

[DESCRIPTION]

[TITLE OF INVENTION]

Cr-Ti ALLOY SPUTTERING TARGET MATERIAL AND METHOD FOR
PRODUCING SAME

5 [Technical Field]

[0001]

The present invention relates to a Cr-Ti alloy sputtering target material for forming a Cr-Ti alloy layer used as a base layer of a magnetic recording medium, and a method of preparing the same.

10 [Background Art]

[0002]

Research on increasing a density of a magnetic recording medium have been actively conducted in order to miniaturize and increase the capacity of a hard disk drive. In recent years, a perpendicular magnetic recording method has been put to practical use as a method capable of realizing a high recording density, and has become mainstream. Further, for further increasing the recording density, new recording methods such as patterned media, a thermally assisted recording method and the like are under development.

[0003]

20 A perpendicular magnetic recording method is a method suitable for high recording density, in which a magnetic film of a perpendicular magnetic recording medium is formed such that an axis of easy magnetization thereof is oriented perpendicular to a medium surface, a demagnetizing field in bits is small even when a recording density is increased, and deterioration in recording and reproducing characteristics is low. A perpendicular magnetic recording medium generally has a

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multilayer structure including a base layer/a soft magnetic backing layer/a seed layer/a Ru intermediate layer/a CoPtCr-SiO₂ magnetic layer/a protective layer on a substrate formed of glass or aluminum. A Cr-Ti layer is formed on a part of the base layer.

[0004]

5 The multilayer structure of the perpendicular magnetic recording medium is formed by film formation using a magnetron sputtering method. A magnetron sputtering method is a method in which a permanent magnet is disposed on a back surface of a parent material called a sputtering target material, a magnetic flux leaks to the surface of the target material, and a glow discharge plasma converges in the leaked
10 magnetic flux region, thereby enabling high-speed film formation. The magnetic recording medium is produced by using a sputtering apparatus having independent film forming chambers for each layer.

[0005]

 The sputtering target material is a plate material adjusted to have a desired thin
15 film composition and is generally produced by a melt casting method or a powder sintering method. The Cr-Ti alloy sputtering target material used for forming the Cr-Ti layer is produced by a powder sintering method.

 However, the Cr-Ti alloy sputtering target material tends to form an intermetallic compound phase (TiCr₂ phase) having a lower sputtering rate than a pure Cr phase or a
20 pure Ti phase during sintering. The TiCr₂ phase generates an aggregated foreign substance called particles, which adheres to a film-formed recording medium, thereby lowering product yield. For this reason, attempts to improve the structure of the Cr-Ti alloy sputtering target material have been made. For example, it has been proposed that, in a Cr-Ti alloy sputtering target material containing 40 to 60 atom% of Ti, the number of
25 particles generated during sputtering be reduced by controlling the amount of the TiCr₂

phase formed at the time of powder sintering such that it is a trace amount.

[Prior Art Document]

[Patent Document]

[0006]

5 [Patent Document 1]

Japanese Unexamined Patent Application Publication No. 2011-252227

[Summary of Invention]

[Problem to be solved by the present invention]

[0007]

10 The Cr-Ti alloy sputtering target material disclosed in the above-described
Patent literature 1 is effective in that generation of coarse particles due to a TiCr_2 phase
can be suppressed.

However, with the recent increase in the recording density of magnetic recording
media, fine particles which did not affect the quality of the recording medium in the past
15 have become one of the causes of reduction in product yield.

The inventors of the present invention confirmed that a lot of fine particles are
generated from the sputtering target material when the Cr-Ti alloy sputtering target
material disclosed in Patent literature 1 is sputtered. Further, as a main cause thereof, a
phenomenon in which minute protrusions which have a major axis of 0.1 μm or more and
20 less than 5.0 μm and are called nodules are generated locally on the sputtering surface of
the sputtering target material is confirmed.

The objective of the present invention is to solve the above-described problem
and to provide a Cr-Ti alloy sputtering target material which can suppress generation of
fine particles during sputtering.

