = 2,400 \text{ G}$, $H_c = 1,400 \text{ Oe}$, $(BH)_{\max} = 0.9 \times 10^6 \text{ G.Oe}$

Comparison of these values of magnetic characteristics with those obtained in the similar experiment in Example 4, B_r was found about 20% lower in the preferred direction of magnetisation, $(BH)_{\max}$ about one half, and the degree of angularity of the magnetisation curve in the second quadrant was lessened, showing a lesser degree of anisotropy than that of Example 4.

No further improvement in the magnetic characteristics was obtained when the above-mentioned conditions of the temperature, pressure and the degree of deformation, and the tempering condition after pressure were varied.

When the pressure direction was widely altered, the test piece as compared with those of Example 4, gave a B_r value about 10 to 30% lower and $(BH)_{\max}$ of about one half, showing an essential difference from the results of Example 4 due to the existence of the Mn_3AlC phase.

The causes of the difference in the magnetic characteristics between Example 4 and Example 7 were investigated by optical microscope and X-ray diffraction. It was determined that in the process of deformation at elevated temperature in Example 4, the lamellar Mn_3AlC phase had the effect of enhancing the orientation of the ϵ' phase by inhibiting the development of multi-directional ϵ' phases such as the twin of the matrix ϵ' phase; accordingly, the orientation of the matrix τ_c phase, after being tempered and as observed in Example 4, was superior to that of Example 7, showing a remarkable improvement in magnetic characteristics compared with the results of Example 7.

As described above, the Mn_3AlC phase separated out in lamellae by the M treatment has the effect not only of facilitating the slip of the atomic plane in the Mn—Al—C alloys, so that it is possible to deform the material using low pressure, but also enhancing the directional effect by controlling the azimuth in the formation of the crystal. Accordingly, the existence of the lamellar Mn_3AlC phase is very important in obtaining highly anisotropic magnets with good magnetic characteristics.

Example 8.

An attempt was made to manufacture the ϵ monocrystal from an Mn—Al alloy having a composition of Mn 71.81%, and Al 28.19%, as chemically analysed, by the melting and cooling method, as in Example 1. The alloy obtained was a polycrystal in which the remaining ϵ phase was present in only a very small amount; the material consisted principally of the β -Mn phase and the $AlMn(\gamma)$ phase, though some part was recognised as the τ phase. A similar tendency was observed when the composition of Mn and Al, melting conditions and cooling conditions were widely varied. There was marked crack development when the alloy was quenched in water from such a high temperature, above 900°C , to obtain the ϵ phase. On the other hand, a Mn—Al binary alloy of the same composition mentioned was heated for one week at a temperature of $1,100^\circ$ to $1,200^\circ\text{C}$, to accelerate its recrystallisation in the ϵ phase, and was then quenched in water from this temperature; the test specimen was heavily cracked, but the ϵ phase, with a particle diameter of about 3 to 5 mm, could be obtained. From this crystal in the ϵ phase, cubic test pieces $3 \times 3 \times 3 \text{ mm}$ having surfaces parallel to (3304), (1120) and (3308) were cut from parts showing relatively large crystalline grains. The test pieces were subjected to pressure to produce a deformation of -14.7% using a pressure of 40 kg/mm^2 , at a temperature of 530°C , with force applied in the direction $\theta_1 = 55^\circ$ and $\theta_2 = 0^\circ$, that is, in the direction perpendicular to the (3304) plane.

The test piece was found out to be an isotropic magnet; its elongation was isotropic, and its magnetic characteristics were:

$B_r = 1,350 \text{ G}$, $H_c = 650 \text{ Oe}$, $(BH)_{\max} = 0.2 \times 10^6 \text{ G.Oe}$

The test piece after deformation as described was examined by X-ray diffraction, which showed diffraction lines from the τ phase, β -Mn phase and $AlMn(\gamma)$ phase but the orientation of the τ phase was barely apparent.

Widely different temperatures, pressures and degrees of deformation were tried, but the tendency described above prevailed, and test pieces in the τ phase only could not be obtained, indicating lack of anisotropy. The effect is believed to be due to the low stability of the ϵ phase and the τ phase. It is a difficulty that in the Mn—Al alloys, unlike the Mn—Al—C alloys, the τ phase exists at above 530°C

and that transition to the $\text{AlMn}(\gamma)$ phase and the β -Mn phase is accelerated by the deformation at elevated temperature. Moreover, the directional control effect due to the lamellar Mn_3AlC phase as described above, is absent.

Example 9.

There were prepared a number of samples of a monocrystal or a polycrystal with large crystalline grains in ϵ or $\epsilon_c(\text{M})$ phase of Mn—Al—C alloys, the proportions of Mn, Al and C being varied within the range of Mn 67.0 to 74.0% and C 0.1 to 2.5%. From these crystals, monocrystal test pieces in ϵ or $\epsilon_c(\text{M})$ phase were cut, and subjected to a pressure of 40 kg/mm² at a temperature of 570°C in the direction $\theta_1 = 55^\circ$ and $\theta_2 = 0^\circ$, and then tempered.

Table 4 gives the composition of the samples obtained by chemical analysis, and the values of the magnetic characteristics in the preferred direction of magnetisation, measured after tempering.

The test pieces of S_{23} and S_{24} containing carbon in amounts falling short of the solubility limit (1/10 Mn — 6.6)% were barely anisotropic, and with the $\text{AlMn}(\gamma)$ and the β -Mn phases separated, their magnetic characteristics showed low isotropy. The test piece of S_{23} had a large amount of the β -Mn phase, and that of S_{30} much of the $\text{AlMn}(\gamma)$ phase; both were of low degree of anisotropy, and showed low magnetic characteristics. The test specimens of S_{31} , S_{32} and S_{33} containing carbon in amounts in excess of the value (1/3 Mn — 22.2)% showed an Al_4C_3 phase before being subjected to deformation, also showed a low degree of anisotropy even after deformation and had nearly isotropic magnetic characteristics. In all of test specimens, S_{31} , S_{32} and S_{33} , the decay phenomenon was present. In test specimen S_{29} , the presence of the $\text{AlMn}(\gamma)$ phase was slight.

The pressure conditions were varied as to direction, temperature and degree of deformation, and the tempering conditions were also varied; the test pieces with $(\text{BH})_{\text{max}}$ less than 2.0×10^6 G.Oe, gave low magnetic characteristics, below this value.

TABLE 4

	Mn (%)	Al (%)	C (%)	Br (G)	B _{Hc} (Oe)	(BH) _{max} ($\times 10^6$ G.Oe)
S_{23}	72.02	27.43	0.55	1400	900	0.4
S_{24}	69.77	30.04	0.19	1100	550	0.2
S_{25}	73.44	25.53	1.03	2500	1250	0.9
S_{26}	72.89	25.86	1.25	6450	2350	6.4
S_{27}	71.58	27.22	1.20	6900	2250	9.0
S_{28}	70.72	28.29	0.99	6750	2200	8.0
S_{29}	68.14	31.41	0.45	6550	1900	6.8
S_{30}	67.63	32.17	0.20	1800	850	0.5
S_{31}	71.40	26.42	2.18	2500	1400	1.1
S_{32}	70.78	27.77	1.45	2750	1300	1.1
S_{33}	69.90	28.77	1.33	2600	1250	1.0

These experimental results make it clear that to attain excellent magnetic characteristics with $(\text{BH})_{\text{max}}$ higher than 6.0×10^6 G.Oe, the composition should be limited to the following ranges: Mn 68.0 to 73.0%, C (1/10 Mn — 6.6) to (1/3 Mn — 22.2)%, and the remainder Al.

Example 10.

A mixture of Mn 72%, Al 27% and C 1% was prepared. The mixture was melted at about 1,400°C for 20 minutes, and was then cast in a chill mould. The casting obtained had a composition of Mn 71.83%, Al 27.19% and C 0.98%, as chemically analysed, and under an optical microscope, columnar crystals were observed in the initially solidified parts. This casting was subjected to the M treatment at 850°C for 20 minutes, and was then quenched from this temperature; a separation of lamellar Mn₃AlC was apparent in the columnar crystalline grains, the lamellar pattern showing abounding crystalline grains at approximately right angles to the growing direction of the columnar crystals. The casting was examined by X-ray diffraction, and the diffraction lines from the ϵ_c phase and the lamellar Mn₃AlC phase were detected.

From this casting, a cubic test piece 6 × 6 × 6 mm was cut, having a surface perpendicular to the growing direction of the columnar crystal; the test piece was subjected to a pressure of 45 kg/mm², at a temperature of 650°C. The degree of reduction of the test piece in the pressure direction was found to be -25.5%. The test piece after deformation was nonmagnetic, but when tempered at 570°C for 4 hours, it turned into an anisotropic magnet with its preferred direction of magnetisation at right angles to the pressure direction. Its magnetic characteristics, as measured in the pressure direction, were found to be:

$$Br = 2,800 \text{ G}, \quad H_c = 1,500 \text{ Oe}, \quad (BH)_{\max} = 1.1 \times 10^6 \text{ G.Oe}$$

In one direction at right angles to the pressure direction and parallel to the growing direction of the columnar crystal before pressure, the magnetic characteristics were:

$$Br = 4,300 \text{ G}, \quad H_c = 2,350 \text{ Oe}, \quad (BH)_{\max} = 3.6 \times 10^6 \text{ G.Oe},$$

and in another direction at right angles to the pressure direction:

$$Br = 4,750 \text{ G}, \quad H_c = 2,400 \text{ Oe}, \quad (BH)_{\max} = 4.9 \times 10^6 \text{ G.Oe}$$

Example 11.

