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(54) **METHOD FOR PRODUCING METAL-BASED MATERIALS FOR MAGNETIC COOLING OR HEAT PUMPS**

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(57) **ABSTRACT**

The process for preparing metal-based materials for magnetic cooling or heat pumps comprises the following steps:
 a) reacting chemical elements and/or alloys in a stoichiometry which corresponds to the metal-based material in the solid phase and/or liquid phase,
 b) if appropriate converting the reaction product from stage a) to a solid,
 c) sintering and/or heat treating the solid from stage a) or b),
 d) quenching the sintered and/or heat treated solid from stage c) at a cooling rate of at least 100 K/s.

METHOD FOR PRODUCING METAL-BASED MATERIALS FOR MAGNETIC COOLING OR HEAT PUMPS

[0001] The present invention relates to processes for preparing metal-based materials for magnetic cooling or heat pumps, to materials of this type and to the use thereof. The materials prepared in accordance with the invention are used in magnetic cooling, in heat pumps or in air conditioning systems.

[0002] Materials of this type are known in principle and are described, for example, in WO 2004/068512. Magnetic cooling techniques are based on the magnetocaloric effect (MCE) and may constitute an alternative to the known vapor circulation cooling methods. In a material which exhibits a magnetocaloric effect, the alignment of randomly aligned magnetic moments by an external magnetic field leads to heating of the material. This heat can be removed from the MCE material to the surrounding atmosphere by a heat transfer. When the magnetic field is then switched off or removed, the magnetic moments revert back to a random arrangement, which leads to cooling of the material below ambient temperature. This effect can be exploited for cooling purposes; see also Nature, vol. 415, Jan. 10, 2002, pages 150 to 152. Typically, a heat transfer medium such as water is used for heat removal from the magnetocaloric material.

[0003] Customary materials are prepared by solid phase reaction of the starting elements or starting alloys for the material in a ball mill. and subsequent pressing, sintering and heat treatment under inert gas atmosphere and subsequent gradual cooling to room temperature. Such a process is described, for example, in J. Appl. Phys. 99, 2006, 08Q107.

[0004] Processing by means of melt spinning is also possible. This makes possible a more homogeneous element distribution, which leads to an improved magnetocaloric effect; cf. Rare Metals, vol. 25, October 2006, pages 544 to 549. In the process described there, the starting elements are first induction-melted in an argon gas atmosphere and then sprayed in the molten state through a nozzle onto a rotating copper roller. There follow sintering at 1000° C. and gradual cooling to room temperature.

[0005] The materials obtained by the known process frequently exhibit high thermal hysteresis. For example, in compounds of the Fe_2P type which are substituted by germanium or silicon, large values for thermal hysteresis in a wide range of 10 K or more are observed. These materials are therefore not very suitable for magnetocaloric cooling.

[0006] It is an object of the present invention to provide a process for preparing metal-based materials for magnetic cooling, which leads to a reduction in the thermal hysteresis. At the same time, a large magnetocaloric effect (MCE) should be achieved.

[0007] The object is achieved in accordance with the invention by a process for preparing metal-based materials for magnetic cooling or heat pumps, comprising the following steps:

[0008] a) reacting chemical elements and/or alloys in a stoichiometry which corresponds to the metal-based material in the solid phase and/or liquid phase,

[0009] b) if appropriate converting the reaction product from stage a) to a solid,

[0010] c) sintering and/or heat treating the solid from stage a) or b),

[0011] d) quenching the sintered and/or heat treated solid from stage c) at a cooling rate of at least 100 K/s.

[0012] It has been found in accordance with the invention that the thermal hysteresis can be reduced significantly when the metal-based materials, after sintering and/or heat treatment, are not cooled gradually to ambient temperature but rather are quenched with a high cooling rate. This cooling rate is at least 100 K/s. The cooling rate is preferably from 100 to 10 000 K/s, more preferably from 200 to 1300 K/s. Especially preferred cooling rates are from 300 to 1000 K/s.