25 [Technical means to solve the problem]

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[0008]

For the Cr-Ti alloy sputtering target material which is represented by a composition formula $\text{Cr}_{100-X}\text{-Ti}_X$ ($40 \leq X \leq 60$) in terms of an atomic ratio with the balance consisting of unavoidable impurities, the inventors of the present invention have

5 investigated variously the causes of generation of particles during sputtering, and as a result, have confirmed that Mg, Al, Si, Mn, Ni, Cu, and Sn which are contained impurities, are the origin of generation of nodules. Further, the inventors found that the generation of nodules can be minimized by using a high-purity Cr-Ti alloy sputtering target material with the amount of impurities controlled to be within a specific range, and

10 the Cr-Ti alloy sputtering target material could be prepared using Ti powder and Cr powder in which the amount of above-described elements is reduced, thereby completing the present invention. In the present invention, the generation of fine particles during sputtering can be suppressed by suppressing the generation of nodules.

[0009]

15 That is, the present invention relates to a Cr-Ti alloy sputtering target material, which is represented by a composition formula $\text{Cr}_{100-X}\text{-Ti}_X$ ($40 \leq X \leq 60$) in terms of an atomic ratio, with the balance consisting of unavoidable impurities that include Mg, Al, Si, Mn, Ni, Cu and Sn in an amount of 1 ppm by mass or more and 50 ppm by mass or less in total.

20 Further, preferably, in the Cr-Ti alloy sputtering target material of the present invention, $\text{Mg} \leq 1$ ppm by mass, $\text{Al} \leq 10$ ppm by mass, $\text{Si} \leq 10$ ppm by mass, $\text{Mn} \leq 1$ ppm by mass, $\text{Ni} \leq 10$ ppm by mass, $\text{Cu} \leq 1$ ppm by mass, and $\text{Sn} \leq 5$ ppm by mass.

[0010]

Further, the Cr-Ti alloy sputtering target material of the present invention may

25 be obtained by mixing a Ti powder that contains, as impurities, Mg, Al, Si, Mn, Ni, Cu

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and Sn in an amount of 1 ppm by mass or more and 50 ppm by mass or less in total, and a Cr powder that contains, as impurities, Mg, Al, Si, Mn, Ni, Cu and Sn in an amount of 1 ppm by mass or more and 50 ppm by mass or less in total, and sintering the mixture under pressure.

5 In the Ti powder, preferably, $\text{Mg} \leq 1$ ppm by mass, $\text{Al} \leq 2$ ppm by mass, $\text{Si} \leq 10$ ppm by mass, $\text{Mn} \leq 2$ ppm by mass, $\text{Ni} \leq 10$ ppm by mass, $\text{Cu} \leq 10$ ppm by mass, and $\text{Sn} \leq 2$ ppm by mass.

 Further, in the Cr powder, preferably, $\text{Mg} \leq 1$ ppm by mass, $\text{Al} \leq 10$ ppm by mass, $\text{Si} \leq 10$ ppm by mass, $\text{Mn} \leq 1$ ppm by mass, $\text{Ni} \leq 10$ ppm by mass, $\text{Cu} \leq 1$ ppm by mass, and
10 $\text{Sn} \leq 10$ ppm by mass.

[Advantageous Effects of Invention]

[0011]

 The present invention can provide a Cr-Ti alloy sputtering target material in which the generation of fine particles during sputtering can be minimized, and a method
15 of preparing the same, and thus is a useful technique for the production of a magnetic recording medium.

[Brief Explanation of Drawings]

[0012]

 Fig. 1 is a secondary electron image of a Cr-Ti alloy sputtering target material of
20 Inventive example 1 taken by a scanning electron microscope.

 Fig. 2 is a secondary electron image of a Cr-Ti alloy sputtering target material of Inventive example 2 taken by a scanning electron microscope.

 Fig. 3 is a secondary electron image of a Cr-Ti alloy sputtering target material of Comparative example 1 taken by a scanning electron microscope.

Fig. 4 is a secondary electron image of a Cr-Ti alloy sputtering target material of Comparative example 2 taken by a scanning electron microscope.

[Description of Embodiments]

[0013]

- 5 The important feature of the present invention is controlling the amounts of Mg, Al, Si, Mn, Ni, Cu and Sn such that they are within a specific range as impurities of a Cr-Ti alloy sputtering target material, which is represented by a composition formula $\text{Cr}_{100-X}\text{-Ti}_X$ ($40 \leq X \leq 60$) in terms of atomic ratio and has a balance consisting of impurities, to minimize the generation of nodules which is the origin of particles during sputtering.
- 10 The generation of fine particles during sputtering can be minimized by minimizing the generation of nodules.

