

1

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FERROMAGNETIC Mn-Ga ALLOY AND METHOD OF PRODUCTION

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This invention is concerned with new ferromagnetic materials and methods for their preparation. More particularly, this invention is concerned with ferromagnetic manganese-gallium compositions and with methods for their preparation.

Various ferromagnetic alloys are known which derive magnetic properties from the presence of manganese. Among these are ternary Heusler alloys as well as such binary compositions as manganese bismuthide. These compositions, especially manganese bismuthide which possesses outstanding characteristics as a permanent magnet material, have found utility in magnetic applications. However, in spite of the fact that manganese is responsible for the magnetic properties of these products, the manganese content thereof is relatively low.

The present invention provides highly useful, manganese-rich ferromagnetic compositions consisting essentially of 55-70 atom percent manganese and 45-30 atom percent gallium. These compositions include (1) compositions having a tetragonal crystal structure and (2) compositions having a cubic structure.

The tetragonal manganese-gallium compositions of this invention are prepared by fusing a mixture of manganese and gallium in the desired proportions within the above stated range, solidifying the molten mass by cooling, annealing the solid at a temperature of 500-600° C., and quenching. The solid, before annealing, exhibits a cubic crystal structure, consists essentially of 55-70 atom percent manganese and 45-30 atom percent gallium, and is ferromagnetic at low temperatures. This cubic manganese-gallium composition is a feature of the present invention.

The properties of tetragonal manganese-gallium compositions depend upon the proportions of manganese and gallium employed. For example, Curie temperature increases with increasing manganese content from about 385° C. for the 55:45 (manganese:gallium) composition to about 475° C. for the 70:30 composition. The magnetic moment per gram or sigma value measured in a field of 4000 oersteds (σ_{4000}) also varies with the manganese:gallium ratio and is a maximum in the neighborhood of the 60:40 composition. Somewhat higher proportions of manganese in the range of 65-67 atom percent produce compositions having high remanence. At the extreme limits of the broad composition range, i.e., for manganese:gallium ratios of 70:30 and 55:45, the presence of minor amounts of other phases besides tetragonal phase becomes apparent. In order to avoid these other phases, it is preferred that the proportion of manganese:gallium be in the range of 68:32 to 60:40.

The cubic manganese-gallium compositions of this invention are obtained directly by solidifying the melt and can be stabilized by cooling the solid rapidly to a temperature below 400° C. The cubic composition can also be obtained by annealing the tetragonal composition at a temperature of 800° C. or above and then cooling rapidly. The properties of the cubic composition like those of the tetragonal composition, described above, depend upon the relative proportions of manganese and gallium present. For example, Curie temperature for the cubic composition increases with increasing manganese content from about -120° C. for the 55:45 composition (manganese:gal-

2

lium) to about -60° C. for the 70:30 composition. Compositions containing 60-68 atom percent manganese and 40-32 atom percent gallium are particularly desirable. The sigma value (σ_{4000}) for the cubic compositions is very high.

In preparing the compositions of this invention, manganese and gallium in the desired proportions, are thoroughly mixed and placed in a container, e.g., an alumina crucible or in a quartz tube. If desired, the container may be hermetically sealed. The container and contents are heated to a temperature and for a time sufficient to melt the ingredients completely. This temperature will usually be in the range of 1000°-1400° C. Prolonged heating is unnecessary provided complete melting is achieved. Heating is carried out in an inert surrounding environment, such as: vacuum, in which case the pressure will not exceed the autogenous pressure of the reactants; or an inert atmosphere such as argon or helium. When an inert atmosphere is employed the pressure will be approximately atmospheric pressure, i.e., in the range of 0.5-1.5 atmospheres.

After complete melting has occurred, the composition is caused to solidify by cooling to a temperature below the melting point, usually to 700-900° C. When it is desired to prepare the cubic manganese-gallium compositions, the solid is then cooled rapidly to a temperature below 400° C. When, on the other hand, the tetragonal manganese-gallium compositions are prepared, the solid is cooled to a temperature in the range of 500-600° C. and held within this temperature range until transformation to the tetragonal phase has occurred. Usually this anneal will require from 1-200 hours. After annealing, the tetragonal composition is cooled rapidly, i.e., quenched, to a temperature below 400° C. As indicated above, the tetragonal phase can be converted to the cubic phase by annealing at a temperature of 800-900° C., followed by quenching.