[0013] This quenching can be achieved by any suitable cooling processes, for example by quenching the solid with water or aqueous liquids, for example cooled water or ice/water mixtures. The solids can, for example, be allowed to fall into ice-cooled water. It is also possible to quench the solids with subcooled gases such as liquid nitrogen. Further processes for quenching are known to those skilled in the art. What is advantageous here is controlled and rapid cooling.

[0014] Without being bound to a theory, the reduced hysteresis can be attributed to smaller particle sizes for the quenched compositions.

[0015] In the processes known to date, sintering and heat treatment have in each case been followed by gradual cooling, which leads to the formation of greater particle sizes and hence to an increase in the thermal hysteresis.

[0016] The rest of the preparation of the metal-based materials is less critical, provided that, in the last step, the sintered and/or heat treated solid is quenched at the inventive cooling rate. The process can be applied to the preparation of any suitable metal-based materials for magnetic cooling. Typical materials for magnetic cooling are multimetal mixtures which often comprise at least three metallic elements and additionally, if appropriate, nonmetallic elements. The expression "metal-based materials" indicates that the predominant proportion of these materials is formed from metals or metallic elements. Typically, the proportion in the overall material is at least 50% by weight, preferably at least 75% by weight, especially at least 80% by weight. Suitable metal-based materials are explained in detail hereinafter.

[0017] In step (a) of the process according to the invention, the elements and/or alloys which are present in the later metal-based material are converted in a stoichiometry which corresponds to the metal-based material in the solid or liquid phase.

[0018] Preference is given to performing the reaction in stage a) by heating the elements and/or alloys together in a closed vessel or in an extruder, or by solid phase reaction in a ball mill. Particular preference is given to performing a solid phase reaction, which is effected especially in a ball mill. Such a reaction is known in principle; cf. the documents cited in the introduction. Typically, powders of the individual elements or powders of alloys of two or more of the individual elements which are present in the later metal-based material are mixed in pulverulent form in suitable proportions by weight. If necessary, the mixture can additionally be ground in order to obtain a microcrystalline powder mixture. This powder mixture is preferably heated in a ball mill, which leads to further comminution and also good mixing, and to a solid phase reaction in the powder mixture.

[0019] Alternatively, the individual elements are mixed as a powder in the selected stoichiometry and then melted.

[0020] The combined heating in a closed vessel allows the fixing of volatile elements and control of the stoichiometry.

Specifically in the case of use of phosphorus, this would evaporate easily in an open system.

[0021] The reaction is followed by sintering and/or heat treatment of the solid, for which one or more intermediate steps can be provided. For example, the solid obtained in stage a) can be pressed before it is sintered and/or heat treated. This allows the density of the material to be increased, such that a high density of the magnetocaloric material is present in the later application. This is advantageous especially because the volume within which the magnetic field exists can be reduced, which may be associated with considerable cost savings. Pressing is known per se and can be carried out with or without pressing aids. It is possible to use any suitable mold for this pressing. By virtue of the pressing, it is already possible to obtain shaped bodies in the desired three-dimensional structure. The pressing may be followed by the sintering and/or heat treatment of stage c), followed by the quenching of stage d).

[0022] Alternatively, it is possible to send the solid obtained from the ball mill to a melt-spinning process. Melt-spinning processes are known per se and are described, for example, in Rare Metals, Vol. 25, October 2006, pages 544 to 549, and also in WO 2004/068512.

[0023] In these processes, the composition obtained in stage a) is melted and sprayed onto a rotating cold metal roller. This spraying can be achieved by means of elevated pressure upstream of the spray nozzle or reduced pressure downstream of the spray nozzle. Typically, a rotating copper drum or roller is used, which can additionally be cooled if appropriate. The copper drum preferably rotates at a surface speed of from 10 to 40 m/s, especially from 20 to 30 m/s. On the copper drum, the liquid composition is cooled at a rate of preferably from 10^2 to 10^7 K/s, more preferably at a rate of at least 10^4 K/s, especially with a rate of from 0.5 to 2×10^6 K/s.

[0024] The melt spinning, like the reaction in stage a) too, can be performed under reduced pressure or under an inert gas atmosphere.

