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Target for magnetron cathode sputtering system consisting of a cobalt-base alloy

The invention relates to a target for magnetron cathode sputtering systems consisting of a cobalt-base alloy which contains further elements in concentrations, so that intermetallic phases are formed with at least one of these elements and intermetallic phases are observed on the basis of the phase diagram in the equilibrium state at the operating temperature of the target.

During the magnetron cathode sputtering, in order to optimize the sputtering process, permanent magnets are disposed behind the target (cathode) in such a way that in front of the target, in the discharge space, a magnetic field forms by means of which the discharge plasma is localized. The region of the target surface above which the plasma is localized is preferably sputtered, as a result of which an erosion channel forms there.

Two main problems arise in the case of ferromagnetic targets:

- Firstly, the magnetic flux of the permanent magnets is bunched in the target, so that a small flux can penetrate into the discharge space. This problem therefore necessitates the use of very thin ferromagnetic targets.

- Secondly, the local reduction in cross-sectional area of the target during the cathode sputtering (erosion channel) causes in the case of ferromagnetic targets an increasing magnetic flux directly above the erosion channel. Hence there arises a higher ionization probability of the sputtering gas locally and a higher sputtering rate locally, with the result that the erosion channel becomes very

narrow, combined with only a slight material yield of the target.

Improved magnetic field geometries and a higher penetration of the magnetic field can be obtained by means of expensive target constructions. By means of slits in the target, perpendicular to the direction of the magnetic field, the magnetic resistance in the target can be increased and a larger field in the discharge space be obtained (K. Nakamura et al., IEEE Transactions on Magnetics, Vol. MAG-18, 1982, 5.1080-1082). Kukla et al. (IEEE Transactions on Magnetics, Vol. MAG-23, 1987, 5.137-139) describe a cathode for ferromagnetic materials which consists of several individual targets that are disposed on top of one another in two planes in order to obtain a higher magnetron magnetic field. These constructions are however more expensive and make the magnetron cathode sputtering more difficult.

In DE 38 19 906 a target is described for use in magnetron cathode sputtering systems, in which the magnetic field penetration can be obtained by the adjustment of a hexagonal (0001)-fibre texture perpendicular to the target surface and in which there is achieved with a greater initial thickness a better utilization of the targets. According to DE 38 19 906 this (0001)-fibre texture is obtained by a cold forming at temperatures below 400 °C. It was found, however, that this cold forming is almost if not completely impossible to carry out if the targets contain by virtue of the alloy composition significant portions of intermetallic phases.

In EP 252 478 B1, finally, a sputter target consisting of a cobalt-base alloy is described, which exhibits only a single cubic phase at temperatures slightly below the melting point. By suitable roller formings at temperatures below the martensite transformation point, a target is then obtained the x-ray diffraction pattern of which exhibits distinctly more

hexagonal phase portions than that of the material obtained directly after the casting. It was found that the cold formings described are once again almost if not completely impossible to carry out if the cobalt-base alloys contain significant portions of intermetallic phases. In all cases serious cracks appeared in the roller plates even with small reductions in thickness.

It is therefore the object of the present invention to develop a target for magnetron cathode sputtering systems consisting of cobalt-base alloys which contain further elements in concentrations, so that intermetallic phases are formed with at least one of the elements and intermetallic phases are detectable on the basis of the phase diagram and the solidification kinetics in the equilibrium state at the operating temperature of the target. The intention is to ensure that the target exhibits a high magnetic field penetration without it having to be subjected to the cold formings described above. It is intended that in this way higher target yields are also obtained and greater target thicknesses can also be used for the class of cobalt-base alloys which contain intermetallic phases.

This object is achieved according to the invention by the fact that the target material exhibits at least one of the following two features:

a) A matrix of primary cobalt mixed crystals is present, the grain boundaries, fines boundaries or twin grain boundaries or slip bands of which are decorated with the elements forming the intermetallic phases. There are, embedded in the matrix, eutectic zones of a greater or lesser eutectic character, consisting of the cobalt mixed crystals and intermetallic phases.

b) The x-ray diffraction pattern exhibits x-ray reflections of an intermetallic phase which is not encountered as

cast and which is formed by a solids reaction below the solidus temperature of the alloy used.

This particular microstructure is obtained by heat treating the target material after the casting and after any hot-roll forming at temperatures of not more than 300 °C below the temperature for the solid-solid transformation reaction. This temperature has to be determined afresh for each alloy with some manual tests. Conventionally it lies for the cobalt-base alloys discussed in the range from 700 °C to 1100 °C. Heat treatments far below the transformation temperature lead on account of the very low diffusion rate at that time to very slow transformation reactions and correspondingly long and uneconomic heat treatment times.