The time required for quenching is related to the amount of material. While very short times, i.e., a few seconds, can be achieved with small objects, longer times are required for larger objects. Quenching time usually will not exceed 1-2 minutes, or, in other words, the rate of temperature decrease during quenching will preferably be no less than 100° C./minute. It is preferred that quenching be carried out in less than one minute.

The examples below are illustrative of this invention. In these examples commercially available materials are employed and quantities are given in parts by weight except as noted. The magnetic properties described are the magnetic moment per gram measured in a 4000 oersted field (σ_{4000}), the remanence (σ_r), the remanence ratio ($\sigma_r:\sigma_{4000}$), the Curie temperature and the intrinsic coercive force, H_{ci} . These properties are described in "Ferromagnetism," by Bozorth, D. Van Nostrand Co., Inc., New York, 1951, pp. 5-8. The sigma values given herein are determined on apparatus similar to that described by T. R. Bardell on pp. 226-228 of "Magnetic Materials in the Electric Industry," Philosophical Library, New York, 1955. Values for coercive force herein are determined on a D.C. ballistic-type apparatus which is a modified form of the apparatus described by Davis and Hartenheim in the "Review of Scientific Instruments," 7, 147 (1936). The Curie temperature, T_c , is determined from measurements of the sigma value (σ_{4000}) at various temperatures.

EXAMPLE I

A blend of 2.20 g. of manganese powder and 1.39 g. of gallium cut in small pieces (Mn:Ga atom ratio, 66.7:33.3) contained in a quartz tube was heated to 200° C. during 40 minutes. In the course of this heating, the tube was alternately evacuated and flushed with

argon to eliminate air. Heating was then continued under argon to a temperature of 1150° C. which was attained after 4 hours. The sample was maintained at 1150° C. for 3.5 hours, whereupon the furnace was turned off and the sample, still in the furnace, allowed to cool. The product after removal from the quartz tube was a very hard, metallic slug which upon fracture showed a silvery interior.

This product was pulverized by grinding and the powder separated into two fractions by exposure to a magnetic field (magnetic separation) at room temperature. One fraction so obtained was strongly magnetic at room temperature and possessed a Curie temperature of 470° C. The other fraction was non-magnetic at room temperature but became strongly magnetic on cooling. The Curie temperature of this second fraction was -66° C.

In a second preparation, a composition containing manganese and gallium in the above proportions was prepared by heating the ingredients in a sealed and evacuated quartz tube to a temperature of 1107° C. over a 9-hour period, maintaining this temperature for 16.5 hours, cooling slowly to 837° C. during a 7-hour period and finally cooling to room temperature. This product also contained magnetic materials of high and low Curie temperature. X-ray diffraction analysis showed the material of low Curie temperature (-66° C.) to have a cubic crystal structure and the material of high Curie temperature to have a tetragonal crystal structure.

In a further preparation of the above manganese-gallium composition, the ingredients were heated in vacuo to 1092° C. over a 9-hour period, held at this temperature for 14 hours, slowly cooled to 700° C. over a 7.5-hour period, and finally cooled to room temperature. The material was pulverized to a particle size below 80 mesh and magnetically separated at room temperature to remove approximately 10% of the sample. The remaining 90% was a strongly magnetic material having a Curie temperature of 475° C. The X-ray diffraction pattern of this material showed it to have a tetragonal crystal structure. For determination of magnetic properties, a portion of the material was heated to 500° C. and slowly cooled to room temperature in a 5000 oersted field. The magnetic properties (measured in a field of 4000 oersted) were as follows: σ_{4000} , 28 gauss cm.³/g.; σ_r , 25 gauss cm.³/g.; remanence ratio, 0.89; intrinsic coercive force, 3060 oersteds. Analysis of the material showed Mn, 59.91; Ga, 37.62. (Mn:Ga atom ratio, 66.87:33.13).

EXAMPLE II

A mixture of manganese and gallium (atom ratio, 60:40) was placed in a quartz tube, closed at one end, which was in turn placed in a larger quartz tube. After evacuation, the outer tube was sealed, and the assembly heated to 1051° C. over a 6-hour period. Heating was continued to a temperature of 1090° C. during 15 hours. The assembly was then slowly cooled to 850° C. during 8.75 hours, and finally allowed to cool to room temperature. The product was a silvery metallic slug which was pulverized to a fine powder by grinding. This powder was shown by X-ray diffraction to consist of a cubic phase, present in major amount, and a tetragonal phase. The respective Curie temperatures were approximately -110° C. and 390° C.