Rod shape castings were made, by melting and casting nine types of Mn—Al—C alloys, designated P₁ to P₉, having compositions as given in Table 5. Melting was carried out by holding a temperature of 1,430°C for 30 minutes, to cause the carbon to melt well into its solid solution. Cylindrical test pieces of 20 mm × 25 mm were cut out from the castings. Each test piece cut out was subjected to heat treatment in which it was heated at a temperature of 1,150°C for 2 hours, and then gradually cooled from this temperature to 830°C at a cooling rate of 10° to 15°C/min; it was held at 830°C for 20 minutes, and then quenched from 830°C at a cooling rate of 300° to 3,000°C/min. It was further subjected to a heat treatment of tempering at 600°C for 1 hour. Each test specimen subjected to this heat treatment was examined for its phase structure, by X-ray diffraction, optical microscopy and electron microscopy. In test pieces of the compositions of P₃ to P₉, containing carbon in excess of its solubility limit (1/10 Mn - 6.6)%, the lamellar Mn₃AlC phase and/or similar face centred cubic phase was clearly apparent especially in test pieces of compositions P₃, P₄, P₅ and P₆. In test pieces of compositions of P₁ and P₂, where the amount of carbon fell short of the solubility limit, the lamellar Mn₃AlC phase and/or similar face centred cubic phase was not present. In test pieces of compositions P₄ and P₅, where the amount of carbon was in excess of the value (1/3 Mn - 22.2)%, separation of Al₄C₃ occurred and the τ_c phase and lamellar Mn₃AlC, and/or similar face centred cubic phase was observed. In the test piece of composition P₃, the β -Mn phase, and in the test piece of composition P₇, the AlMn(p) phase, were respectively found existing in a substantial amount. In the test piece of composition P₆, the AlMn(p) phase was faintly observed.

These test specimens were subjected respectively to the following deformation at raised temperature.

A test piece of composition P₁ was pressed under a pressure of 50 kg/mm² in the axial direction of the cylinder, at a temperature of 680°C, which produced a deformation of -25% in the pressure direction. After this deformation step numerous cracks were found to be developing in the test piece, and its magnetic characteristic greatly declined. Before deformation the test piece had a value $(BH)_{\max} = 0.6 \times 10^6 \text{ G.Oe}$; after deformation it has the characteristics:

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$$Br = 1,700 \text{ G}, \quad H_c = 700 \text{ Oe}, \quad (BH)_{\max} = 0.3 \times 10^6 \text{ G.Oe}$$

indicating it to be isotropic. This test piece was examined by X-ray diffraction and large amounts of the β -Mn phase and AlMn(ν) phase were apparent, apart from a small amount of remaining τ phase. Additional tempering heat treatment merely caused a further decline in magnetic characteristics.

TABLE 5

	Mn	Al	C
P ₁	72.08	27.45	0.47
P ₂	70.21	29.55	0.24
P ₃	73.44	25.51	1.05
P ₄	72.36	26.40	1.24
P ₅	71.63	27.23	1.14
P ₆	68.86	30.78	0.40
P ₇	67.86	31.81	0.33
P ₈	71.66	26.35	1.99
P ₉	69.90	28.67	1.43

A test piece of composition P₂ was subjected to a deformation, using a pressure of 55 kg/mm² applied in the axial direction of the cylinder at a temperature of 710°C, to produce a deformation of -50%. The test piece subjected to this treatment was found to disintegrate, and its lumpy granules showed barely any magnetism, as a permanent magnet was brought near to it. This same test piece was examined by X-ray diffraction, and no τ phase was detected, only the AlMn(ν) phase and β -Mn phase. It was considered that this was due to the fact that its decomposition from the τ phase to the AlMn(ν) phase and β -Mn phase was accelerated by this deformation at elevated temperature as in the case of the P₁ test piece described above.

A test piece of composition P₃ was subjected to a compressive deformation using a pressure of 50 kg/mm² applied in the axial direction of the cylinder at a temperature of 630°C, to produce a deformation of -40%. This test piece showed a preferred direction of magnetisation in the direction of its diameter but the magnetic characteristics found in this direction were only:

$$Br = 2,600 \text{ G}, \quad H_c = 1,500 \text{ Oe}, \quad (BH)_{\max} = 1.0 \times 10^6 \text{ G.Oe}$$

Its magnetic characteristics were not improved by an additional tempering treatment. The test piece subjected to this deformation was examined by X-ray diffraction and the β -Mn phase was found present in large amounts; this is considered to have militated against improvement of the magnetic characteristics.

A test piece of composition P₄ was extruded to a degree of 65%, the degree of extrusion being expressed as the percentage decrease of sectional area of the test piece, before and after extrusion. A pressure of 40 kg/mm² was used, applied in the axial direction of the cylinder, at a temperature of 720°C. The test piece subjected to extrusion was found to be an excellent anisotropic magnet with a preferred direction of magnetisation in the extruding direction, that is, along the axis of the cylindrical test piece. The magnetic characteristics in the preferred direction of magnetisation were:

$$Br = 6,100 \text{ G}, \quad H_c = 2,200 \text{ Oe}, \quad (BH)_{\max} = 5.5 \times 10^6 \text{ G.Oe}$$

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The test piece subjected to extrusion was examined as to its phase structure by X-ray diffraction and optical microscopic observation. It was found to be in the τ_c phase and the lamellar Mn_3AlC phase, with a streak pattern of the lamellar Mn_3AlC phase nearly parallel to the extruding direction. Another test piece of composition P_4 was subjected to compression by applying a pressure of 45 kg/mm² in the direction along the axis of the cylinder, at 650°C, to produce a deformation of -53%. The preferred direction of magnetisation of the specimen after deformation was found to be in the diametral direction, with magnetic characteristics:

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$$Br = 4,900 \text{ G}, \quad B_{Hc} = 2,600 \text{ Oe}, \quad (BH)_{\max} = 4.3 \times 10^6 \text{ G.Oe}$$

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A test piece of composition P_3 was subjected to compression by applying a pressure of 45 kg/mm² in the direction along the axis of the cylinder, at 680°C, to produce a deformation of -65%. The preferred direction of magnetisation of the specimen was found in the diametral direction, with magnetic characteristics:

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$$Br = 5,050 \text{ G}, \quad B_{Hc} = 2,600 \text{ Oe}, \quad (BH)_{\max} = 4.6 \times 10^6 \text{ G.Oe}$$

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A test piece of composition P_3 was subjected to extrusion by applying a pressure of 40 kg/mm² in the direction along the axis of the cylinder, at 630°C, to produce a degree of extrusion of 65%. The preferred direction of magnetisation of the extruded specimen was in the direction of extrusion, with magnetic characteristics:

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$$Br = 5,850 \text{ G}, \quad B_{Hc} = 2,250 \text{ Oe} \quad (BH)_{\max} = 5.7 \times 10^6 \text{ G.Oe}$$

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A test piece of composition P_3 was subjected to an extrusion to produce a degree of extrusion in the direction along the axis of the cylinder, of 50%, and the temperature of extrusion was varied over the range of 500°C to 850°C. Table 6 shows the relation between the extrusion temperature and the magnetic properties in the preferred direction of magnetisation. At extrusion temperatures below 500°C, as in Example 4, the test piece had little plasticity; extrusion was difficult; the development of cracks was marked, and the test piece failed to become anisotropic. At temperatures above 830°C also, decreasing plasticity was shown with crack formation, and failure to become anisotropic. In the range of extrusion temperatures of 580° to 830°C, excellent anisotropic magnets were obtained with $(BH)_{\max}$ in excess of $4.8 \times 10^6 \text{ G.Oe}$.

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TABLE 6

Temperature (°C)	Br (G)	B_{Hc} (Oe)	$(BH)_{\max}$ ($\times 10^6 \text{ G.Oe}$)
500	2,700	1,400	1.1
530	5,850	2,050	5.0
630	6,050	2,150	5.6
730	6,000	2,100	5.5
830	5,500	2,000	4.8
850	2,550	950	0.7

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A test piece of composition P_6 was subjected to an extrusion using a pressure of 40 kg/mm² and applied in the direction along the axis of the cylinder, at a temperature of 700°C, to produce a 31% extrusion. The test piece subjected to this working showed the following magnetic characteristics in the direction of extrusion:

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$Br = 4,350 \text{ G}, H_c = 1,600 \text{ Oe}, (BH)_{\max} = 2.4 \times 10^6 \text{ G.Oe}$

This test piece, subjected to extrusion, was further subjected to extrusion by applying a pressure of 25 kg/mm^2 in the same direction, at a temperature of 700°C , to produce a degree of extrusion of 25%. The magnetic characteristics in the direction of extrusion were:

$Br = 5,700 \text{ G}, H_c = 1,950 \text{ Oe}, (BH)_{\max} = 5.0 \times 10^6 \text{ G.Oe}$

A test piece of composition P_7 was subjected to extrusion by applying a pressure of 45 kg/mm^2 in the direction of the axis of the cylinder, at a temperature of 780°C , to produce a degree of extrusion of 50%. On the test piece subjected to extrusion, cracks developed approximately perpendicular to the direction of extrusion. The magnetic characteristics in the direction of extrusion, and hence in the preferred direction of magnetisation were:

$Br = 2,750 \text{ G}, H_c = 1,700 \text{ Oe}, (BH)_{\max} = 1.8 \times 10^6 \text{ G.Oe}$

A test piece of composition P_8 was subjected to compression by applying a pressure of 50 kg/mm^2 in the direction of the axis of the cylinder, at a temperature of 750°C , to produce a degree of deformation of -76%. On the test piece subjected to this compression, cracks developed in the diametral direction, around its periphery. The preferred direction of magnetisation was found to be in the diametral direction of the test piece, with magnetic characteristics:

$Br = 3,800 \text{ G}, H_c = 1,800 \text{ Oe}, (BH)_{\max} = 2.1 \times 10^6 \text{ G.Oe}$

This test piece showed Al_4C_3 separated in it, and after several days began to disintegrate. A test piece of composition P_9 was subjected to a compression by applying a pressure of 55 kg/mm^2 in the direction of the axis of the cylinder, at 700°C , to produce a degree of deformation of -35%. The preferred direction of magnetisation of the specimen after deformation was found in the diametral direction with magnetic characteristics:

$Br = 3,400 \text{ G}, H_c = 1,700 \text{ Oe}, (BH)_{\max} = 1.9 \times 10^6 \text{ G.Oe}$

This specimen also showed Al_4C_3 separated in it, and after several days began to disintegrate.