[0025] The melt spinning achieves a high processing rate, since the subsequent sintering and heat treatment can be shortened. Specifically on the industrial scale, the production of the metal-based materials thus becomes significantly more economically viable. Spray-drying also leads to a high processing rate. Particular preference is given to performing melt spinning.

[0026] Alternatively, in stage b), spray cooling can be carried out, in which a melt of the composition from stage a) is sprayed into a spray tower. The spray tower may, for example, additionally be cooled. In spray towers, cooling rates in the range from 10^3 to 10^5 K/s, especially about 10^4 K/s, are frequently achieved.

[0027] The sintering and/or heat treatment of the solid is effected in stage c) preferably first at a temperature in the range from 800 to 1400° C. for sintering and then at a temperature in the range from 500 to 750° C. for heat treatment. These values apply especially to shaped bodies, whereas lower sintering and heat treatment temperatures can be employed for powders. For example, the sintering can then be effected at a temperature in the range from 500 to 800° C. For shaped bodies/solids, the sintering is more preferably effected at a temperature in the range from 1000 to 1300° C., especially from 1100 to 1300° C. The heat treatment can then be effected, for example, at from 600 to 700° C.

[0028] The sintering is performed preferably for a period of from 1 to 50 hours, more preferably from 2 to 20 hours, especially from 5 to 15 hours. The heat treatment is performed preferably for a period in the range from 10 to 100 hours, more preferably from 10 to 60 hours, especially from 30 to 50 hours. The exact periods can be adjusted to the practical requirements according to the material.

[0029] In the case of use of the melt-spinning process, sintering can frequently be dispensed with, and the heat treatment can be shortened significantly, for example to periods of from 5 minutes to 5 hours, preferably from 10 minutes to 1 hour. Compared to the otherwise customary values of 10 hours for sintering and 50 hours for heat treatment, this results in a major time advantage.

[0030] The sintering/heat treatment results in partial melting of the particle boundaries, such that the material is compacted further.

[0031] The melting and rapid cooling in stage b) thus allows the duration of stage c) to be reduced considerably. This also allows continuous production of the metal-based materials.

[0032] Particular preference is given in accordance with the invention to the process sequence of

[0033]   a) solid phase reaction of chemical elements and/or alloys in a stoichiometry which corresponds to the metal-based material in a ball mill,

[0034]   b) melt spinning the material obtained in stage a),

[0035]   c) heat treating the solid from stage b) at a temperature in the range from 430 to 1200° C., preferably from 800 to 1000° C., for a period of from 10 seconds or 1 minute to 5 hours, preferably from 30 minutes to 2 hours,

[0036]   d) quenching the heat treated shaped body from stage c) at a cooling rate of from 200 to 1300 K/s.

[0037] The process according to the invention can be used for any suitable metal-based materials.

[0038] The metal-based material is more preferably selected from

[0039]   (1) compounds of the general formula (I)

$$(A_yB_{y-1})_{2+\delta}C_wD_xE_z \qquad (I)$$
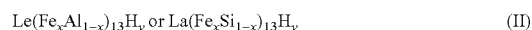
where

[0040]   A is Mn or Co,

[0041]   B is Fe, Cr or Ni,

[0042]   C, D, E at least two of C, D, E are different, have a non-vanishing concentration and are selected from P, B, Se, Ge, Ga, Si, Sn, N, As and Sb, where at least one of C, D and E is Ge or Si,

[0043]   δ is a number in the range from −0.1 to 0.1,

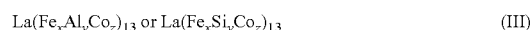[0044]   w, x, y, z are numbers in the range from 0 to 1, where w+x+z=1;

[0045]   (2) La- and Fe-based compounds of the general formulae (II) and/or (III) and/or (IV)

$$Le(Fe_xAl_{1-x})_{13}H_y \text{ or } La(Fe_xSi_{1-x})_{13}H_y \qquad (II)$$

where

[0046]   x is a number from 0.7 to 0.95;

[0047]   y is a number from 0 to 3, preferably from 0 to 2;

$$La(Fe_xAl_yCo_z)_{13} \text{ or } La(Fe_xSi_yCo_z)_{13} \qquad (III)$$

where

[0048]   x is a number from 0.7 to 0.95;

[0049]   y is a number from 0.05 to 1−x;

[0050]   z is a number from 0.005 to 0.5;

$$LaMn_xFe_{2-x}Ge \qquad (IV)$$

where

[0051] x is a number from 1.7 to 1.95 and

[0052] (3) Heusler alloys of the MnTP type where T is a transition metal and P is a p-doping metal with an electron count per atom e/a in the range from 7 to 8.5.