Further, a feature of the present invention is to mix a Ti powder and a Cr powder in which each of the impurities is controlled such that they are within a specific range and to sinter the mixture under pressure to prepare the Cr-Ti alloy sputtering target material.

[0014]

The Cr-Ti alloy sputtering target material of the present invention is represented by a composition formula $\text{Cr}_{100-X}\text{-Ti}_X$ ($40 \leq X \leq 60$) in terms of the atomic ratio, and has a balance consisting of unavoidable impurities.

- 20 The content of Ti is defined as the range in which a film with high adhesion and high crystallinity can be formed and a magnetic recording medium with high recording and reproducing characteristics can be produced when a Cr-Ti alloy is used as a part of the base layer or the seed layer of the magnetic recording medium.

[0015]

- 25 In the Cr-Ti alloy sputtering target material of the present invention, in terms of

controlling an amount of Mg, Al, Si, Mn, Ni, Cu and Sn as impurities which are the origin of nodules to a trace amount, a total content of the impurities is defined as 1 ppm by mass or more and 50 ppm by mass or less. Further, the total content of impurities is preferably 1 ppm by mass or more and 17 ppm by mass or less, more preferably 1 ppm by mass or more and 13 ppm by mass or less.

Among the above-described impurities, Ni forms a Ni-Ti compound having a small sputtering rate especially in the refining process of Ti, and thus tends to be the origin of abnormal discharge and causes the generation of nodules during sputtering. Therefore, Ni $\leq$ 10 ppm by mass is preferable in the Cr-Ti alloy sputtering target material of the present invention.

[0016]

Further, among the above impurities, Mg, Al, Si and Mn have high affinity with oxygen, and thus when these impurities are contained in a large amount in the Ti powder or the Cr powder which are raw material powders, oxides may be easily formed in the storage and manufacturing processes of the raw material powders. These oxides form chemically stable bonds, and have a lower sputtering rate than the surrounding metallic structure, and thus tend to be the origin of nodules. Therefore, Mg $\leq$ 1 ppm by mass, Al $\leq$ 10 ppm by mass, Si $\leq$ 10 ppm by mass and Mn $\leq$ 1 ppm by mass are preferable in the Cr-Ti alloy sputtering target material of the present invention.

[0017]

Further, Cu and Sn as impurities form a liquid phase at a temperature of 500 °C or less, which is the surface temperature of the sputtering target material in sputtering, and thus tend to be the origin of nodules. Therefore, Cu $\leq$ 1 ppm by mass and Sn $\leq$ 5 ppm by mass are preferable in the Cr-Ti alloy sputtering target material of the present invention.

Further, even from the viewpoint of controlling the amount of Mg, Al, Si, Mn, Ni, Cu, and Sn to a trace amount, these impurities are inevitably included, and the lower limit thereof is 1 ppm by mass or more in total in the Cr-Ti alloy sputtering target material of the present invention.

5 Further, the amount of inevitable metal impurities excluding gas components other than Mg, Al, Si, Mn, Ni, Cu and Sn is preferably adjusted to 100 ppm by mass or less in total in the Cr-Ti alloy sputtering target material of the present invention.

[0018]

The above-described Cr-Ti alloy sputtering target material of the present
10 invention may be obtained by mixing a Ti powder and a Cr powder that contain, as impurities, Mg, Al, Si, Mn, Ni, Cu and Sn in an amount of 1 ppm by mass or more and 50 ppm by mass or less in total, and sintering the mixture under pressure.

Since the Ti powder used as the raw material powder is prepared through a sponge Ti which is generally prepared by the Kroll method, the Ti powder is likely to
15 contain impurities such as Mg, Al and Si. For this reason, it is preferable to use a Ti raw material ingot prepared by press-molding the above-described sponge Ti in a briquette shape to obtain a molded body, and further subjecting the molded body to secondary refining by a vacuum arc melting method or the like, as a raw material of the Ti powder used in the present invention. Further, it is preferable to collect cut chips from the
20 secondarily refined Ti raw material ingot, temporarily hydrogenate and crush the cut chips, and then subject the crushed cut chips to dehydrogenation treatment to obtain the Ti powder. As a result, the Ti powder to be obtained is controlled such that $Mg \leq 1$ ppm by mass, $Al \leq 2$ ppm by mass, $Si \leq 10$ ppm by mass, $Mn \leq 2$ ppm by mass, $Ni \leq 10$ ppm by mass, $Cu \leq 10$ ppm by mass, and $Sn \leq 2$ ppm by mass.