As demonstrated by these examples, test pieces in the phase of $\tau_c(M)$ showed excellent plasticity in the temperature range from 530° to 830°C , and became highly anisotropic by the deformation at raised temperature. The test pieces thus yielded anisotropic magnets of excellent magnetic characteristics. On the other hand, when the lamellar Mn_3AlC phase was absent in the test pieces or when phases other than the τ_c phase, for example, the phases of Al_4C_3 , $\beta - Mn$ or $AlMn(\gamma)$ existed, plasticity was impaired; the degree of their anisotropy was slight, and their magnetic characteristics were low.

Accordingly, to obtain excellent anisotropic magnets, it is necessary to use compositions falling within the ranges of $Mn 68.0$ to 73.0% , $C (1/10 Mn - 6.6)\%$ to $(1/3 Mn - 22.2)\%$ and remainder Al , preferably within the ranges of $Mn 70.5$ to 72.5% , $C (1/10 Mn - 6.6)$ to $(1/3 Mn - 22.2)\%$ and the remainder Al . Also, it is necessary to subject the $\tau_c(M)$ phase within such composition ranges to a plastic deformation at raised temperature in the range of 530° to 830°C , especially with extrusion to a degree of 40 to 65%. The resultant anisotropic magnets have excellent magnetic characteristics, for example $(BH)_{\max}$ in excess of $4.8 \times 10^6 \text{ G.Oe}$. Furthermore, the mechanical strength measured after deformation showed a marked improvement, and also the machinability was excellent.

Example 12.

From a casting similar to that of Example 11 of composition P_3 , a cylindrical test piece 20 mm in diameter $\times 35 \text{ mm}$ long was cut. The test piece was held at a temperature of $1,000^\circ\text{C}$ for 5 hours, and was then cooled to 835°C at a cooling rate of 10°C/min . It was then further quenched from this temperature at a cooling rate of 300° to $3,000^\circ\text{C/min}$. The test piece was held at 500°C for 10 minutes, and it was confirmed by X-ray diffraction and optical microscopic observation of its phase structure that about 70% was the $\tau_c(M)$ phase, and the remainder the $\tau_c(M)$ phase.

This test piece was extruded by applying a pressure of 40 kg/mm^2 in the direction of the axis of the cylinder, at a temperature of 730°C to produce a degree of extrusion of 40%. The magnetic characteristics in the direction of extrusion of the test piece, after being extruded were found low, and the existence of the ϵ'_c



phase was established by X-ray diffraction. The test piece was further tempered at 600°C for 2 hours, and in this way, there was obtained an anisotropic magnet of very excellent magnetic characteristics, with a preferred direction of magnetisation in its axial direction. The magnetic characteristics in the preferred direction of magnetisation were:

$$Br = 6,200 \text{ G}, \quad H_c = 2,300 \text{ Oe}, \quad (BH)_{\max} = 6.0 \times 10^6 \text{ G.Oe}$$

The test piece had a very high mechanical strength and good machinability after extrusion, giving values equal to or higher than those obtained in Example 11.

Example 13.

From the casting of Example 11 of composition P₃, a cylindrical test piece of 20 mm in diameter and 35 mm long was cut. It was held at a temperature of 1,150°C for 2 hours, cooled down to 1,000°C, and then quenched from this temperature at a cooling rate in the range 300° to 3,000°C/min.

This test piece, in the ϵ_c phase after being quenched, was extruded by applying a pressure of 60 kg/mm² in the direction of the axis of the cylinder at a temperature of 730°C, to produce a degree of extrusion of 40%. Its deformation velocity was lower than the corresponding velocity in the extrusion of the τ_c (M) phase test piece of the same composition in Example 11, indicating lower deformability. The test piece, after being extruded, was found to be in the ϵ_c phase and ϵ'_c phase, on examination by X-ray diffraction.

After tempering the test piece at 600°C for 2 hours, the magnetic characteristics, in the extruding direction, were found to be:

$$Br = 5,200 \text{ G}, \quad H_c = 1,950 \text{ Oe}, \quad (BH)_{\max} = 4.8 \times 10^6 \text{ G.Oe}$$

The material was identified as an anisotropic magnet with its preferred direction of magnetisation in the direction of extrusion. This test piece had a very high mechanical strength and good machinability, giving values equal or better than those obtained in Examples 11 and 12.

Example 14.

From the castings of Example 11 in compositions P₁ to P₉, as given in Table 5, cylindrical test pieces of 20mm diameter x 35 mm long were cut. These test pieces were held at 1,150°C for 2 hours, and then gradually cooled down to 830°C at a cooling rate of 10°C/min. They were then subjected to the M treatment in which they were held at a temperature of 830°C for 20 minutes and subsequently quenched at a cooling rate of 1,000°C/min from this temperature.

The phase structure of these test pieces after being quenched were examined by X-ray diffraction, optical microscopy and electron microscopy. The test pieces of compositions P₃ to P₉, containing carbon in excess of its solubility limit of (1/10 Mn - 6.6)%, showed the lamellar Mn₃AlC phase and/or similar face centred cubic phase, but the test pieces of compositions P₁ and P₂, containing carbon falling short of this solubility limit, the lamellar Mn₃AlC phase and/or similar face centred cubic phase was not detected. The test pieces of compositions P₄ and P₅, containing carbon in excess of (1/3 Mn - 22.2)%, the existence of Al₄C₃, as well as the ϵ_c phase and the lamellar Mn₃AlC phase and/or similar face centred cubic phase was observed. In the test piece of composition P₃, the presence of the β - Mn phase, and in the test piece of composition P₇, the presence of the AlMn(γ) phase, were marked. The test piece of composition P₁ was found to have a small amount of the ϵ phase and large amounts of the AlMn(γ) phase and the β - Mn phase, while in the test piece of composition P₂, nearly equal amounts respectively of the τ phase, β - Mn phase and AlMn(γ) phase existed in admixture, but the ϵ phase was not detected at all.

These test pieces after being heat treated were respectively subjected to the deformation at raised temperature as described hereinafter, and then further subjected to tempering appropriate to the respective test pieces.

A test piece of composition P₁ was extruded by applying a pressure of 50 kg/mm² in the direction of the axis of the cylinder, at a temperature of 630°C, to produce a degree of extrusion of 40%. The test piece after such extrusion disintegrated into fragments of 0.5 to 2 mm, the original shape being lost. From a larger fragment a 1 mm cube was cut and further tempered at 500°C for 30 minutes. Measurements of its magnetic characteristics showed it to be isotropic, giving the following magnetic values:

$$Br = 1,200 \text{ G}, \quad H_c = 400 \text{ Oe}, \quad (BH)_{\max} = 0.1 \times 10^6 \text{ G.Oe}$$

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Examination of this test piece by X-ray diffraction showed that it was mostly in the β - Mn phase and the AlMn(γ) phase, with the small remainder of the τ phase. This is considered to be due to the fact that decomposition from the ϵ phase and the τ phase to the AlMn(γ) phase and the β - Mn phase was accelerated by the deformation at raised temperature.

A test piece of composition P₂ was compressed by applying a pressure of 45 kg/mm² in the direction of the axis of the cylinder at a temperature of 780°C, to produce a degree of deformation of -20%. The test piece, after being compressed was found to be disintegrated to an extent to have lost its original shape. Examination of this test piece after being compressed showed no existence of the τ phase, but only the AlMn(γ) phase and the β - Mn phase. This was considered to be due to the fact that decomposition from the τ phase to the AlMn(γ) phase and β - Mn phase was accelerated by the deformation at raised temperature.

A test piece of composition P₃ was compressed by applying a pressure of 40 kg/mm² in the direction of the axis of the cylinder, at a temperature of 580°C, to produce a degree of deformation of -50%. On the test piece after being compressed, a small number of cracks were detected in its diametral direction around its periphery, the same showing slight magnetism. After tempering this test piece at 570°C for 3 hours, the test piece showed a preferred direction of magnetisation in its diametral direction, but the magnetic characteristics were low:

$$Br = 2,580 \text{ G}, \quad H_c = 1,400 \text{ Oe}, \quad (BH)_{\max} = 1.3 \times 10^6 \text{ G.Oe}$$

Examination of the test piece after having been compressed and tempered showed it to have a large amount of the β - Mn phase, and this was taken to explain the failure to achieve improvement in magnetic characteristics.