[0053] Materials particularly suitable in accordance with the invention are described, for example, in WO 2004/068512, Rare Metals, Vol. 25, 2006, pages 544 to 549, J. Appl. Phys. 99, 08Q107 (2006), Nature, Vol. 415, Jan. 10, 2002, pages 150 to 152 and Physica B 327 (2003), pages 431 to 437.

[0054] In the aforementioned compounds of the general formula (I), C, D and E are preferably identical or different and are selected from at least one of P, Ge, Si, Sn and Ga.

[0055] The metal-based material of the general formula (I) is preferably selected from at least quaternary compounds which, as well as Mn, Fe, P and if appropriate Sb, additionally comprise Ge or Si or As or Ge and Si or Ge and As or Si and As or Ge, Si and As.

[0056] Preferably at least 90% by weight, more preferably at least 95% by weight, of component A is Mn. Preferably at least 90% by weight, more preferably at least 95% by weight, of B is Fe. Preferably at least 90% by weight, more preferably at least 95% by weight, of C is P. Preferably at least 90% by weight, more preferably at least 95% by weight, of D is Ge. Preferably at least 90% by weight, more preferably at least 95% by weight, of E is Si.

[0057] The material preferably has the general formula $MnFe(P_wGe_xSi_z)$.

[0058] x is preferably a number in the range from 0.3 to 0.7, w is less than or equal to 1−x and z corresponds to 1−x−w.

[0059] The material preferably has the crystalline hexagonal Fe_2P structure. Examples of suitable structures are $MnFeP_{0.45}$ to 0.7, $Ge_{0.55}$ to 0.30 and $MnFeP_{0.5}$ to 0.70, $(Si/Ge)_{0.5}$ to 0.30.

[0060] Suitable compounds are additionally $M_{n1+x}Fe_{1-x}P_{1-y}Ge_y$ with x in the range from −0.3 to 0.5, y in the range from 0.1 to 0.6. Likewise suitable are compounds of the general formula $Mn_{1+x}Fe_{1-x}P_{1-y}Ge_{y-z}Sb_z$ with x in the range from −0.3 to 0.5, y in the range from 0.1 to 0.6 and z less than y and less than 0.2. Also suitable are compounds of the formula $Mn_{1+x}Fe_{1-x}P_{1-y}Ge_{y-z}Si_z$ with x in the range from 0.3 to 0.5, y in the range from 0.1 to 0.66, z less than or equal to y and less than 0.6.

[0061] Preferred La- and Fe-based compounds of the general formulae (II) and/or (III) and/or (IV) are $La(Fe_{0.90}Si_{0.10})_{13}$, $La(Fe_{0.89}Si_{0.11})_{13}$, $La(Fe_{0.880}Si_{0.120})_{13}$, $La(Fe_{0.877}Si_{0.123})_{13}$, $LaFe_{11.8}Si_{1.2}$, $La(Fe_{0.88}Si_{0.12})_{13}H_{0.5}$, $La(Fe_{0.88}Si_{0.12})13$, $La(Fe_{0.877}Si_{0.123})_{13}$, $LaFe_{11.57}Si_{1.43}H_{1.3}$, $La(Fe_{0.88}Si_{0.12})H_{1.5}$, $LaFe_{11.2}Co_{0.7}Si_{1.1}$, $LaFe_{11.5}Al_{1.5}C_{0.1}$, $LaFe_{11.5}Al_{1.5}C_{0.2}$, $LaFe_{11.5}Al_{1.5}C_{0.4}$, $LaFe_{11.5}Al_{1.5}Co_{0.5}$, $La(Fe_{0.94}Co_{0.06})_{11.83}Al_{1.17}$, $La(Fe_{0.92}Co_{0.08})_{11.83}Al_{1.17}$.