25 Further, even when the secondarily refined Ti raw material ingot is applied to a

non-contact type inert gas atomization method in which refractories are not used, the amount of the impurities of the Ti powder can be controlled within the above-described range.

Further, the Ti powder used in the present invention is preferably controlled to have a content of Fe contained as an impurity of 100 ppm by mass or less and a content of oxygen of 900 ppm by mass or less so as to minimize the generation of coarse particles which has been a problem in the prior art. Further, the Ti powder preferably has a particle size of 100 mesh or less and 325 mesh or more. Accordingly, the Cr-Ti alloy sputtering target material of the present invention can reduce a TiCr_2 phase which is a cause of coarse particles.

[0019]

When the Cr powder is prepared by a general aluminum thermite production method, it is difficult to control the amount of impurities such as Al, Si or the like within the above-described range. Therefore, it is preferable that the Cr powder used as the raw material powder in the present invention is obtained by subjecting a high purity electrolytic Cr pulverized powder to reduction heat treatment in a hydrogen atmosphere. Accordingly, the Cr powder to be obtained is controlled such that $\text{Mg} \leq 1$ ppm by mass, $\text{Al} \leq 10$ ppm by mass, $\text{Si} \leq 10$ ppm by mass, $\text{Mn} \leq 1$ ppm by mass, $\text{Ni} \leq 10$ ppm by mass, $\text{Cu} \leq 1$ ppm by mass, and $\text{Sn} \leq 10$ ppm by mass.

Further, it is possible to minimize the amount of a coarse pure Cr phase remaining in the structure of the sputtering target material of the present invention by using Cr powder with a particle size of 32 mesh or less. Further, it is possible to suppress an increase in the specific surface area to suppress a TiCr_2 phase formed at the grain boundary with Ti, which contributes to coarse particles, by using a Cr powder having a particle size of 325 mesh or more. Therefore, the Cr powder used in the

present invention preferably has a particle size of 32 mesh or less and 325 mesh or more. Accordingly, the Cr-Ti alloy sputtering target material of the present invention can reduce the TiCr_2 phase and suppress the generation of coarse particles.

[0020]

5 A hot isostatic pressing method, a hot press method, an electric current sintering method and the like may be applied to the sintering under pressure in the present invention. Particularly preferably, a sintered body in which the formation of the TiCr_2 phase is sufficiently suppressed can be obtained by setting the sintering temperature to 750 °C or more and 900 °C or less. In this case, excellent sintering can be performed
10 without decreasing a sintered density by setting a pressurizing pressure to 20 MPa or more.

[Examples]

[0021]

First, a Cr powder subjected to reduction treatment in a hydrogen atmosphere is
15 sieved with a 100 mesh sieve to prepare a Cr powder. On the other hand, a Ti powder used in Inventive example 1 is prepared by sieving a Ti powder, which is obtained by collecting cut chips from a Ti raw material ingot obtained by secondary refining of a sponge Ti, temporarily hydrogenating and crushing the cut chips, and then subjecting the crushed cut chips to dehydrogenation treatment, using a 100 mesh sieve. Further, a Ti
20 powder used in Inventive example 2 is prepared by sieving a Ti powder which is obtained by melting the Ti raw material ingot and performing a non-contact type inert gas atomization method in which refractories are not used, using a 100 mesh sieve.

The powders prepared above is mixed together such that an atomic ratio in terms of Cr to Ti is 55:45, filled into a soft iron capsule, degassed and sealed, and then
25 subjected to pressure-sintering using hot isostatic pressing under conditions of a

temperature of 850 °C, a holding pressure of 120 MPa, and a holding time of 1 hour, and thereby a sintered body is prepared.

The obtained sintered body is machined to a diameter of 180 mm and a thickness of 10 mm to prepare a Cr-Ti alloy sputtering target material.

5 [0022]

As Comparative example 1, a commercially available Ti powder having a purity of 99.9 mass% and the above-described Cr powder are mixed to be 55 to 45 in terms of the atomic ratio of Cr to Ti, and the pressure-sintering under the same sintering conditions as above is performed thereon to prepare a Cr-Ti alloy sputtering target material.