A test piece of composition P₄ was extruded by applying a pressure of 40 kg/mm² in the direction of the axis of the cylinder, at a temperature of 720°C, to produce a degree of extrusion of 50%. The test piece, after being extruded, was examined by X-ray diffraction which showed the existence of the ϵ' phase, besides the Mn₃AlC phase. The magnetic characteristics of this test piece, in the direction of extrusion and measured after tempering it at 550°C for 10 hours, were found to be:

$$Br = 6,400 \text{ G}, \quad H_c = 2,550 \text{ Oe}, \quad (BH)_{\max} = 6.2 \times 10^6 \text{ G.Oe}$$

The test piece was a very excellent anisotropic magnet with its preferred direction of magnetisation in the direction of extrusion. The phase structure of this test piece was examined by X-ray diffraction and optical microscopic observation, and was found to be in the τ_c phase and the Mn₃AlC phase, and the streak pattern of the lamellar Mn₃AlC phase running nearly parallel to the direction of extrusion was also observed.

A test piece of composition P₄ was compressed, to produce a degree of deformation of -45%, by applying a pressure of 45 kg/mm² in the direction of the axis of the cylinder, at a temperature of 650°C. After being compressed the test piece was tempered at 600°C for 3 hours, and its magnetic characteristics were measured. It was an anisotropic magnet with its preferred direction magnetisation in its diametral direction. Its magnetic characteristics in the preferred direction of magnetisation were:

$$Br = 5,300 \text{ G}, \quad H_c = 2,600 \text{ Oe}, \quad (BH)_{\max} = 4.7 \times 10^6 \text{ G.Oe}$$

A test piece of composition P₅ was extruded, to produce a degree of extrusion of 50%, by applying a pressure of 45 kg/mm² in the direction of the axis of the cylinder, at a temperature of 630°C. After tempering the test piece at 550°C for 20 hours, it was an anisotropic magnet with its preferred direction of magnetisation in the direction of extrusion. Its characteristics were:

$$Br = 6,250 \text{ G}, \quad H_c = 2,500 \text{ Oe}, \quad (BH)_{\max} = 6.3 \times 10^6 \text{ G.Oe}$$

$$4\pi I_{10,000} = 6,800 \text{ G}, \quad H_c = 2,800 \text{ Oe}, \quad Br/4\pi I_{10,000} = 0.92$$

A test piece of composition P₅ was extruded to produce a degree of extrusion of 40% in the direction of the axis of the cylinder, at temperatures varied in the range of 500°C to 850°C. Table 7 shows the magnetic characteristics in the direction of extrusion measured after tempering the test piece following extrusion, for the different working temperature. With a temperature of deformation below 500°C, there was little plasticity, as in Examples 4 and 11. This posed difficulty in extrusion; there was marked development of cracks, and tempering did not render

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it anisotropic. At temperatures above 830°C, it showed diminishing plasticity, with concomitant development of cracks, and failed to become anisotropic. In the temperature ranges of 530° to 830°C, an excellent anisotropic magnet with $(BH)_{\max}$ in excess of 5.2×10^6 G.Oe was obtained, at lower degrees of extrusion than in Example 11.

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TABLE 7

Deforming temperature (°C)	Br (G)	B _{Hc} (Oe)	(BH) _{max} (×10 ⁶ G.Oe)
500	2700	1200	1.0
530	6000	1950	5.5
630	6300	2450	6.3
730	6150	2200	6.1
830	5700	2000	5.1
850	2800	1350	1.2

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A test piece of composition P₆ was extruded to produce a degree of extrusion of 31% by applying a pressure of 40 kg/mm² in the direction of the axis of the cylinder, at 650°C. After being extruded, it was tempered at 620°C for 2 hours, and was then an anisotropic magnet with its preferred direction of magnetisation in the direction of extrusion. Its magnetic characteristics in that direction were found to be:

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$$Br = 6,300 \text{ G}, \quad B_{Hc} = 2,150 \text{ Oe}, \quad (BH)_{\max} = 5.3 \times 10^6 \text{ G.Oe}$$

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A test piece of composition P₇ was compressed to a degree of deformation of -35% by applying a pressure of 45 kg/mm² in the direction of the axis of the cylinder, at a temperature of 800°C. After being compressed the test piece was tempered at 550°C for 12 hours; it was then an anisotropic magnet with its preferred direction of magnetisation in the diametral direction. Its magnetic characteristics, however, were low:

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$$Br = 1,950 \text{ G}, \quad B_{Hc} = 1,050 \text{ Oe}, \quad (BH)_{\max} = 0.7 \times 10^6 \text{ G.Oe}$$

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A test piece of composition P₈ was compressed to a degree of deformation of -18% by applying a pressure of 50 kg/mm² in the direction of the axis of the cylinder, at a temperature of 730°C. After being compressed the test piece was tempered at 570°C for 6 hours, and it was then an anisotropic magnet with its preferred direction of magnetisation in the diametral direction. Its magnetic characteristics, however, were low:

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$$Br = 3,350 \text{ G}, \quad B_{Hc} = 1,900 \text{ Oe}, \quad (BH)_{\max} = 1.7 \times 10^6 \text{ G.Oe}$$

This test piece began to disintegrate after several days.

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A test piece of composition P₉ was extruded to produce a degree of extrusion of 31%, by applying a pressure of 55 kg/mm² at 780°C in the direction of the axis of the cylinder. After being extruded the test piece showed lamellar cracks perpendicular to the direction of extrusion. After tempering this alloy at 600°C for 4 hours, it was an anisotropic magnet with its preferred direction of magnetisation in the extrusion direction, but its magnetic characteristics were found to be low:

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$$Br = 3,700 \text{ G}, \quad B_{Hc} = 2,200 \text{ Oe}, \quad (BH)_{\max} = 2.1 \times 10^6 \text{ G.Oe}$$

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This test piece also began to disintegrate after several days.

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Disc shaped test pieces were cut from the test pieces having the magnetic characteristics mentioned, with the preferred direction of magnetisation in the direction parallel to the major disc surfaces, and the magnetic torques were measured. Every test piece gave a unidirectional magnetic torque curve, the

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torques falling within the range of 0.63 to 0.86×10^7 dyne/cm/cm³. Expressing the degree of anisotropy as the ratio of this magnetic torque to the value of 1.07×10^7 dyne-cm/cm² for the τ_c monocrystal of Example 3, all the test pieces gave high degrees of anisotropy with ratios above about 0.6. In particular, the test piece with $(BH)_{\max} = 6.3 \times 10^6$ G.Oe and obtained by extruding an alloy of the P₃ composition, was found to have a magnetic torque of 0.86×10^7 dyne-cm/cm³, and excellent orientation, and was therefore an anisotropic magnet with a very high degree of anisotropy.

The above described examples indicate that the Mn—Al—C alloys having the $\epsilon_c(M)$ phase showed excellent plasticity in the temperature range of 530° to 830°C , and from these alloys, anisotropic magnets having excellent magnetic characteristics were obtained by a process of deformation at raised temperature, followed by tempering. With the examples given, with a degree of deformation 20 to 30% less than that used in Example 11, anisotropic magnets could be obtained having magnetic characteristics equal or 10 to 20% superior to those of Example 11, compared with the magnetic characteristics of the test piece in the $\tau_c(M)$ phase, given in Example 11.

Accordingly, it again appears that good anisotropic magnets can be obtained which have a composition falling within the range of Mn 68.0 to 73.0%, C (1/10 Mn - 6.6)% to (1/3 Mn - 22.2)% and the remainder Al, and preferably those within the range of Mn 70.5 to 72.5%, C (1/10 Mn - 6.6) to (1/3 Mn - 22.2)% and the remainder Al, when the conditions specified are observed. Anisotropic magnets having such excellent magnetic characteristics as $(BH)_{\max}$ greater than 5.2×10^6 G.Oe were obtained, with deformation, by way of extrusion, with a degree of extrusion of 30 to 50%. The mechanical strength and machinability of the materials measured after the deformation and subsequent tempering, were notably improved, reaching values equal or better than those of Examples 11, 12 and 13.

The magnetic torques of the test pieces having $(BH)_{\max}$ higher than 4.8×10^6 G.Oe, obtained in the above mentioned Examples 11, 12, 13, 14, were measured, and all gave values greater than 0.43×10^7 dyne-cm/cm³. All the test pieces thus showed a high degree of anisotropy, above a ratio of about 0.4, as defined above.

Example 15.

Mn, Al and C starting materials were thoroughly mixed, and melted together at about $1,450^\circ\text{C}$ for 30 minutes, thereby causing the carbon to melt fully into its solid solution; the melt was then cast to form rod shape castings of a Mn—Al—C alloy. The composition of the castings thus obtained was found by chemical analysis and is given in Table 8.

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TABLE 8

Sample No.	Mn %	Al %	C %
1	67.51	32.37	0.22
2	67.55	31.95	0.50
3	68.03	31.88	0.09
4	68.04	31.66	0.30
5	67.91	31.66	0.43
6	68.04	31.41	0.55
7	68.48	31.40	0.12
8	68.53	31.27	0.20
9	68.49	31.22	0.29
10	68.53	30.95	0.52
11	68.55	30.80	0.65
12	68.45	30.80	0.75
13	68.50	30.59	0.91
14	69.02	30.85	0.13
15	69.00	30.76	0.24
16	69.04	30.64	0.32
17	68.99	30.49	0.52
18	68.97	30.28	0.75
19	68.98	30.14	0.88
20	69.55	30.35	0.10
21	69.50	30.30	0.20
22	69.48	30.23	0.29
23	69.50	29.95	0.55
24	69.53	29.79	0.68
25	69.49	29.60	0.91
26	69.51	29.40	1.09
27	69.97	29.91	0.12
28	69.96	29.82	0.22
29	69.95	29.72	0.33
30	70.04	29.41	0.55
31	69.98	29.30	0.72
32	69.95	29.12	0.73

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TABLE 9

Sample No.	Br (G)	B _{Hc} (Oe)	(BH) _{max} ($\times 10^6$ G.Oe)
1	100	50	0.0
2	500	150	0.0
3	1300	200	0.1
4	2600	550	0.5
5	1950	500	0.3
6	2500	550	0.4
7	1450	250	0.1
8	2200	450	0.3
9	3200	550	0.6
10	3200	600	0.7
11	3150	600	0.7
12	2950	550	0.6
13	2750	550	0.5
14	1500	250	0.1
15	2400	500	0.4
16	3250	500	0.6
17	3200	650	0.8
18	3150	600	0.7
19	2900	600	0.6
20	1300	200	0.1
21	2350	400	0.3
22	2450	450	0.4
23	3200	600	0.7
24	3200	650	0.8
25	3000	650	0.7
26	2800	600	0.6
27	1250	250	0.1
28	2300	450	0.3
29	2600	450	0.4
30	3050	700	0.7
31	3100	850	0.9
32	2950	900	0.8

TABLE 8 (Cont.)