[0062] Suitable manganese-comprising compounds are $MnFeGe$, $MnFe_{0.9}Co_{0.1}Ge$, $MnFe_{0.8}Co_{0.2}Ge$, $MnFe_{0.7}Co_{0.3}Ge$, $MnFe_{0.6}Co_{0.4}Ge$, $MnFe_{0.5}Co_{0.5}Ge$, $MnFe_{0.4}Co_{0.6}Ge$, $MnFe_{0.3}Co_{0.7}Ge$, $MnFe_{0.2}Co_{0.8}Ge$, $MnFe_{0.15}Co_{0.85}Ge$, $MnFe_{0.1}Co_{0.9}Ge$, $MnCoGe$, $Mn_5Ge_{2.5}Si_{0.5}$, Mn_5Ge_2Si, $Mn_5Ge_{1.5}Si_{1.5}$, Mn_5GeSi_2, Mn_5Ge_3, $Mn_5Ge_{2.9}Sb_{0.1}$, $Mn_5Ge_{2.8}Sb_{0.2}$, $Mn_5Ge_{2.7}Sb_{0.3}$, $LaMn_{1.9}Fe_{0.1}Ge$, $LaMn_{1.85}Fe_{0.15}Ge$, $LaMn_{1.8}Fe_{0.2}Ge$, $(Fe_{0.9}Mn_{0.1})_3C$, $(Fe_{0.8}Mn_{0.2})_3C$, $(Fe_{0.7}Mn_{0.3})_3C$, Mn_3GaC, $MnAs$, $(Mn, Fe)As$, $Mn_{1+\delta}As_{0.8}Sb_{0.2}$, $MnAs_{0.75}Sb_{0.25}$, $Mn_{1.1}As_{0.75}Sb_{0.25}$, $Mn_{1.5}As_{0.75}Sb_{0.25}$.

[0063] Heusler alloys suitable in accordance with the invention are, for example, $Fe_2MnSi_{0.5}Ge_{0.5}$, $Ni_{52.9}Mn_{22.4}Ga_{24.7}$, $Ni_{50.9}Mn_{24.7}Ga_{24.4}$, $Ni_{55.2}Mn_{18.6}Ga_{26.2}$, $Ni_{51.6}Mn_{24.7}Ga_{23.8}$, $Ni_{52.7}Mn_{23.9}Ga_{23.4}$, $CoMnSb$, $CoNb_{0.2}Mn_{0.8}Sb$, $CoNb_{0.4}Mn_{0.6}SB$, $CoNb_{0.6}Mn_{0.4}Sb$, $Ni_{50}Mn_{35}Sn_{15}$, $Ni_{50}Mn_{37}Sn_{13}$, $MnFeP_{0.45}As_{0.55}$, $MnFeP_{0.47}As_{0.53}$, $Mn_{1.1}Fe_{0.9}P_{0.47}As_{0.53}$, $MnFeP_{0.89-x}Si_xGe_{0.11}$, X=0.22, X=0.26, X=0.30, X=0.33.

[0064] The invention also relates to a metal-based material for magnetic cooling, which is obtainable by a process as described above.

[0065] In addition, the invention relates to a metal-based material for magnetic cooling as defined above with reference to the composition, excluding As-comprising materials, with an average crystal size in the range from 10 to 400 nm, more preferably from 20 to 200 nm, especially from 30 to 80 nm. The average crystal size can be determined by X-ray diffraction. When the crystal size becomes too small, the maximum magnetocaloric effect is reduced. When the crystal size, in contrast, is too great, the hysteresis of the system rises.

[0066] The inventive metal-based materials are preferably used in magnetic cooling, as has been described above. A corresponding refrigerator comprises, in addition to a magnet, preferably a permanent magnet, metal-based materials as described above. The cooling of computer chips and solar power generators is also possible. Further fields of use are heat pumps and air conditioning systems.