The cobalt-base alloy contains in addition to elements such as Ni, Pt, Pd, Cr, also elements such as Ta, B, Mo, W, Hf, V, Nb, which form intermetallic phases with at least one of the aforementioned elements, wherein the content in elements forming intermetallic phases must be sufficiently high that in the equilibrium state at the operating temperature of the target they are no longer present fully dissolved in the cobalt mixed crystal.

It has been found, surprisingly, that targets which comprise in addition to the Co mixed crystals also intermetallic phases exhibit, after a heat treatment at a suitable temperature to be selected according to the phase diagram, a distinctly higher magnetic field penetration than targets of identical composition which have been manufactured directly out of the cast ingot or out of a plate rolled slightly below the solidus temperature.

In contrast to this, a heat treatment in the case of targets which by virtue of their composition do not exhibit any precipitations of intermetallic phases does not lead to any improvement in the magnetic field penetration. If such targets

are however subjected to one of the cold formings described in the literature, the anticipated improvement in the magnetic field penetration is obtained. A subsequent heat treatment at temperatures in the range 700 °C - 1100 °C, in accordance with the present invention, even leads in this case to a partial or complete destruction of this improvement in the magnetic field penetration. Even more astonishing, therefore, is the observed improvement in the magnetic field penetration for cobalt-base alloys which differ from these alloys only to the extent that they contain slightly higher portions of the elements Ta, B, Mo, W, Hf, V, Nb, so that intermetallic precipitation phases now form.

Careful structural and phase studies of cobalt-base alloys treated according to the present invention have shown that as a result of the heat treatment precipitations form which decorate the grain boundaries or twin grain boundaries or slip bands of the cobalt mixed crystals. These precipitations contain distinct portions of the elements which also form the intermetallic phases (see Fig. 1). In addition, phase investigations by means of x-ray diffractometry and electron microprobe analyser show that as a result of the heat treatment the composition of the intermetallic phases changes or new intermetallic phases are formed. This would seem to suggest a solid-solid transformation, such as is described e.g. also for the Co-Ta system (Binary Alloy Phase Diagrams, Second Edition, T.M. Massalski (ed.), ASM International, 1990).

Targets which possess a microstructure according to the present invention show a distinctly higher magnetic field penetration than untreated targets with the same composition and geometry. They are even in some cases superior to targets which on account of the absence of the intermetallic phases have to be manufactured by means of the cold formings described in the literature.

Table 1 summarizes the experimental results which have been obtained with examples according to the present invention and with comparison examples. All the targets were manufactured by melting of the corresponding alloy components under vacuum or protective gas and subsequent pouring into an ingot mould.

In order to characterise the magnetic target properties, the magnetic field component parallel to the target surface was measured while the target lay on a set of magnets for a PK150 cathode (ϕ 150 mm). The field strength H_x was recorded approx. 1 mm above the target. Without a target, i.e. measured directly on the cathode bath, the maximum value was $H_{x,max}$ = 95 kA/m.

Figure 1 shows a microprobe analyser shot of the microstructure of a target according to the present invention. Grey matrix: cobalt mixed crystal; clear patches: intermetallic phases of the coarsened eutectic; fine clear lines: decoration of the grain boundaries, fines boundaries or twin grain boundaries or slip bands. Magnification 1000:1.

Figure 2 shows a microprobe analyser shot of the microstructure of a comparison target. Grey matrix: cobalt mixed crystal; clear patches: intermetallic phases of the coarsened eutectic. Magnification 1000:1.

Figure 3 shows a microprobe analyser shot of the microstructure of a comparison target without intermetallic phases. Magnification 1000:1.

Table 1: Manufacturing parameters, magnetic properties and structural characterisation of targets according to the present invention, and of targets which were produced by comparison methods. Target geometry for determining $H_{x,max}$: ϕ 150 x 6 mm.

	Compos-ition	Rolling Heat temp.	Heat treat. temp.	treat. time	$H_{x,max}$	Micro-structure
	(at %)	(°C)	°C)	(h)	(kA/m)	
A	CoCr(10.5)Ta(4)	1150	850	86	50	as Fig. 1
A	CoCr(10.5)Ta(4)	--	880	8	44	as Fig. 1
A	CoCr(10.5)Ta(4)	1150	750	360	39	as Fig. 1
B	CoCr(10.5)Ta(4)	1) 1200 2) 700	--	--	29	as Fig. 2, cracks
A	CoCr(10)Ta(6)	1200	875	22	48	as Fig. 1
B	CoCr(10)Ta(6)	1) 1250 2) 700	--	--	36	as Fig. 2, serious cracks
	CoCr(12)Ta(2)	1) 1150 2) 350	-- --	-- --	44	as Fig. 3
C	CoCr(12)Ta(2)	1100	900	16	27	as Fig. 3
A	CoCr(9)Pt(9)Ta(2)	1150	840	8	46	as Fig. 1
B	CoCr(9)Pt(9)Ta(2)	1) 100 2) 750	--	--	25	as Fig. 2, serious cracks
C	CoCr(11)Pt(10)Ta(1)	1150	820	12	28	as Fig. 3
A	CoCr(10)Ta(5)	1100	800	20	41	as Fig. 1
D	CoCr(10)Ta(5)	1200	1000	8	26	as Fig. 2
C	CoNi(18)Cr(8)	1) 1100 2) 300	--	--	42	as Fig. 3