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Further, as Comparative example 2, a Ti powder prepared by temporarily hydrogenating and crushing a sponge Ti and performing the dehydrogenation treatment thereon, and the above-described Cr powder are mixed to be 50 to 50 in terms of the atomic ratio of Cr to Ti, and the pressure-sintering under the same sintering conditions as above is performed thereon to prepare a Cr-Ti alloy sputtering target material.

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[0023]

The contents of Mg, Al, Si, Mn, Ni, Cu and Sn are measured by glow discharge mass spectrometry for each powder and each Cr-Ti alloy sputtering target material prepared above. Further, a density is measured by a water substitution method, and a relative density is calculated using a theoretical density for each of the Cr-Ti alloy sputtering target materials described above. The analysis values of impurities of each powder are shown in Table 1, and the analysis values of impurities and relative densities of each of the Cr-Ti alloy sputtering target materials are shown in Table 2.

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[0024]

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Each of the Cr-Ti alloy sputtering target materials prepared above is placed in a

chamber of a DC magnetron sputtering apparatus (model: C3010) manufactured by Canon ANELVA Corporation, and sputtering is performed for 5 hours under the conditions of an Ar gas pressure of 0.3 Pa and an input power of 1500 W after reducing the pressure in the chamber to 1×10^{-6} Pa or less.

5 Next, the number of nodules having a major axis of 5.0 μm or more and the number of nodules having a major axis of 0.1 μm or more and less than 5.0 μm , which are observed at 600 times magnification with a field of view of $157 \mu\text{m} \times 209 \mu\text{m}$ using a scanning electron microscope (model: S-3600N) manufactured by Hitachi High-Technologies Corporation, are measured with respect to a sputtering surface of
10 each of the Cr-Ti alloy sputtering target materials. The measurement results are shown in Table 2.

[0025]

[Table 1]

Sample No.	Impurities in Cr powder (ppm by mass)								Impurities in Ti powder (ppm by mass)								Note
	Mg	Al	Si	Mn	Ni	Cu	Sn	Total	Mg	Al	Si	Mn	Ni	Cu	Sn	Total	
1	0.2	3.6	5.6	0.4	1.1	0.3	1.1	12.3	0.3	0.9	2.7	0.8	4.6	1.2	0.5	11.0	Inventive example 1
2	0.2	3.6	5.6	0.4	1.1	0.3	1.1	12.3	0.4	1.8	1.4	0.5	0.5	0.9	0.5	6.0	Inventive example 2
3	0.2	3.6	5.6	0.4	1.1	0.3	1.1	12.3	0.8	13.0	49.0	28.0	180.0	12.0	36.0	218.8	Comparative example 1
4	0.2	3.6	5.6	0.4	1.1	0.3	1.1	12.3	290.0	3.9	11.0	6.8	26.0	5.6	34.0	377.3	Comparative example 2

[0026]

[Table 2]

Sample No.	Product composition (atom%)	Impurities in target material (ppm by mass)								Relative density (%)	Number of nodules		Note
		Mg	Al	Si	Mn	Ni	Cu	Sn	Total		Major axis		
											Less than 5.0 μm and 0.1 μm or more	5.0 μm or more	
1	Cr ₅₅ -Ti ₄₅	0.1	3.2	8.9	0.8	2.2	0.5	0.8	16.5	99.65	0	0	Inventive example 1
2	Cr ₅₅ -Ti ₄₅	0.6	2.8	5.4	0.5	1.5	0.9	0.7	12.4	100.06	0	0	Inventive example 2
3	Cr ₅₅ -Ti ₄₅	0.8	12.0	27.0	8.2	18.0	2.3	21.0	89.3	100.10	24	9	Comparative example 1
4	Cr ₅₅ -Ti ₉₀	60.0	13.0	17.0	2.9	22.0	2.4	14.0	131.3	100.30	47	8	Comparative example 2

[0027]

Figs. 1 and 2 show secondary electron images of the sputtering surface of the Cr-Ti alloy sputtering target materials of Inventive examples 1 and 2 after sputtering, and Figs. 3 and 4 show the secondary electron images of the sputtering surface of the Cr-Ti alloy sputtering target materials of Comparative examples 1 and 2 after sputtering.

In Comparative Examples 1 and 2, 9 and 8 nodules with a major diameter of 5.0 μm or more are respectively detected on the sputtering surface, and the number of nodules having a major axis of 0.1 μm or more and less than 5.0 μm is confirmed to be 24 and 47, respectively, which is a significantly high number.