[0067] The metal-based materials prepared by the process according to the invention may be in any desired solid form. They may also be present in the form of flakes, ribbons, wire, powders, or else in the form of shaped bodies. Shaped bodies such as monoliths or honeycombs can be produced, for example, by a hot extrusion process. It is possible, for example, for cell densities of from 400 to 1600 CPI or more to be present. Thin sheets obtainable by rolling processes are also preferred in accordance with the invention. Advantageous non-porous shaped bodies are those formed from shaped thin material, for example tubes, plates, meshes, grids or rods. Shaping by metal injection molding (MIM) processes is also possible in accordance with the invention.

[0068] The invention is illustrated in detail by the examples which follow.

EXAMPLES

Example 1

[0069] Evacuated quartz ampoules which comprised pressed samples of MnFePGe were kept at 1100° C. for 10 hours in order to sinter the powder. This sintering was followed by heat treatment at 650° C. for 60 hours in order to bring about homogenization. Instead of slow cooling in the oven to room temperature, the samples were, however, immediately quenched in water at room temperature. The quenching in water caused a certain degree of oxidation at the sample surfaces. The outer oxidized shell was removed by etching with dilute acid. The XRD patterns showed that all samples crystallized in a structure of the Fe_2P type.

[0070] The following compositions were obtained:

[0071] $Mn_{1.1}Fe_{0.9}P_{0.81}Ge_{0.19}$; $Mn_{1.1}Fe_{0.9}P_{0.78}Ge_{0.22}$, $Mn_{1.1}Fe_{0.9}P_{0.75}Ge_{0.25}$ and $Mn_{1.2}Fe_{0.8}P_{0.81}Ge_{0.19}$. The values observed for the thermal hysteresis are 7 K, 5 K, 2 K and 3 K for these samples in the given sequence. Compared to a slowly cooled sample, which has a thermal hysteresis of more than 10 K, the thermal hysteresis has been greatly reduced.

[0072] The thermal hysteresis was determined in a magnetic field of 0.5 tesla.

[0073] FIG. 1 shows the isothermal magnetization of $Mn_{1.1}Fe_{0.9}B_{0.78}Ge_{0.22}$ close to the Curie temperature with a rising magnetic field. Field-induced transition behavior which leads to a large MCE is observed for magnetic fields of up to 5 tesla.

[0074] The Curie temperature can be adjusted by varying the Mn/Fe ratio and the Ge concentration, as can the value of the thermal hysteresis.

[0075] The change in the magnetic entropy, calculated from the direct current magnetization using the Maxwell relationship, for a maximum field change of from 0 to 2 tesla, is 14 J/kgK, 20 J/kgK and 12.7 J/kgK respectively for the first three samples.

[0076] The Curie temperature and the thermal hysteresis decrease with increasing Mn/Fe ratio. As a result, the MnFePGe compounds exhibit relatively large MCE values in a low field. The thermal hysteresis of these materials is very low.

Example 2

Melt Spinning of MnFeP(GeSb)

[0077] The polycrystalline MnFeP(Ge, Sb) alloys were first produced in a ball mill with high energy input and by solid phase reaction methods, as described in WO 2004/068512 and J. Appl. Phys. 99, 08 Q107 (2006). The material pieces were then introduced into a quartz tube with a nozzle. The chamber was evacuated to a vacuum of 10^{-2} mbar and then filled with high-purity argon gas. The samples were melted by means of a high frequency and sprayed through the nozzle owing to a pressure difference to a chamber containing a rotating copper drum. The surface speed of the copper wheel was adjustable, and cooling rates of about 10^5 K/s were achieved. Subsequently, the spun ribbons were heat treated at 900° C. for one hour.

[0078] X-ray diffractometry reveals that all samples crystallize in the hexagonal Fe_2P structure pattern. In contrast to samples not produced by the melt-spinning method, no smaller contaminant phase of MnO was observed.

[0079] The resulting values for the Curie temperature, the hysteresis and the entropy were determined for different peripheral speeds in the melt-spinning. The results are listed in Tables 1 and 2 which follow. In each case, low hysteresis temperatures were determined.