Sample No.	Mn %	Al %	C %
33	70.06	28.84	1.10
34	70.52	29.39	0.09
35	70.56	29.26	0.18
36	70.47	28.98	0.55
37	70.45	28.66	0.89
38	71.02	28.07	0.91
39	72.05	26.90	1.05

From each of these castings, a test specimen was cut, cubic in shape and $10 \times 10 \times 10$ mm, and was brought to the uniform ϵ phase or ϵ_s phase by heat treatment at $1,150^\circ\text{C}$ for 2 hours followed by quenching from 900°C or higher at a cooling rate exceeding $10^\circ\text{C}/\text{min.}$ in the temperature range of 830° to 900°C . After this heat treatment was carried out, each test specimen was examined by X-ray diffraction, optical microscopy and electron microscopy to determine its phase structure. The results were as follows:

(1) Test specimens in which the existence of Al_4C_3 was apparent included Nos. 2, 6, 12, 13, 19 and 26.

(2) Of the test specimens 2, 6, 12, 13, 19 and 26 mentioned in (1), those which had a matrix of ϵ_s single phase included Nos. 6, 12, 13, 19 and 26.

(3) Test specimens in which deposition of $\text{AlMn}(\nu)$ phase was apparent included Nos. 1, 2, 3 and 5.

(4) Test specimens other than those mentioned in (1), (2) and (3) were all found to be ϵ or ϵ_s single phase.

These test specimens were tempered in the temperature range of 480° to 830°C . With a tempering time of 30 minutes, there was an appreciable decrease of magnetic properties above 780°C for all test specimens, Nos. 1 to 39. The temperature range where the τ or τ_s phase existed stably varied greatly depending on the composition; with the tempering time of 30 minutes, the temperature was below 750°C .

The magnetic characteristics of each test specimen obtained when tempered at 700°C for 30 minutes were measured and are given in Table 9.

TABLE 9 (Cont.).

Sample No.	Br (G)	B _{Hc} (Oe)	(BH) _{max} (×10 ⁶ G.Oe)
33	2800	1200	1.0
34	1000	200	0.1
35	1550	450	0.2
36	2700	1150	0.9
37	2600	1300	1.0
38	3200	1300	1.2
39	3150	1400	1.3

5 The phase structure of each test specimen of Table 9 after being tempered was determined and it was found that in each of the specimens Nos. 1, 2, 3, 5, 7, 14, 20 27, 34 and 35, that is, the specimens containing Mn less than 68.0% or C less than 0.2%, the AlMn(γ) phase or the β - Mn phase, or both, were observed, and the Br of these specimens was found to be less than the figure of 2000 G. In contrast, in specimens containing above 0.2%, with tempering up to 750°C for 30 minutes, the τ or τ_c phase was stable and the value of Br was 2,000 G or more, but as 750°C was exceeded, the transformation to the AlMn(γ) phase and β - Mn phase began, as confirmed by the X-ray diffraction, and optical and electron microscopy. 10

The magnetic characteristics and principal phase of specimen No. 17, were determined after the specimen had been tempered for 30 minutes in the temperature range of 480 to 830°C. The results are given in Table 10.

TABLE 10

Code	Tempering temperature (°C)	Br (G)	B _{Hc} (Oe)	(BH) _{max} (×10 ⁶ G.Oe)	Phase structure
a	480	2600	400	0.4	τ_c
b	500	2800	450	0.5	τ_c
c	550	3000	560	0.6	τ_c
d	600	3200	650	0.8	τ_c
e	650	3200	650	0.8	τ_c
f	700	3200	650	0.8	τ_c
g	750	3150	600	0.7	τ_c
h	780	1800	500	0.3	$\tau_c + \text{AlMn}(\gamma) + \beta\text{-Mn}$
i ₁	800	1000	250	0.1	$\tau_c + \text{AlMn}(\gamma) + \beta\text{-Mn}$
j	830	100	50	0.0	$\text{AlMn}(\gamma) + \beta\text{-Mn} + \epsilon_c$

Example 16.

From each of the castings of specimens Nos. 1 to 39 of Example 15, a cylindrical test specimen of 20 mm in diameter and 35 mm long was cut. It was subjected to heat treatment to bring it to a uniform phase, followed by quenching, as in Example 15. The specimen was then tempered at 600°C for 30 minutes; thereafter, it was extruded in the temperature range of 500° to 800°C, by an oil operated hydraulic press at an extrusion pressure of 12.6 tons, using a die giving a surface reduction of 75%.

At an extrusion temperature below 530°C, all test specimens were reduced to small fragments, so that no test pieces were available for measurement of the magnetic characteristics. At temperatures above 530°C but below 600°C, some test pieces cracked and some did not. Even when cracking did not occur, deformability was low, and the degree of anisotropy as given by the ratio of $(BH)_{\max}$ in the direction of extrusion to that in the direction at right angles was small.

With temperatures exceeding 780°C, in all specimens except for Nos. 38 and 39, transformation to the AlMn(γ) phase and β - Mn phase took place; the magnetic property rapidly decreased, and the degree of anisotropy also diminished.

On the other hand, as regards the relationship between composition and magnetic characteristics, when C was 0.2 to (1/3 Mn - 22.2)%, the degree of anisotropy was high; for the range of 68.0 to 70.5% Mn, there was obtained an anisotropic magnet with a preferred direction of magnetisation in the direction of extrusion.

With Mn present in an amount exceeding 70.5% but less than 73.0%, only a small degree of anisotropy, or none, occurred.

Test specimen No. 17 of Example 15 was subjected to heat treatment and quenching as in Example 15, and was tempered at 600°C for 30 minutes after quenching as in the preceding example. It was then similarly extruded, with an extrusion pressure of 12.6 tons with a surface reduction of 75%. The magnetic characteristics in the direction of extrusion obtained after this treatment were measured and are given in Table 11.

TABLE 11

Code	Processing temperature (°C)	Br (G)	B _H C (Oe)	(BH) _{max} (×10 ⁶ G.Oe)
a	500	—	—	—
b	530	3150	1350	1.5
c	580	3200	1500	1.8
d	590	5050	1650	3.3
e	600	6200	1960	6.5
f	650	6450	2500	6.7
g	700	6450	2550	6.8
h	750	6350	2400	6.5
i	780	6350	2300	6.3
j	790	4950	1900	3.7
k	800	2300	1300	0.8

The test specimen Code (a) was reduced to fragments such that its magnetic characteristics could not be measured. The test specimens Codes (b), (c) and (k)

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were almost isotropic, and test specimens (d) and (j) had a lower degree of anisotropy than Codes (e) to (i). Thus, only by deformation at a temperature of 600° to 780°C, preferably 650° to 780°C, were anisotropic magnets with a high degree of anisotropy obtained.

5 All the test specimens Nos. 1 to 39 of Example 15 were tempered at 600°C for 30 minutes after subjecting them to the heat treatment and quenching as in Example 15, and were then, extruded at 700°C under a pressure of 12.5 tons with a surface reduction of 75%. The magnetic characteristics in the direction of extrusion of the specimens treated in this way were measured and are given in Table 12. 5

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TABLE 12

Sample No.	Br (G)	BHc (Oe)	(BH) _{max} ($\times 10^6$ G. Oe)
1	0	0	0
2	200	50	0.0
3	1050	400	0.1
4	6200	2200	6.0
5	1500	700	0.4
6	4350	1700	3.8
7	1150	500	0.2
8	4900	1600	4.1
9	6300	2300	6.2
10	6400	2400	6.5
11	6250	2400	6.3
12	4300	1800	4.0
13	3350	2200	2.2
14	1200	550	0.3
15	4950	1850	4.3
16	6400	2400	6.5
17	6450	2550	6.8
18	6300	2500	6.4
19	5050	2350	4.7
20	1200	450	0.2
21	4500	1600	3.7
22	4800	1900	4.5
23	6500	2600	7.1
24	6450	2600	7.0
25	6300	2550	6.3
26	6350	2250	4.8
27	1150	600	0.3
28	4550	1700	4.0
29	4800	1950	4.2
30	6000	2400	5.9
31	6250	2450	6.4

TABLE 12 (Cont.)