On the other hand, in Invention Example 1 and Invention Example 2, the number of nodules having a long diameter of 5.0 μm or more is 0, and the number of each nodules having a major axis of 0.1 μm or more and less than 5.0 μm is also 0, and the generation of nodules is greatly reduced, and thereby the effectiveness of the present invention is confirmed. According to the Cr-Ti alloy sputtering target material of the present invention, the generation of fine particles can be suppressed during sputtering using the Cr-Ti alloy sputtering target material.

[CLAIMS]

[Claim 1]

A Cr-Ti alloy sputtering target material, which is represented by a composition formula $\text{Cr}_{100-x}\text{-Ti}_x$ ($40 \leq x \leq 60$) in terms of an atomic ratio, with the balance consisting of
5 unavoidable impurities that comprise Mg, Al, Si, Mn, Ni, Cu and Sn in an amount of 1 ppm by mass or more and 50 ppm by mass or less in total.

[Claim 2]

The Cr-Ti alloy sputtering target material according to claim 1, wherein $\text{Mg} \leq 1$ ppm by mass, $\text{Al} \leq 10$ ppm by mass, $\text{Si} \leq 10$ ppm by mass, $\text{Mn} \leq 1$ ppm by mass, $\text{Ni} \leq 10$ ppm
10 by mass, $\text{Cu} \leq 1$ ppm by mass, and $\text{Sn} \leq 5$ ppm by mass.

[Claim 3]

A method of preparing a Cr-Ti alloy sputtering target material, comprising:
mixing a Ti powder that comprises, as impurities, Mg, Al, Si, Mn, Ni, Cu and Sn
in an amount of 1 ppm by mass or more and 50 ppm by mass or less in total, and a Cr
15 powder that comprises, as impurities, Mg, Al, Si, Mn, Ni, Cu and Sn in an amount of 1 ppm by mass or more and 50 ppm by mass or less in total; and

sintering under pressure to obtain a Cr-Ti alloy sputtering target material, which is represented by a composition formula $\text{Cr}_{100-x}\text{-Ti}_x$ ($40 \leq x \leq 60$) in terms of the atomic ratio, with the balance consisting of unavoidable impurities that comprises Mg, Al, Si,
20 Mn, Ni, Cu and Sn in an amount of 1 ppm by mass or more and 50 ppm by mass or less in total.

[Claim 4]

The method according to claim 3, wherein, in the Ti powder, $\text{Mg} \leq 1$ ppm by mass, $\text{Al} \leq 2$ ppm by mass, $\text{Si} \leq 10$ ppm by mass, $\text{Mn} \leq 2$ ppm by mass, $\text{Ni} \leq 10$ ppm by mass,

$\text{Cu} \leq 10$ ppm by mass, and $\text{Sn} \leq 2$ ppm by mass.

[Claim 5]

The method according to claim 4, wherein, in the Cr powder, $\text{Mg} \leq 1$ ppm by mass, $\text{Al} \leq 10$ ppm by mass, $\text{Si} \leq 10$ ppm by mass, $\text{Mn} \leq 1$ ppm by mass, $\text{Ni} \leq 10$ ppm by mass, $\text{Cu} \leq 1$ ppm by mass, and $\text{Sn} \leq 10$ ppm by mass.

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[ABSTRACT]

Provided are: a Cr-Ti alloy sputtering target material, which is capable of suppressing the generation of fine particles during sputtering; and a method for producing this Cr-Ti alloy sputtering target material. A Cr-Ti alloy sputtering target material which is represented by a composition formula $\text{Cr}_{100-X}\text{-Ti}_X$ ($40 \leq X \leq 60$) in terms of the atomic ratio, with the balance made up of unavoidable impurities that include Mg, Al, Si, Mn, Ni, Cu and Sn in an amount of from 1 ppm by mass to 50 ppm by mass (inclusive) in total. A method for producing a Cr-Ti alloy sputtering target material, wherein a Ti powder that contains, as impurities, Mg, Al, Si, Mn, Ni, Cu and Sn in an amount of from 1 ppm by mass to 50 ppm by mass (inclusive) in total and a Cr powder that contains, as impurities, Mg, Al, Si, Mn, Ni, Cu and Sn in an amount of from 1 ppm by mass to 50 ppm by mass (inclusive) in total are mixed with each other and sintered under pressure.