TABLE 1

	V (m/s)	T_c (K)	ΔT_{hys} (K)	$-\Delta S$ (J/kgK)
Ribbons				
$Mn_{1.2}Fe_{0.8}P_{0.73}Ge_{0.25}Sb_{0.02}$	30	269	4	12.1
$Mn_{1.2}Fe_{0.8}P_{0.70}Ge_{0.20}Sb_{0.10}$	30	304	4.5	19.0
	45	314	3	11.0
$MnFeP_{0.70}Ge_{0.20}Sb_{0.10}$	20	306	8	17.2
	30	340	3	9.5
$MnFeP_{0.75}Ge_{0.25}$	20	316	9	13.5
	40	302	8	—
$Mn_{1.1}Fe_{0.9}P_{0.78}Ge_{0.22}$	20	302	5	—
	40	299	7	—
$Mn_{1.1}Fe_{0.9}P_{0.75}Ge_{0.25}$	30	283	9	11.2
$Mn_{1.2}Fe_{0.8}P_{0.75}Ge_{0.25}$	30	240	8	14.2
$Mn_{1.1}Fe_{0.9}P_{0.73}Ge_{0.27}$	30	262	5	10.1
Bulk				
$MnFeP_{0.75}Ge_{0.25}$		327	3	11.0
$Mn_{1.1}Fe_{0.9}P_{0.81}Ge_{0.19}$		260	7	14.0
$Mn_{1.1}Fe_{0.9}P_{0.78}Ge_{0.22}$		296	5	20.0
$Mn_{1.1}Fe_{0.9}P_{0.75}Ge_{0.25}$		330	2	13.0

TABLE 1-continued

	V (m/s)	T_c (K)	ΔT_{hys} (K)	$-\Delta S$ (J/kgK)
$Mn_{1.2}Fe_{0.8}P_{0.81}Ge_{0.19}$		220	3	7.7
$Mn_{1.2}Fe_{0.8}P_{0.75}Ge_{0.25}$		305	3	—
$Mn_{1.2}Fe_{0.8}P_{0.73}Ge_{0.27}$		313	5	—
$Mn_{1.3}Fe_{0.7}P_{0.78}Ge_{0.22}$		203	3	5.1
$Mn_{1.3}Fe_{0.7}P_{0.75}Ge_{0.25}$		264	1	—

TABLE 2

	T_c (K)	ΔT_{hys} (K)	$-\Delta S$ (J/kgK)
Bulk			
$MnFeP_{0.75}Ge_{0.25}$	327	3	11.0
$Mn_{1.16}Fe_{0.84}P_{0.75}Ge_{0.25}$	330	5	22.5
$Mn_{1.18}Fe_{0.82}P_{0.75}Ge_{0.25}$	310	3	16.1
$Mn_{1.20}Fe_{0.80}P_{0.75}Ge_{0.25}$	302	1	12.0
$Mn_{1.22}Fe_{0.78}P_{0.75}Ge_{0.25}$	276	4	11.7
$Mn_{1.26}Fe_{0.74}P_{0.75}Ge_{0.25}$	270	1	8.5
$Mn_{1.1}Fe_{0.9}P_{0.81}Ge_{0.19}$	260	6	13.8
$Mn_{1.1}Fe_{0.9}P_{0.78}Ge_{0.22}$	296	4	20.0
$Mn_{1.1}Fe_{0.9}P_{0.77}Ge_{0.23}$	312	2	14.6
$Mn_{1.1}Fe_{0.9}P_{0.75}Ge_{0.25}$	329	2	13.0
Ribbons			
$Mn_{1.20}Fe_{0.80}P_{0.75}Ge_{0.25}$	288	1	20.3
$Mn_{1.22}Fe_{0.78}P_{0.75}Ge_{0.25}$	274	2	15.3
$Mn_{1.24}Fe_{0.76}P_{0.75}Ge_{0.25}$	254	2	16.4
$Mn_{1.26}Fe_{0.74}P_{0.75}Ge_{0.25}$	250	4	14.4
$Mn_{1.30}Fe_{0.70}P_{0.75}Ge_{0.25}$	230	0	9.8

1. A process for preparing a metal-comprising material, the process comprising:

  a) reacting at least one chemical element and/or at least one alloy in a stoichiometry which corresponds to the metal-comprising material, in solid phase and/or liquid phase, to yield a first reaction product;

  b) optionally., converting the first reaction product from a) to a solid;

  c) sintering and/or heat treating the first reaction product from a) or the solid from b), to give a second solid; and

  d) quenching the second solid from c) at a cooling rate in a range from 200 to 1300 K/s.