Sample No.	Br (G)	B _{Hc} (Oe)	(BH) _{max} ($\times 10^6$ G.Oe)
32	6100	2400	6.0
33	5800	2350	5.5
34	800	450	0.1
35	1500	700	0.4
36	5950	2250	5.5
37	5700	2100	5.2
38	3300	2450	2.4
39	3350	2500	2.5

Examination of the phase structure of the samples by X-ray diffraction, optical microscopy and electron microscopy showed that:

5 (1) Tests specimens in which one or both of the AlMn(γ) or β - Mn phases were present in large quantities included Nos. 1, 2, 3, 5, 7, 14, 20, 27, 34 and 35, that is those test specimens containing Mn being less than 68.0% or C less than 0.2%. The X-ray diffraction examination of those specimens showed that the amount of τ phase was found to be appreciably less than of those given in Table 9. 5

10 (2) Test specimens in which Al₄C₃ was observed by optical microscopy included Nos. 2, 6, 12, 13, 19 and 26, that is the test specimens in which the amount of C exceeded the value (1/3 Mn - 22.2)%. 10

These test specimens began to decay several days to several weeks later. Test specimens in which Al₄C₃ existed, showed diminished plasticity, and a diminished degree of anisotropy.

15 (3) Test specimens other than those mentioned in (1) and (2) above, that is specimens Nos. 4, 8, 9, 10, 11, 15, 16, 17, 18, 21, 22, 23, 24, 25, 26, 28, 29, 30, 31, 32, 33, 36, 37, 38, and 39, showed in the main, only τ or τ_c phase. 15

20 (4) Of the test pieces mentioned in (3), Mn₃AlC and/or a similar face centred cubic phase were found in test pieces Nos. 4, 9, 10, 11, 16, 17, 18, 23, 24, 25, 30, 31, 32, 33, 36, 37, 38, and 39, these test pieces having a composition including carbon in an amount exceeding (1/10 Mn - 6.6)% and a tendency was also noticed that the amounts of Mn₃AlC and/or similar face centred cubic phase were slightly greater after deformation at raised temperature. 20

25 Similarly, with compositions in the range of Mn 68.0 to 70.5%, C (1/10 Mn - 6.6)% to (1/3 Mn - 22.2)% and remainder Al, anisotropic magnets were obtained by plastically deforming the alloys, quenching and tempering. The magnets had excellent magnetic characteristics compared to anisotropic magnets obtained by plastically deforming the alloys tempered after M treatment, as described in Example 11. 25

30 The cause of this is not certain, but in the case of Example 11, it is surmised that the presence of a small amount of the AlMn(γ) phase reduces the degree of anisotropy, because in this composition range, the AlMn(γ) phase could be found in the phase existing in the test pieces of Example 11 before plastic deformation, but could not be found in the phase of this present example. 30

35 Also, test pieces of a composition in the range Mn 70.5 to 73.0%, C (1/10 Mn - 6.6) to (1/3 Mn - 22.2)%, and the remainder Al, were rendered anisotropic only slightly or not at all. It is considered that the reason for this is the presence of substantial amounts of spheroidised Mn₃AlC, and only small amounts of lamellar Mn₃AlC and/or similar face centred cubic phase in the alloys before plastic deformation. 35

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Example 17.

Test specimen No. 23 of Example 16 was further tempered at 550°C for 30 to

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240 minutes after having been extruded as in Example 16. The magnetic characteristics in the extrusion direction were measured and the results are given in Table 13.

TABLE 13

Code	Tempering time (min)	Br (G)	B _{Hc} (Oe)	(BH) _{max} (× 10 ⁶ G.Oe)
a	30	6600	2750	7.8
b	60	6600	2750	7.8
c	120	6500	2600	7.1
d	240	6150	2200	5.9

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Example 18.

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From the casting of sample No. 24 of Example 15, cylindrical test specimens were cut, each 20 mm diameter and 35 mm long. The specimens were subjected to quenching as in Example 15 and tempered at 600°C for 30 minutes. Thereafter, one part was extruded through a die, under a pressure of 12.5 tons, at a temperature of 730°C, to give a surface reduction of 65%. The magnetic characteristics in the extrusion direction were measured and were:

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$$Br = 6450 \text{ G, } B_{Hc} = 2250 \text{ Oe, } (BH)_{max} = 6.8 \times 10^6 \text{ G.Oe}$$

The other part of the sample was similarly extruded but to a surface reduction of 25% at 730°C, and was then further extruded at the same temperature, so that the surface reduction would be a total of 65%.

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After the second extrusion, the magnetic characteristics in the direction of extrusion were measured and were:

$$Br = 6450 \text{ G, } B_{Hc} = 2600 \text{ Oe, } (BH)_{max} = 7.1 \times 10^6 \text{ G.Oe}$$

The test specimen twice extruded was tempered at 550°C for 30 minutes and the magnetic characteristics in the direction of extrusion were:

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$$Br = 6500 \text{ G, } B_{Hc} = 2700 \text{ Oe, } (BH)_{max} = 7.5 \times 10^6 \text{ G.Oe}$$

Example 19.

Test specimen No. 39 of Example 15 was extruded under the conditions described in Example 18. After a single extrusion to a surface reduction of 65% the magnetic characteristics both in the direction of extrusion and in the direction at right angles were measured and were:

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$$Br = 3300 \text{ G, } B_{Hc} = 2450 \text{ Oe, } (BH)_{max} = 2.3 \times 10^6 \text{ G.Oe}$$

After the second extrusion, to a total surface reduction of 65%, extrusion being carried out as in Example 18, the magnetic characteristics both in the direction of extrusion and in the direction at right angles were measured and were:

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$$Br = 3350 \text{ G, } B_{Hc} = 2400 \text{ Oe, } (BH)_{max} = 2.3 \times 10^6 \text{ G.Oe}$$

After the test specimen had been subjected to the second extrusion, it was further tempered at 550°C for 30 minutes and the magnetic characteristics in the direction of extrusion were measured and were:

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$$Br = 3200 \text{ G, } B_{Hc} = 2200 \text{ Oe, } (BH)_{max} = 2.0 \times 10^6 \text{ G.Oe}$$

Example 20.

A series of rod shaped test specimens having different compositions within the limits, Mn 67.5 to 73.0%, C (1/5 Mn - 13.3) ± 0.03% with respect to the amount of Mn and the balance being Al, were cast as in Example 15. From each of these castings, a cylindrical test piece of 20 mm diameter and 35 mm long was cut. It was subjected to heat treatment and quenching, as in Example 15 and was then tempered at 600°C for 30 minutes. The tempered test piece was extruded at 730°C

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under a pressure of 12.5 tons to a surface reduction of 75%. The relationship between the proportion of Mn and the degree of anisotropisation in a typical one of these test pieces was found to be as shown in Figure 7. A very high degree of anisotropy was achieved for Mn in the range of 68.0 to 70.5%.

5 The degree of anisotropy is expressed, as before, by the ratio of $(BH)_{max}$ in the direction of extrusion, that is, along the axis of the test cylinder, and the direction at right angles, that is, the diametral direction. 5

Example 21.

10 From the casting of sample No. 24 of Example 15, a cylindrical test piece 20 mm in diameter and 35 mm long was cut. It was subjected to the heat treatment and quenching as in Example 15, extruded at 700°C at a pressure of 15 tons, using a die having a reduction of 75% and tempered at 600°C for 30 minutes. The magnetic characteristics in the direction of extrusion of the test piece obtained in this way were: 10

15 $Br = 6600 \text{ G}$, $H_c = 2300 \text{ Oe}$, $(BH)_{max} = 6.8 \times 10^6 \text{ G.Oe}$ 15

Example 22.

20 From the casting of sample No. 10 of Example 15, a cylindrical test piece of 20 mm in diameter and 35 mm long was cut. It was subjected to the heat treatment and quenching as in Example 15, and tempered at 550°C for 30 minutes. It was then upset, using a die of 40 mm diameter, at 750°C, to form a test piece 40 mm in diameter and 8.8 mm long, which showed no cracks. From the outer peripheral part of this test piece, a cube $8.8 \times 8.8 \times 8.8 \text{ mm}$ was cut and by measurement of its magnetic characteristics, it was found to be an anisotropic magnet with its preferred direction of magnetisation in the diametral direction. The observed magnetic characteristics in the preferred direction of magnetisation were: 20

25 $Br = 5500 \text{ G}$, $H_c = 2400 \text{ Oe}$, $(BH)_{max} = 5.3 \times 10^6 \text{ G.Oe}$ 25

By plastic deformation as described, predetermined shapes of magnetically anisotropic material could be obtained.

Example 23.

30 A square rod-shaped test piece $30 \times 30 \times 150 \text{ mm}$ was cast, of a composition of Mn 69.28%, Al 30.28% and C 0.49%, as chemically analysed. After subjecting it to a heat treatment at 1,150°C for 2 hours, and quenching from 1,000°C to 600°C at a cooling rate of about 400°C/min., it was then tempered at 600°C for 30 minutes. This test piece was rolled at 650°C in five cycles to a thickness of 10 mm using grooved rolls with a 30 mm groove width, without producing cracks. 30

35 The formed test piece was found to be an anisotropic magnet with its preferred direction of magnetisation in the rolling direction, and the magnetic characteristics in this preferred direction of magnetisation were: 35

$Br = 6450 \text{ G}$, $H_c = 2500 \text{ Oe}$, $(BH)_{max} = 6.6 \times 10^6 \text{ G.Oe}$

Example 24. 40

40 From the casting of sample No. 16 of Example 15, a cylindrical test piece of 20 mm in diameter and 35 mm long was cut. It was subjected to heat treatment and quenching as in Example 15, and was then extruded at 700°C under a pressure of 12.5 tons, while applying a magnetic field of 3,000 Oe in the extrusion direction by means of a solenoid. It was then tempered at 600°C for 30 minutes. The test piece obtained in this way was shown to be an anisotropic magnet with its preferred direction of magnetisation in the extruding direction. The magnetic characteristics in the extrusion direction were: 45

$Br = 6550 \text{ G}$, $H_c = 2250 \text{ Oe}$, $(BH)_{max} = 6.8 \times 10^6 \text{ G.Oe}$

Example 25. 50

50 From the casting of sample No. 10 of Example 15, a cylindrical test piece of 10 mm in diameter and 20 mm long was cut. After subjecting it to the heat treatment and quenching as in Example 15, it was tempered at 600°C for 30 minutes. It was then extruded at 700°C, using a die giving reduction of 75%, ultrasonic vibration being applied, either on the die or punch, during extrusion. The magnetic characteristics in the extruding direction using a vibration frequency of 27 KHz were: 55

$$Br = 6350 \text{ G}, \quad H_c = 2600 \text{ Oe}, \quad (BH)_{\max} = 6.8 \times 10^6 \text{ G.Oe}$$

Example 26.