A portion of the unseparated powder was pelleted, sealed in a quartz tube under vacuum, and annealed at a temperature of 843° C. for 71 hours. At the conclusion of this period, the pellet was quenched in ice water. X-ray diffraction analysis showed that the annealed pellet now consisted predominantly of the cubic phase. The Curie point measured on this pellet was -120° C.

A second portion of the above powder, pelleted and sealed in a quartz tube under vacuum, was annealed at 576° C. for 135 hours and then quenched in ice water. This pellet exhibited an X-ray diffraction pattern characteristic of the tetragonal crystal structure and had a

Curie temperature of 390° C. After cooling slowly from a temperature of 500° C. in a field of 5000 oersteds, the pellet had the following magnetic properties: σ_{4000} , 37.6 gauss cm.³/g.; σ_r , 19.2 gauss cm.³/g.; intrinsic coercive force, 1150 oersteds.

In another preparation of the manganese-gallium composition (Mn:Ga atom ratio, 60:40) carried out as described above, the product, after grinding and pelleting, was annealed at 560° C. for 162 hours in a quartz tube under vacuum, and quenched in ice water. The annealed pellet was composed entirely of crystals having a tetragonal structure as shown by its X-ray diffraction pattern and exhibited a Curie point of 390° C. The X-ray diffraction pattern indicating a tetragonal structure with cell constants: $a_0=2.75$ Å.; $c_0=3.64$ Å., is shown in Table I below.

Table I

X-RAY DIFFRACTION PATTERN OF TETRAGONAL PHASE (60:40 Mn:Ga)

Intensity ¹	Interplanar spacing ²	Intensity ¹	Interplanar spacing ²
V.....	2.753	M ₃	1.110
S.....	2.199	M ₂	1.099
M ₁	1.943	F.....	0.972
M ₃	1.823	F.....	0.889
M ₃	1.372	M ₁	0.865
M ₂	1.328	F.....	0.858
M ₂	1.165	M ₃	0.786

¹ S indicates the strongest line in the pattern, M₁, M₂, M₃ and M₄ indicate lines of moderate intensity (decreasing in the order M₁ to M₄), F indicates faint lines, and V indicates very faint lines.

² In Angstrom units.

EXAMPLE III

A composition containing manganese and gallium in the proportions 62.5:37.5 (atom ratio) was prepared by the general procedure described in Example II. The mixture was heated to a temperature of 1078° C. during 8.25 hours, then slowly heated to 1105° C. during 15.25 hours, slowly cooled to 700° C. over 8.67 hours, and finally cooled to room temperature. The silvery metallic slug obtained was pulverized. The product was strongly magnetic at low temperature and exhibited a Curie temperature of -65° C. The magnetic moment per gram (σ_{4000}) measured at -180° C. was 49 gauss cm.³/g.

The X-ray diffraction pattern of this product showed that the predominant constituent was material having a cubic crystal structure with $a_0=9.03$ Å. A little material of tetragonal structure was also present. The X-ray diffraction pattern of the cubic material is shown in Table II.

Table II

X-RAY DIFFRACTION PATTERN OF CUBIC PHASE (62.5:37.5 Mn:Ga)

Intensity ¹	Interplanar spacing ²	Intensity ¹	Interplanar spacing ²
M ₄	3.025	V.....	1.278
M ₂	2.604	M ₁	1.229
M ₃	2.421	V.....	1.152
S.....	2.130	M ₃	1.111
M ₃	1.928	M ₄	1.064
F.....	1.854	F.....	0.950
F.....	1.773	F.....	0.913
F.....	1.646	F.....	0.893
M ₂	1.507	F.....	0.868
M ₃	1.362	F.....	0.843
M ₃	1.333		

¹ S indicates the strongest line in the pattern, M₁, M₂, M₃ and M₄ indicate lines of moderate intensity (decreasing in the order M₁ to M₄), F indicates faint lines, and V indicates very faint lines.

² In Angstrom units.

EXAMPLES IV-VI

These examples illustrate the preparation of various manganese-gallium compositions. The products were prepared by heating the appropriate mixture of manganese and gallium, contained in an alumina crucible, in an atmosphere of argon under about 0.6 atmosphere pressure.