2. The process according to claim 1, wherein the reacting in a) is effected by heating the at least one element and/or alloy together in a closed vessel or in an extruder, or by solid phase reaction in a ball mill.

3. The process according to claim 1, wherein the converting to a solid in b) is effected by melt spinning or spray cooling.

4. The process according to claim 1, wherein, in c), first sintering is effected at a temperature in a range from 800 to 1400° C. and then heat treating at a temperature in a range from 500 to 750° C.

5. The process according to claim 1, wherein the metal-comprising is at least one selected from the group consisting of

  (1) a compound of formula (I)

$$(A_yB_{y-1})_{2+\delta}C_wD_xE_z \qquad (I),$$

wherein

  A is Mn or Co,

  B is Fe, Cr, or Ni,

  C, D, E at least two of C, D, E are different, have a non-vanishing concentration and are selected from the group

consisting of P, B, Se, Ge, Ga, Si, Sn, N, As, and Sb, whereby at least one of C, D, and E is Ge or Si,

δ is a number in a range from −0.1 to 0.1,

w, x, y, z are numbers in a range from 0 to 1, whereby w+x+z=1;
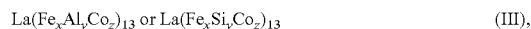
(2a) an La- and Fe-based compound of formulae (II)

$$La(Fe_xAl_{1-x})_{13}H_y \text{ or } La(Fe_xSi_{1-z})_{13}H_y \qquad (II),$$
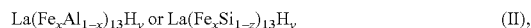
wherein

x is a number from 0.7 to 0.95, and

y is a number from 0 to 3;

(2b) an La- and Fe-based compound of formula III

$$La(Fe_xAl_yCo_z)_{13} \text{ or } La(Fe_xSi_yCo_z)_{13} \qquad (III),$$

wherein

x is a number from 0.7 to 0.95,

y is a number from 0.05 to 1−x, and

z is a number from 0.005 to 0.5;

(2c) an La- and Fe-based compound of formula IV

$$LaMn_xFe_{2-x}Ge \qquad (IV),$$

wherein

x is a number from 1.7 to 1.95; and

(3) a Heusler alloy of MnTP composition, wherein T is a transition metal and P is a p-doping metal with an electron count per atom, e/a, in a range from 7 to 8.5.

6. The process according to claim **5**, wherein the metal-comprising material is at least one at least quaternary compound of formula (I) which, as well as Mn, Fe, P, and optionally Sb, additionally comprises

Ge or Si or As, or

Ge and As, or

Si and As, or

Ge, Si and As.

7. The process according to claim **1**, wherein

a) is a solid phase reaction of the at least one element and/or alloy in a ball mill, to give a first material;

b) is melt spinning the first material obtained in a) to give a second solid;

c) is heat treating the second solid from b) at a temperature in a range from 430 to 1200° C., for a period of from 10 seconds or 1 minute to 5 hours, to give a heat treated shaped body; and

d) is quenching the heat treated shaped body from c) at a cooling rate of from 200 to 1300 K/s.

8. (canceled)

9. A metalized material, obtained by a process as defined in claim **5**, excluding As-comprising materials, with an average crystal size in a range from 10 to 400 nm.

10. (canceled)

11. The process according to claim **2**, wherein the converting to a solid in b) is effected by melt spinning or spray cooling.

12. The process according to claim **2**, wherein, in c), first sintering is effected at a temperature in a range from 800 to 1400° C. and then heat treating at a temperature in a range from 500 to 750° C.

13. The process according to claim **3**, wherein, in c), first sintering is effected at a temperature in a range from 800 to 1400° C. and then heat treating at a temperature in a range from 500 to 750° C.

14. The process according to claim **11**, wherein, in c), first sintering is effected at a temperature in a range from 800 to 1400° C. and then heat treating at a temperature in a range from 500 to 750° C.

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