5 From the casting of sample No. 16 of Example 15, a cylindrical test piece of 10 mm in diameter and 20 mm long was cut. After subjecting it to the heat treatment and quenching as in Example 15, it was tempered at 600°C for 1 hour. It was then extruded at high speed, at 750°C using a die giving a reduction of 75%. With an extrusion speed of 10 m/sec., the magnetic characteristics in the direction of extrusion were: 5

$$Br = 6200 \text{ G}, \quad H_c = 2600 \text{ Oe}, \quad (BH)_{\max} = 6.4 \times 10^6 \text{ G.Oe}$$

10 The test piece could be produced without the development of cracks. 10

Example 27.

15 In studying mechanical properties, conventional isotropic Mn—Al—C magnets were superior to those of the Mn—Al magnets, but they could be machined, for example on a lathe, only with difficulty, the mechanical strength of the materials being at a low level, for example a tensile strength 2 kg/mm², elongation 0 and transverse strength 7 kg/mm². 15

20 On the other hand, test pieces which had undergone the respective treatments described in the embodiments of the invention, had mechanical strengths which were markedly improved, for example tensile strength 20 to 30 kg/mm², elongation 3 to 5% and transverse strength 30 to 40 kg/mm²; machinability was improved such that machining operations such as turning and drilling using conventional drilling machines could be performed with ease even on the magnetised materials. 20

Example 28.

25 A rod shape casting of an Mn—Al alloy having a composition of Mn 71.62% and Al 28.38%, as chemically analysed, was manufactured by melting and casting. From this casting, a cylindrical test piece of 20 mm in diameter and 36 mm long was cut. It was held at a temperature of 1,000°C for 1 hour, and was quenched in water. The test piece after being quenched showed numerous cracks. After quenching the test piece was examined by X-ray diffraction and its phase structure, and was found to consist of the ϵ phase only. 30

This ϵ phase test piece was compressed to a degree of deformation of -50% by applying a pressure of 45 kg/mm² in the direction of the axis of the cylinder, at a temperature of 650°C. The test piece after deformation was found to be isotropic, with low magnetic characteristics:

$$35 \quad Br = 1,300 \text{ G}, \quad H_c = 800 \text{ Oe}, \quad (BH)_{\max} = 0.3 \times 10^6 \text{ G.Oe} \quad 35$$

The test piece after compression was examined by X-ray diffraction and showed the β - Mn phase and AlMn(γ) phase to be present in large amounts.

40 From a rod shape casting of Mn—Al alloy having a composition of Mn 69.05% and Al 30.96%, as chemically analysed, a cylindrical test piece of 20 mm in diameter and 35 mm long was cut. The test piece was held at 1,000°C for 1 hour and quenched in water. The phase structure of the quenched test piece was found by X-ray diffraction to be in the ϵ single phase. The test piece was tempered to the τ phase, and then extruded at 650°C under a pressure of 16 tons, to a reduction of 64%. The test piece formed was isotropic, and its magnetic characteristics were: 40

$$45 \quad Br = 900 \text{ G}, \quad H_c = 450 \text{ Oe}, \quad (BH)_{\max} = 0.1 \times 10^6 \text{ G.Oe} \quad 45$$

As revealed by X-ray diffraction of the test piece after having been thus treated, large amounts of β - Mn phase and AlMn(γ) phase were present, but the τ phase was found in only a very small amount.

50 Results nearly the same were obtained when the composition of Mn and Al, the conditions of heat treatment and the conditions of treatments were altered; it was not found possible to obtain a magnetic characteristic of $(BH)_{\max}$ above 1.0×10^6 G.Oe; its mechanical strength was considered very brittle. 50

55 As described above, with the Mn—Al alloys, the stability of the ϵ phase and τ phase was not only lower than in Mn—Al—C alloys containing carbon in an amount in excess of its solubility limit, but the strain-induced transformation was promoted when the treatment was performed in temperature ranges above 530°C, so that it was virtually impossible to preserve the τ phase, and moreover, anisotropy was not obtained because of absence of the orientation control effect 55

whereby the degree of orientation is increased by the presence of the lamellar Mn₃AlC or similar phase.

Example 29.

An experiment similar to those of Example 11, 14 and 16 was carried out with Mn—Al—C—X alloys manufactured by adding an additive element X to the Mn—Al—C alloy.

An Mn—Al—C—Nb alloy, that is, where the additive X is Nb, in the shape of a cylinder 20 mm in diameter and 35 mm long and having a composition of Mn 71.47%, Al 25.06%, C 1.03% and Nb 2.44%, as chemically analysed, was manufactured by melting, casting and heat treatment as in Example 11. This alloy was determined by X-ray diffraction and optical microscopy to be mainly in the $\tau_c(M)$ phase.

This test piece was compressed to a degree of deformation of -65% in the direction of the axis of the cylinder under a pressure of 45 kg/mm² and at a temperature of 680°C. The test piece after being worked was found to be an anisotropic magnet with its preferred direction of magnetisation in the diametral direction, having the following magnetic characteristics in that direction:

$$Br = 5,200 \text{ G}, \quad H_c = 2,800 \text{ Oe}, \quad (BH)_{\max} = 4.9 \times 10^6 \text{ G.Oe}$$

This represents an improvement in $(BH)_{\max}$ over the magnetic characteristic obtained in the similar experiment with an Mn—Al—C alloy of Example 11.

Next, a cylindrical Mn—Al—C—Nb alloy test piece 20 mm in diameter and 35 mm long of a composition Mn 69.59%, Al 29.14%, C 0.72% and Nb 0.55%, as chemically analysed, was melted and cast, and then subjected to the heat treatment and quenching as in Example 15. The test piece was tempered at 600°C for 30 minutes, and its phase structure was examined by X-ray diffraction. The AlMn(γ) phase and β —Mn were not observed and substantially only the τ phase was present.

This test piece was extruded at 700°C under a pressure of 15 tons, to produce a reduction of 75%. The resulting test piece formed proved to be an anisotropic magnet with its preferred direction of magnetisation in the direction of extrusion. Its magnetic characteristics in the preferred direction of magnetisation were:

$$Br = 6200 \text{ G}, \quad H_c = 2600 \text{ Oe}, \quad (BH)_{\max} = 6.7 \times 10^6 \text{ G.Oe}$$

This represents an improvement in $(BH)_{\max}$ compared with the results obtained with test piece No. 31 of Example 16.

In further experiments, various Mn—Al—C—X alloys were prepared by adding up to 6%, based on the weight of the Mn—Al—C alloy, of one or more of β , N, Ti, Pd, Bi, V, Ag, Fe, Mo, Ni, Ge, Nb, Co, Pb, Zn, S, Ce and Sm to Mn—Al—C alloys consisting of Mn = 68.0 to 73.0%; C = (1/10 Mn - 6.6)% to (1/3 Mn - 22.2)% and the remainder Al.

Experiments similar to those of Examples 11, 14 and 16 were conducted with these alloys. Results especially notable were that an Mn—Al—C—(Nb + Mo) alloy, with 2.0% Nb and 0.5% Mo, showed an improvement of about 10% in $(BH)_{\max}$ over the results obtained in Examples 11 and 14, and that with Mn—Al—C—X alloys containing as additive elements B, Ti, Fe, Mo, Ge, Co, Ni and Nb singly or in combination of two or more, improvements in magnetic characteristics were noted.

Further Mn—Al—C—Pb alloys, with Pb added in a ratio of 3.0% by weight, had magnetic characteristics nearly equal or somewhat inferior to those obtained in Examples 11 and 14, but their plasticity was notably better. Such a tendency was also observed in Mn—Al—C—Zn alloys, containing Zn as the additive.

Also, improved magnetic characteristics were observed in Mn—Al—C—B—Ti alloys with 0.2% Ti and 0.3% B; the $(BH)_{\max}$ was improved by about 10% over that of the alloy of Example 16. Also, in Mn—Al—C—X alloys containing additive elements of B, Ti, Ni, Fe, Mo, Ge, Nb and Co, added singly or in combination within 3% by weight with respect to Mn—Al—C alloy, improved magnetic characteristics were recognised.

Further Mn—Al—C—Pb alloys with Pb added in 2.0% weight ratio, had magnetic characteristics nearly equal to or slightly less than those of Example 16, but they had notably enhanced plasticity. The similar tendency was observed where Zn was added, that is in Mn—Al—C—Zn alloys.

