SPUTTERING TARGET

TECHNICAL FIELD

[0001]

The present disclosure relates to a sputtering target and an alloy suitable for the sputtering target, and a method of producing a magnetic thin film.

BACKGROUND ART

[0002]

Tunnel magnetoresistance films are used in a magnetic head, a magnetic random access memory (MRAM), and the like. In such a tunnel magnetoresistance film, the tunnel magnetoresistance (TMR) signal is high, and the switching current density (Jc) is low. A common tunnel magnetoresistance film includes two magnetic thin films and a barrier layer sandwiched between the thin films. A typical material forming the barrier layer is MgO. On the other hand, a typical material forming the thin films is an alloy containing a large amount of B. Such an alloy further contains Fe or Co. Because the alloy contains a sufficient amount of B, a high tunnel magnetoresistance signal can be achieved in the tunnel magnetoresistance film. Patent Literature 1 (WO2011/070860) and Patent Literature 2 (JP2020-132995A) disclose alloys suitable for magnetic thin films.

CITATION LIST

PATENT LITERATURE

[0003]

Patent Literature 1: WO2011/070860

Patent Literature 2: JP2020-132995A

SUMMARY OF INVENTION

[0004]

A magnetic thin film can be obtained by sputtering. In the sputtering, cations in plasma collide with a target. As a result of the collision, atoms are ejected from the target. These atoms deposit onto a substrate, thereby forming a thin film.

[0005]

As described above, B can contribute to a high tunnel magnetoresistance signal in the thin film. On the other hand, B may impair toughness of the target. A target containing a large amount of B is prone to cracking during use. Furthermore, defects such as cracking of a molded body may also occur during production of the target. Such defects hinder the yield of the target.

[0006]

An object of the present invention is to provide a sputtering target that can be efficiently produced, has excellent toughness, and can contribute to magnetic properties of a thin film, and to provide an alloy suitable for the sputtering target.

[0007]

The present disclosure provides the following aspects.

[Aspect 1]

An alloy suitable for a sputtering target, the alloy comprising:

50 at% or more and 70 at% or less of B; and

one or two selected from the group consisting of Co and Fe,

wherein the alloy has a metallic structure with a crystal grain size of 30 μm or less,

wherein the metallic structure includes a (CoFe)B phase as a matrix and a plurality of B phases dispersed in the matrix, and

wherein each B phase has an equivalent circular diameter of 30 μm or less.

[Aspect 2]

The alloy according to aspect 1, wherein a total content ratio of Co and Fe in the alloy is 30 at% or more and 50 at% or less.

[Aspect 3]

The alloy according to aspect 1 or 2, further comprising O,

wherein a content ratio of O in terms of ppm by mass is equal to or smaller than a value V_1 calculated by a mathematical formula:

$V_1 = -10 \times B\% + 900$

wherein B% represents a content ratio of B in terms of at%.

[Aspect 4]

A sputtering target, composed of the alloy according to any one of aspects 1 to 3,

[Aspect 5]

A method of producing a magnetic thin film, comprising the steps of:

providing a target composed of the alloy according to any one of aspects 1 to 3; and

subjecting the target to sputtering.

[0008]

Since the sputtering target contains a sufficient amount of B, a thin film excellent in magnetic properties can be obtained from the target. The target has excellent toughness despite containing a large amount of B. Accordingly, the target is less likely to crack during sputtering. Furthermore, defects are less likely to occur during production of the target.

[0009]

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DESCRIPTION OF EMBODIMENTS

[0010]

Preferred embodiments will be described in detail below.

[0011]

[Target]

A sputtering target according to the present embodiment is composed of an alloy containing B as a main component. The alloy further contains Co or Fe. Preferably, the balance of the alloy includes inevitable impurities. The alloy may have a composition that includes Co and is free of Fe, may have a composition that includes Fe and is free of Co, and may have a composition that includes Co and Fe. In other words, the alloy is a Co-B alloy, an Fe-B alloy, or a Co-Fe-B alloy.

[0012]

[Boron (B)]

The target contains a large amount of B. A thin film containing a large amount of B may be formed from the target. B can contribute to magnetism of the thin film. In a tunnel magnetoresistance film including the thin film, B can contribute to a high tunnel magnetoresistance signal. From this viewpoint, the B content ratio in the alloy is preferably 50 at% or more, more preferably 53 at% or more, and particularly preferably 55 at% or more. Excess B promotes precipitation of an excessive B phase or precipitation of a B phase as a matrix. These B phases impair toughness of the target. From the viewpoint of toughness, the B content ratio is preferably 70 at% or less, more preferably 67 at% or less, and particularly preferably 65 at% or less.