A) Targets according to the present invention

B), C), D) Comparison examples

Notes on the examples:

Case A):

Prior to the heat treatment a matrix of primary Co mixed crystals is present, in which eutectic regions of Co mixed crystals and intermetallic phases may be embedded. After the heat treatment the grain boundaries, fines boundaries or twin grain boundaries or slip bands are decorated with elements which also form the intermetallic phases. The heat treatment takes place below the solid-solid transformation. x-ray reflections of a new intermetallic phase occur. If intermetallic phases have already been observed prior to the heat treatment, their stoichiometry and lattice structure changes.

Case B):

The initial condition corresponds to Case A. Instead of the heat treatment, however, a cold forming is now carried out. No decoration of the grain boundaries, fines boundaries or twin grain boundaries or slip bands occurs. The brittleness of the material is such, however, that, owing to the cold forming, macroscopic cracks appear which render the material unusable or make economic manufacture extremely difficult.

Case C):

No intermetallic phases are present, either because no element is included which forms intermetallic phases with the other components, or because the concentration of the elements forming intermetallic phases is so low that the solubility limit has not been exceeded on any occasion. In this case the cold forming described in the literature is very successful, whereas a heat treatment according to the present invention does not bring about any improvement compared with the untreated material. Neither the rolling treatment nor the heat treatment leads to the formation of intermetallic phases.

Case D):

The initial state corresponds to Case A. Since the heat treatment takes place above the solid-solid transformation temperature, no significant change in the microstructure and the structure of the intermetallic phases occurs. On occasions a certain proportion of the intermetallic phases passes into solution.

Claims

1. Target for magnetron cathode sputtering systems consisting of a cobalt-base alloy Co_{1-x-y} M_xR_y, wherein M stands for at least one of the elements Cr, Pt, Ni, Pd or similar elements of the transition metals and $0 \leq x \leq 0.3$, R stands for at least one of the elements Ta, Mo, W, B, Hf, Nb, V or similar metals tending towards the formation of intermetallic phases and $0.015 \leq y \leq 0.20$, consisting of a microstructure of predominantly hexagonal cobalt mixed crystals and optionally intermetallic phases formed with R, wherein the target material exhibits at least one of the following two features:

   a) The grain boundaries, fines boundaries or twin grain boundaries or slip bands of the cobalt mixed crystal forming the matrix are decorated with the elements forming the intermetallic phases.

   b) x-ray diffraction patterns produced by the target exhibit reflections of an intermetallic phase which is in the main absent as cast and forms only during a heat treatment in the temperature range below the solidus temperature of the alloy due to a solids reaction.

2. Target according to claim 1, **characterised in that** the composition is Co_{1-x-y} Cr_xTa_y with $0 \leq x \leq 0.3$; $0.025 \leq y \leq 0.15$.

3. Target according to claim 1, **characterised in that** the composition is $Co_{1-x-y-z}$ Pt_x Cr_y Ta_z with $0 \leq x \leq 0.2$; $0 \leq y \leq 0.25$; $0.015 \leq z \leq 0.15$.

4. Target according to any one of claims 1 - 3, **characterised in that** it is used for manufacturing thin-film media for longitudinal data storage.

* C L M S *

5. Method for manufacturing targets according to any one of claims 1 - 3, **characterised in that** the target is heat treated for 1 to 100 hours at temperatures of not more than 300 °C below the temperature for the solid-solid transformation reaction.