The mixtures employed and the heating conditions used are shown in Table III. The manganese-gallium composition was initially heated to the temperature shown under the heading "Heating," during the period of time indicated. The composition was next cooled to the temperature shown under the heading "Cooling," in the time indicated and finally cooled, while still in the furnace, to room temperature. The product was then annealed at a temperature of 560–570° C. for the time indicated and quenched in ice water. The properties of the products are also shown in Table III.

solid to a temperature below 400° C.; cooling finally to room temperature; and isolating the resulting solid ferromagnetic composition.

6. Process for the formation of a ferromagnetic composition consisting essentially of 55–70 atom percent manganese and 45–30 atom percent gallium, having substantially the tetragonal crystal structure which comprises: mixing the desired portions of manganese and gallium, heating the mixture in an inert environment to a temperature in the range of approximately 1000°–1400° C. to produce complete fusion; solidifying the mixture by

Table III

PREPARATION AND PROPERTIES OF MANGANESE-GALLIUM COMPOSITIONS

Example No.	Mn:Ga ratio (atom percent)	Heat-treatment					Properties of products ¹		
		Heating		Cooling		Annealing time (hrs.)	Coercive force, H _{ci} (oersteds)	Magnetic moment, σ ₄₀₀₀ (gauss cm. ³ /g.)	Curie temp., T _c (° C.)
		Temp. (° C.)	Time (min.)	Temp. (° C.)	Time (min.)				
IV-----	70:30	1350	16	900	14	183	-----	-----	475
V-----	65:35	1204	28	900	32	180	1,680	² 33	435
VI-----	55:45	1040	20	985	10	142	1,200	22	385

¹ All products were shown by X-ray diffraction to have the tetragonal crystal structure.

² Remanence ratio was 0.73.

The manganese-gallium compositions of this invention are prepared by simple processes and provide strongly magnetic materials whose properties render them suitable for use in fabrication of permanent magnets. The massive compositions are readily machined and, after grinding to powder, can be readily fabricated into intricate shapes by powder metallurgy techniques. The compositions of cubic crystal structure are particularly suited for applications requiring a material strongly magnetic at low temperatures but non-magnetic at ordinary temperatures.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows.

I claim:

1. Ferromagnetic compositions consisting essentially of 55–70 atom percent manganese and 45–30 atom percent gallium.

2. Ferromagnetic compositions consisting essentially of 55–70 atom percent manganese and 45–30 atom percent gallium, having a tetragonal crystal structure, and having a Curie temperature in the range 385° C. to 475° C. measured in a field of 4000 oersteds.

3. Ferromagnetic compositions consisting essentially of 55–70 atom percent manganese and 45–30 atom percent gallium having a cubic crystal structure.

4. Ferromagnetic compositions consisting entirely of a tetragonal crystal structure, consisting essentially of 60–68 atom percent manganese and 40–32 atom percent gallium, and having a Curie temperature in the range 385° C. to 475° C. measured in a field of 4000 oersteds.

5. Process for the formation of a ferromagnetic composition consisting essentially of 55–70 atom percent manganese and 45–30 atom percent gallium which comprises: mixing the desired proportions of manganese and gallium; heating the mixture in an inert environment to a temperature in the range of approximately 1000°–1400° C. to produce complete fusion; cooling first to a temperature of 700–900° C. to solidify the melt; cooling the

cooling to a temperature in the range of approximately 700–900° C.; cooling the solid to a temperature in the range of approximately 500–600° C. and annealing at this temperature for 1 to 200 hours until transformation to the tetragonal phase has occurred; quenching at a cooling rate of at least 100° C. per minute to a temperature below 400° C. and isolating the resulting ferromagnetic composition.

7. Process for the formation of a ferromagnetic composition consisting essentially of 55–70 atom percent manganese and 45–30 atom percent gallium having substantially the cubic crystal structure which comprises: mixing the desired proportion of manganese and gallium; heating the mixture in an inert environment to a temperature in the range of approximately 1000–1400° C. to produce complete fusion; solidifying the mixture by cooling to a temperature in the range of approximately 700–900° C.; cooling the solid at a rate of at least 100° C. per minute to a temperature below approximately 400° C., and isolating the resulting ferromagnetic composition.

8. Ferromagnetic compositions consisting essentially of 60–68 atom percent manganese and 40–32 atom percent gallium having a cubic crystal structure.

9. Ferromagnetic compositions consisting essentially of approximately 66.7 atom percent manganese and approximately 33.3 atom percent gallium.

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