[0013]

[Cobalt (Co) and iron (Fe)]

A thin film containing Co or Fe may be formed from the target containing Co or Fe. Co and Fe can contribute to magnetism of the thin film. From this viewpoint, the total content ratio of Co and Fe in the alloy is preferably 30 at% or more, more preferably 33 at% or more, and particularly preferably 35 at% or more. From the viewpoint that the alloy may contain a sufficient amount of B, the total content ratio of Co and Fe is preferably 50 at% or less, more preferably 47 at% or less, and particularly preferably 45 at% or less.

[0014]

[Metallic structure]

The metallic structure of the target is a polycrystalline structure. In other words, the metallic structure has a plurality (or a large number) of crystal grains.

[0015]

The crystal grain size Dg in the metallic structure is 30 μm or less. In other words, the metallic structure is fine. The target is excellent in toughness despite containing a B phase. From the viewpoint of toughness, the crystal grain size Dg is more preferably 22 μm or less, and particularly preferably 17 μm or less. The smaller the crystal grain size Dg, the more preferable. The crystal grain size Dg may be statistically calculated on the basis of

observation of the metallic structure using an optical microscope. Measurement conditions are described later.

[0016]

[(CoFe)B phase]

The (CoFe)B phase contains both Co and Fe, or either Co or Fe. The molar ratio between Co atoms and Fe atoms in the (CoFe)B phase is 0:1 or more and 1:0 or less. In other words, a composition of the matrix is a CoB phase, an FeB phase, or a CoFeB phase. In the CoB phase, a Co atom and a B atom are bonded, and the molar ratio between Co atoms and B atoms is 1:1. In the FeB phase, an Fe atom and a B atom are bonded, and the molar ratio between Fe atoms and B atoms is 1:1. In the CoFeB phase, a B atom is bonded to a Co atom or an Fe atom, and the molar ratio between B atoms and the sum of Co atoms and Fe atoms is 1:1.

[0017]

[B phase]

As described above, the B phase is dispersed in the matrix. The equivalent circular diameter Dc of each B phase is 30 μm or less. In other words, the maximum value Dmax of these equivalent circular diameters Dc is 30 μm or less. These B phases do not significantly impair toughness of the target. The target is less prone to cracking during sputtering. During production of the target, cracking defects in a molded body are less likely to occur. The target exhibits excellent manufacturing yield. From these viewpoints, the maximum value Dmax is more preferably 20 μm or less and particularly preferably 15 μm or less. The smaller the maximum value Dmax, the more preferable. The maximum value Dmax may be statistically calculated on the basis of observation of the metallic structure using a scanning electron microscope. Measurement conditions are described later.

[0018]

[Oxygen (O)]

The alloy may contain O as an impurity. O may be bonded to B to form a B_2O_3 phase. The melting point of the B_2O_3 phase is low. A target containing the B_2O_3 phase has poor toughness. Since the target according to the present embodiment contains a large amount

of B, the B_2O_3 phase is likely to be formed in the target. From the viewpoint of suppressing the B_2O_3 phase, it is important to suppress the O content ratio. From the viewpoint of toughness, the O content ratio (ppm by mass) is preferably equal to or less than a value V_1 calculated by the following formula.

$V_1 = -10 \times B\% + 900$

In the formula, B% represents the B content ratio (at%).

[0019]

The O content ratio (ppm by mass) is more preferably equal to or less than a value V_2 calculated by the following formula.

$V_2 = -10 \times B\% + 800$

[0020]

The O content ratio (ppm by mass) is particularly preferably equal to or less than a value V_3 calculated by the following formula.

$V_3 = -10 \times B\% + 750$

[0021]

The O content ratio is measured by gas analysis using a non-dispersive infrared absorption method after fusion in an inert gas. The size of a test specimen subjected to the analysis is 3 mm × 3 mm × 30 mm. The test specimen having the above size is cut out from the target by a wire-cut method.