The various examples given above indicate abnormally large plasticity at 530° to 830°C for Mn—Al—C alloys consisting of Mn 68.0 to 73.0%, C (1/10 Mn -

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5 6.6)% to (1/3 Mn - 22.2)% and remainder Al, based on the phasal transformation of $\epsilon_c \rightarrow \epsilon'_c = \tau_c$ induced by the plastic deformation, and especially abnormally large anisotropic plasticity of the ϵ'_c phase. This phenomenon of abnormal plasticity can be called transformation plasticity. The marked anisotropy brought about by plastic deformation at raised temperature, taking advantage of this transformation plasticity, results from the slip of the atomic plane in the direction toward [001] on each of the following crystal planes:

$$\epsilon_c(0001) // \epsilon'_c(100) // \tau_c(111)$$

10 particularly on the $\epsilon'_c(100)$ plane, which accompanies the above described phase transformation, as described in detail in Examples 3, 4 and 5. Accordingly, by having the lamellar Mn_3AlC phase on the $\epsilon_c(0001)$ plane, it is possible to give preference to the desirable slip of the atomic plane on the crystal planes mentioned, so that the degree of anisotropy can be appreciably increased by taking advantage of the orientation controlling effect due to the lamellar Mn_3AlC .

15 The improved alloys described are anisotropic Mn—Al—C alloys obtained by subjecting the alloys having compositions within the ranges enclosed by the lines connecting the points A, B, C and D, as represented in the Mn—Al—C ternary diagram of Figure 8, that is the composition range of Mn 68.0 to 73.0%, C (1/10 Mn — 6.6) to (1/3 Mn — 22.2) % and remainder Al, to plastic deformation at 530° to 20 830°C.

Particularly, the degree of magnetic anisotropy of alloys having compositions within the area defined by lines connecting points E, F, C and D in Figure 8, that is, compositions of from 70.5 to 73.0% Mn, (1/10[Mn] - 6.6) to (1/3[Mn] - 22.2)% C, the remainder being Al, can be substantially increased by precipitating the lamellar Mn_3AlC phase before plastic deformation of the alloy.

25 Moreover, alloys having a very high degree of magnetic anisotropy and excellent magnetic characteristics can be obtained by subjecting alloys having compositions within the area defined by lines connecting points A, B, F and E of Figure 8, that is, compositions of from 68.0 to 70.5% Mn, (1/10[Mn] - 6.6) to (1/3[Mn] - 22.2)% C, the remainder being Al, to plastic deformation at elevated temperatures.

30 Although the mechanisms regarding polycrystals can hardly be clarified quantitatively, various phenomena described in the Examples given can be interpreted qualitatively by the similar mechanisms of deformations, transformation and magnetism of monocrystals. Thus, because polycrystals generally require the deformation needed for rotation and movement of the grain boundary, in addition to the anisotropic deformation in each crystal grain, they must be worked to a greater extent than monocrystals. Moreover, their magnetic characteristics are improved at a degree of deformation of 30 to 65%; and because of their being polycrystalline, the degree of anisotropy attained with them is 30 to 40 40% smaller than with monocrystals, but the composition range, phase structure and the deforming temperature range required for the realisation of the above described phenomena were confirmed to be really the common essentials. It was considered that the mechanism of anisotropisation is not only based on the structure induced by working.

45 The examples clearly establish that the presence of carbon in amounts in excess of the solubility limit is among the important factors for attaining such unexpectedly marked anisotropy as described, based on the mechanisms of deformation, transformation and magnetism.

50 With the materials described, the mechanical strength of anisotropic magnets of very high degrees of anisotropy, with $(BH)_{max}$ from 4.8 to 9.2×10^6 G.Oe, were 4 to 10 times as high as those of conventional Mn—Al—C magnets; they had such toughness as enabled them to be machined such as by turning; excelled in weater resistance, corrosion resistance, stability and temperature characteristics, and they were thus of high industrial value.

55 The materials were such as to make possible the use of not only extrusion and compression, but other forms of plastic deformation including, for example, wire drawing, drawing, rolling, die rolling and die upsetting, and making feasible the cutting of magnetised workpieces whilst providing anisotropic magnets with a preferred direction of magnetisation in any desired direction in a particular shape.

WHAT WE CLAIM IS:—

1. A bulk alloy which consists, by weight, of from 68.0% to 73.0% of manganese, and from (1/10[Mn] - 6.6)% to (1/3[Mn] - 22.2)% of carbon, the

46

5 6.6)% to (1/3 Mn - 22.2)% and remainder Al, based on the phasal transformation of $\epsilon_c \rightarrow \epsilon'_c = \tau_c$ induced by the plastic deformation, and especially abnormally large anisotropic plasticity of the ϵ'_c phase. This phenomenon of abnormal plasticity can be called transformation plasticity. The marked anisotropy brought about by plastic deformation at raised temperature, taking advantage of this transformation plasticity, results from the slip of the atomic plane in the direction toward [001] on each of the following crystal planes:

$$\epsilon_c(0001) // \epsilon'_c(100) // \tau_c(111)$$

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15 The improved alloys described are anisotropic Mn—Al—C alloys obtained by subjecting the alloys having compositions within the ranges enclosed by the lines connecting the points A, B, C and D, as represented in the Mn—Al—C ternary diagram of Figure 8, that is the composition range of Mn 68.0 to 73.0%, C (1/10 Mn - 6.6) to (1/3 Mn - 22.2) % and remainder Al, to plastic deformation at 530° to 830°C.

20 Particularly, the degree of magnetic anisotropy of alloys having compositions within the area defined by lines connecting points E, F, C and D in Figure 8, that is, compositions of from 70.5 to 73.0% Mn, (1/10[Mn] - 6.6) to (1/3[Mn] - 22.2)% C, the remainder being Al, can be substantially increased by precipitating the lamellar Mn_3AlC phase before plastic deformation of the alloy.

25 Moreover, alloys having a very high degree of magnetic anisotropy and excellent magnetic characteristics can be obtained by subjecting alloys having compositions within the area defined by lines connecting points A, B, F and E of Figure 8, that is, compositions of from 68.0 to 70.5% Mn, (1/10[Mn] - 6.6) to (1/3[Mn] - 22.2)% C, the remainder being Al, to plastic deformation at elevated temperatures.

30 Although the mechanisms regarding polycrystals can hardly be clarified quantitatively, various phenomena described in the Examples given can be interpreted qualitatively by the similar mechanisms of deformations, transformation and magnetism of monocrystals. Thus, because polycrystals generally require the deformation needed for rotation and movement of the grain boundary, in addition to the anisotropic deformation in each crystal grain, they must be worked to a greater extent than monocrystals. Moreover, their magnetic characteristics are improved at a degree of deformation of 30 to 65%; and because of their being polycrystalline, the degree of anisotropy attained with them is 30 to 40° smaller than with monocrystals, but the composition range, phase structure and the deforming temperature range required for the realisation of the above described phenomena were confirmed to be really the common essentials. It was considered that the mechanism of anisotropisation is not only based on the structure induced by working.

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WHAT WE CLAIM IS:—

1. A bulk alloy which consists, by weight, of from 68.0% to 73.0% of manganese, and from (1/10[Mn] - 6.6)% to (1/3[Mn] - 22.2)% of carbon, the



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remainder being aluminium together with unavoidable impurities, where [Mn] is the percentage of manganese, and which is magnetically anisotropic.

2. An alloy according to claim 1, which contains the compound Mn_3AlC and/or a face-centred cubic phase similar to Mn_3AlC , as herein defined.

3. A modification of the alloy claimed in claim 1 or 2, which further comprises up to 6% by weight, based on the weight of the Mn—Al—C alloy, of one or more of Nb, Mo, B, Ti, Fe, Ge, Ni and Co.

4. A modification of the alloy claimed in claim 1 or claim 2, which further comprises up to 6% by weight, based on the weight of the Mn—Al—C alloy, of one or both of Pb and Zn.

5. An alloy according to claim 1 or 2, substantially as herein described in any of Examples 3 to 7, 9 to 14, and 16 to 26.

6. A modification of the alloy claimed in claim 1 or 2, substantially as herein described in Example 29.

7. A method of making an alloy as claimed in any of claims 1 to 4, which comprises subjecting a Mn—Al—C alloy of the composition specified and which is free of a grainy Mn_3AlC phase (as herein defined) to plastic deformation at a temperature of from 530° to 830°C whereby the alloy is rendered magnetically anisotropic.

8. A method according to claim 7 in which the Mn—Al—C starting alloy has a hexagonal phase.

9. A method according to claim 7 in which the Mn—Al—C starting alloy has an orthorhombic phase.

10. A method according to any of claims 7 to 9, in which lamellae of the compound Mn_3AlC and/or a face-centred cubic phase similar to Mn_3AlC , as herein defined, are precipitated in the Mn—Al—C alloy prior to the deformation treatment.

11. A method according to claim 10, in which the precipitation of the lamellae is effected by cooling the alloy from a higher temperature to a temperature in the range of from 900°C to 830°C at a cooling rate of not more than 10°C/min, followed by quenching.

12. A method according to claim 10, in which the precipitation of the lamellae is effected by holding the alloy at a temperature of from 830°C to 900°C for at least 7 minutes, followed by quenching.

13. A method according to any of claims 7 to 12, in which the deformed alloy is subjected to tempering at a temperature of from 480°C to 750°C.

14. A method according to claim 7, in which the starting alloy contains 68.0% to 70.5% of manganese and in which the starting alloy is quenched from a temperature of at least 900°C and then subjected to plastic deformation at a temperature of from 600°C to 780°C.

15. A method according to claim 14, in which the quenched alloy is subjected to tempering at a temperature of from 480°C to 750°C before deformation.

16. A method according to claim 7, substantially as herein described in any of Examples 3 to 7, 9 to 14, and 16 to 26.

17. A method of making a permanent magnet which is magnetically anisotropic, which comprises magnetising the alloy claimed in any of claims 1 to 5.

18. A permanent magnet which has been made by the method claimed in claim 17.

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