Fig. 1

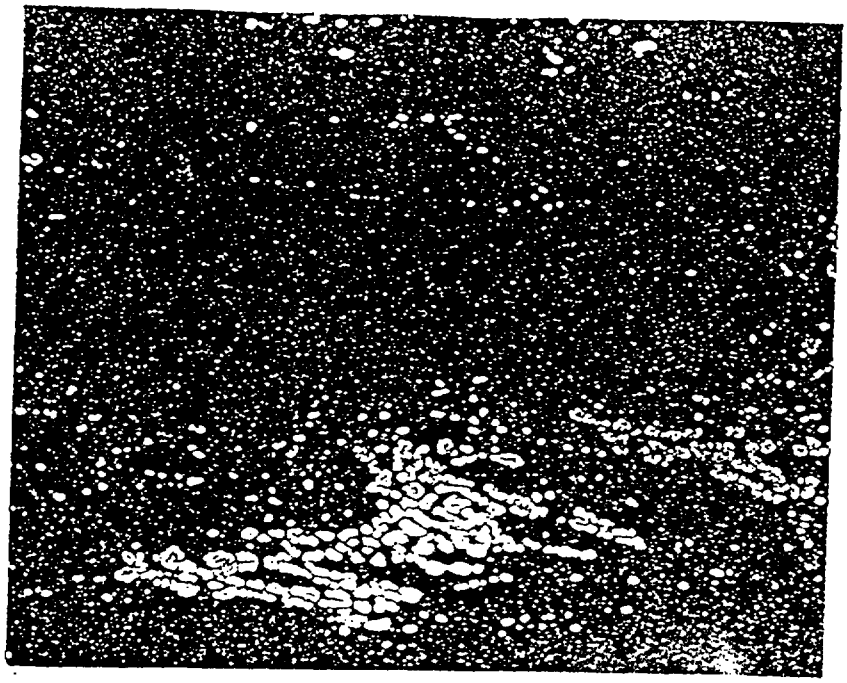

Fig. 2

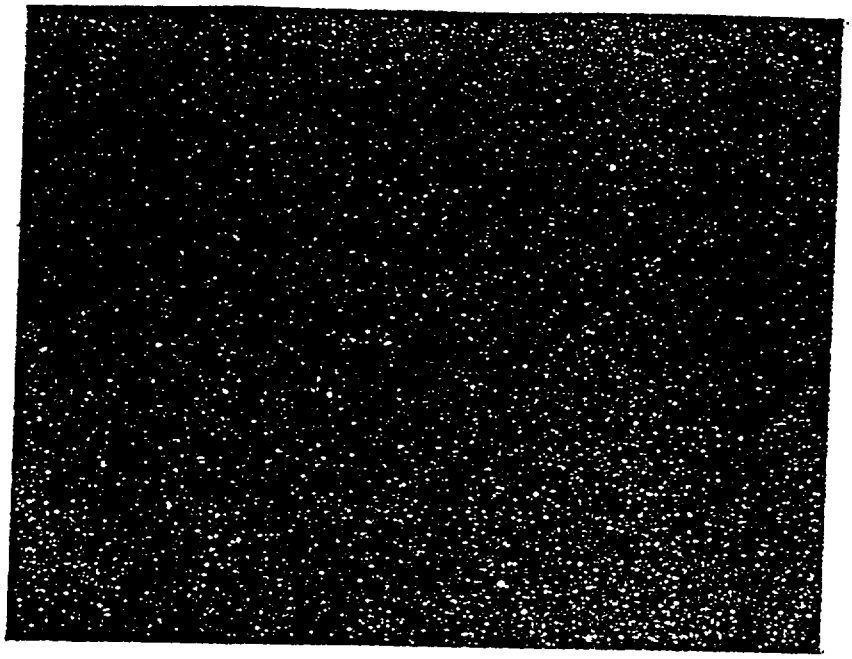

Fig. 3

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Abstract

TARGET FOR MAGNETRON CATHODE SPUTTERING SYSTEM CONSISTING OF A COBALT-BASE ALLOY

A target for magnetron cathode sputtering systems consists of a cobalt-base alloy which contains further elements so that intermetallic phases may be observed on the basis of the phase diagram in the equilibrium state at the operating temperature of the target. The corn boundaries, fines boundaries or twin grain boundaries or slip bands of the cobalt mixed crystal forming the matrix are decorated with the elements forming the intermetallic phases, wherein the X-ray diffraction patterns produced by the target exhibit reflections of an intermetallic phase which is absent in the main as cast and forms only during a heat treatment in the temperature range below the solidus temperature of the alloy due to a solids reaction.

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ABSTRACT

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A target for magnetron cathode sputtering systems consists of a cobalt-base alloy which contains further elements so that intermetallic phases may be observed on the basis of the phase diagram in the equilibrium state at the operating temperature of the target. The corn boundaries, fines boundaries or twin grain boundaries or slip bands of the cobalt mixed crystal forming the matrix are decorated with the elements forming the intermetallic phases, wherein the X-ray diffraction patterns produced by the target exhibit reflections of an intermetallic phase which is absent in the main as cast and forms only during a heat treatment in the temperature range below the solidus temperature of the alloy due to a solids reaction.

(Figure 1)