[0022]

[Target production method]

In production of the target, powder is provided first. The powder may be produced by an atomization method, a pulverization method, or the like. Examples of the atomization method include a gas atomization method, a water atomization method, and a disk atomization method. From the viewpoint of suppressing contamination of impurities into the powder, the gas atomization method and the disk atomization method are preferred. From the viewpoint of suppressing contamination of impurities into the powder, atomization in an inert gas atmosphere is preferred. From the viewpoint of mass productivity, gas atomization is preferred.

[0023]

The powder is subjected to pressurization and heating. The pressurization and heating are preferably performed by hot isostatic pressing (HIP). Through the pressurization and heating, the sputtering target which is a sintered body is obtained. The target is processed to have a predetermined size and subjected to sputtering. The target may be obtained by a hot pressing method, a spark plasma sintering method, a hot extrusion method, or the like.

[0024]

By providing powder having a crystal grain size of 30 μm or less and forming a molded body under conditions under which crystal grains are less likely to be coarsened, a target having a metallic structure with a crystal grain size Dg of 30 μm or less can be obtained. Grain growth can be suppressed by lowering the heating temperature and shortening the heating time during molding within ranges in which excessive pores are not formed in the molded body.

[0025]

By providing powder which has a B content ratio of 70 at% or less and in which the equivalent circular diameter of a pure B phase is 30 μm or less, and forming a molded body under conditions under which the pure B phase is less likely to be coarsened using the powder, a target having a metallic structure in which the maximum value Dmax of the equivalent circular diameter Dc is 30 μm or less can be obtained. Growth of the pure B phase can be suppressed by lowering the heating temperature and shortening the heating time during molding within ranges in which excessive pores are not formed in the molded body.

[0026]

[Sputtering]

The present disclosure is also directed to a method of producing a thin film. The production method includes the steps of: providing a target composed of the alloy of the present disclosure described above; and subjecting the target to sputtering. A magnetic thin film can be obtained by the production method. In the production method, cracking of the target can be suppressed. In particular, the effect of suppressing cracking is significant in sputtering using a magnetron sputtering apparatus. A thin film suitable for a tunnel

magnetoresistance film used in a magnetic head, a magnetic random access memory (MRAM), or the like can be obtained by such sputtering.

EXAMPLES

[0027]

Effects of a sputtering target according to Examples will be clarified below. However, the scope disclosed in the present specification should not be construed as being limited based on the description of Examples.

[0028]

[Example 1]

A raw material metal was put into an alumina crucible. The raw material metal was induction-heated and melted in an argon gas atmosphere. The molten metal was discharged from a nozzle of the crucible, and high-pressure argon was sprayed onto the molten metal to obtain powder. The powder was subjected to classification to adjust the particle size to 300 μm or less. A capsule (outer diameter: 220 mm, inner diameter: 210 mm, length: 200 mm) made of carbon steel (SC) and having a chromium plating layer on the inner surface of the capsule was filled with the powder. The capsule was degassed and then sealed. The powder was subjected to hot isostatic pressing (HIP) at a temperature of 1200°C and a pressure of 140 MPa for 3 hours to obtain a sintered body. The sintered body was subjected to wire cutting and lathe machining, followed by surface polishing to obtain a sputtering target. The target had a disk shape. The target had a diameter of 180 mm and a thickness of 7 mm. The composition of the target is shown in Table 1 below.

[0029]

[Examples 2 to 13 and Comparative Examples 2 and 4]

A sputtering target of each of Examples 2 to 13 and Comparative Examples 2 and 4 was obtained in the same manner as in Example 1 except that a raw material metal with a different composition was used.

[0030]

[Comparative Example 1]

An ingot was obtained by melting. The ingot was subjected to wire cutting and lathe machining, followed by surface polishing to obtain a sputtering target.

[0031]

[Comparative Example 3]

A target of Comparative Example 3 was obtained in the same manner as in Example 1 except that the temperature of the hot isostatic pressing was set to 1350°C.

[0032]

[Crystal grain size]

A test specimen was cut out from the target. A surface of the test specimen was subjected to mirror polishing. The surface was then etched using a nitric acid alcohol-based etchant. The surface was observed with an optical microscope, and an image having a vertical dimension of 170 μm and a horizontal dimension of 220 μm was captured. Three straight lines each having a length L of 220 μm were drawn on the image, and the number N of intersections between the lines and crystal grain boundaries was counted. The crystal grain size Dg was calculated based on the following mathematical formula.

$Dg = (3 \cdot L)/N$

The results are shown in Table 1 below.

[0033]

[Equivalent circular diameter of B phase]

A test specimen was cut out from the target. A surface of the test specimen was subjected to polishing. The surface was observed with a scanning electron microscope (SEM), and an image having a vertical dimension of 100 μm and a horizontal dimension of 140 μm was captured. The equivalent circular diameter Dc of a B phase was measured by image analysis. In the present specification, the term "equivalent circular diameter" means the projected area diameter and is defined as the diameter of a circle having the same area as the projected area of a particle (here, the B phase). Accordingly, the equivalent circular diameter Dc was measured for each of multiple B phases observed within one field of view. In this manner, the equivalent circular diameters Dc were measured in five fields of view, and the maximum value Dmax hereof was determined. The results are shown in Table 1 below. In the target of Comparative Example 2, no B phase was observed.

[0034]

[Transverse rupture strength]

A test specimen was cut out from the target by a wire-cut method. The test specimen was subjected to a transverse rupture test in accordance with "JIS Z 2511, Metallic powders-Determination of green strength by transverse rupture of rectangular compacts." Test conditions were as follows.

Test specimen thickness t: 3 mm

Test specimen width W: 3 mm

Test specimen length: 20 mm

Inter-fulcrum distance: 10 mm

The load P (kN) at which the test specimen fractured was measured, and the transverse rupture strength BS (MPa) was calculated using the following mathematical formula.

$BS = (3/2) \times P \times L/(t^2 \times W)$

BS: Transverse rupture strength (MPa)

t: Test specimen thickness (mm)

W: Test specimen width (mm)

L: Inter-fulcrum distance (mm)

P: Load at fracture (kN)

The average of values obtained from three measurements is shown in Table 1 below.

[0035]

[Table 1]

Table 1 Evaluation results

	Composition (at%)			O	V1	Dg	Dmax	Transverse rupture strength
	Co	Fe	B	ppm		μm	μm	MPa
Example 1	10	30	60	50	300	3	3	340
Example 2	39	0	61	120	290	3	3	250
Example 3	0	36	64	150	260	2	5	280
Example 4	10	20	70	170	200	17	15	220
Example 5	20	30	50	110	400	8	1	200
Example 6	24	25	51	90	390	7	2	220
Example 7	15	30	55	60	350	7	3	240
Example 8	22	10	68	190	220	14	13	240
Example 9	20	15	65	90	250	4	6	290
Example 10	22	12	66	110	240	6	7	270
Example 11	20	18	62	70	280	3	3	300
Example 12	6	31	63	110	270	3	4	310
Example 13	13	20	67	200	230	9	11	250
Comparative Example 1	10	30	60	40	300	66	49	50
Comparative Example 2	21	30	49	80	410	32	N/A	140
Comparative Example 3	10	25	65	100	250	40	25	150
Comparative Example 4	20	8	72	200	180	9	35	70

[0036]

As is apparent from Table 1, the sputtering target of each of the Examples exhibits excellent toughness despite containing a sufficient amount of B. From these evaluation results, superiority of these targets is evident.

[0037]

The sputtering target described above is suitable for production of various magnetic thin films.

CLAIMS

1. An alloy suitable for a sputtering target, the alloy comprising:

50 at% or more and 70 at% or less of B; and

one or two selected from the group consisting of Co and Fe,

wherein the alloy has a metallic structure with a crystal grain size of 30 μm or less,

wherein the metallic structure includes a (CoFe)B phase as a matrix and a plurality of B phases dispersed in the matrix, and

wherein each B phase has an equivalent circular diameter of 30 μm or less.

2. The alloy according to claim 1, wherein a total content ratio of Co and Fe in the alloy is 30 at% or more and 50 at% or less.

3. The alloy according to claim 1 or 2, further comprising O,

wherein a content ratio of O in terms of ppm by mass is equal to or smaller than a value V_1 calculated by a mathematical formula:

$V_1 = -10 \times B\% + 900$

wherein B% represents a content ratio of B in terms of at%.

4. A sputtering target, composed of the alloy according to any one of claims 1 to 3.

5. A method of producing a magnetic thin film, comprising the steps of:

providing a target composed of the alloy according to any one of claims 1 to 3; and

subjecting the target to sputtering.